UNIVERSITI SAINS MALAYSIA

Laporan Akhir Projek Penyelidikan Jangka Pendek

Development of Waste-Derived Siliceous Materials as a Sorbent for Dye and Heavy Metal Removal

By
Dr. Irvan Dahlan
Prof. Hamidi Abdul Aziz
Prof. Ismail Abustan
Dr. Syafalni
Mr. Mohamad Fared Murshed

2011

UNIVERSITI SAINS MALAYSIA

LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA *PENDEK*

FINAL REPORT OF SHORT TERM RESEARCH PROJECT

Sila kemukakan laporan akhir ini melalui Jawatankuasa Penyelidikan di Pusat Pengajian dan Dekan/Pengarah/Ketua Jabatan kepada Pejabat Pelantar Penyelidikan

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1. **Nama Ketua Penyelidik:** *Name of Research Leader* **Dr. Irvan Dahlan**

☐ Profesor Madya/ *Assoc. Prof.* ☑ Dr./ *Dr.* ☐ Encik/Puan/Cik *Mr/Mrs/Ms*

2. **Pusat Tanggungjawab (PTJ):** *School/Department* **Pusat Pengajian Kejuruteraan Awam**

3. **Nama Penyelidik Bersama:** *Name of Co-Researcher*
(1) Prof. Hamidi Abdul Aziz
(2) Prof. Ismail Abustan
(3) Dr. Syafalni
(4) Mohamad Fared Murshed

4. **Tajuk Projek:** *Title of Project* **Development of waste-derived siliceous materials as a sorbent for dye and heavy metal removal.**

5. Ringkasan Penilaian/*Summary of Assessment***:**	Tidak Mencukupi *Inadequate* 1	2	Boleh Diterima *Acceptable* 3	Sangat Baik *Very Good* 4	5
i) **Pencapaian objektif projek:** *Achievement of project objectives*	☐	☐	☐	☐	☑
ii) **Kualiti output:** *Quality of outputs*	☐	☐	☐	☐	☑
iii) **Kualiti impak:** *Quality of impacts*	☐	☐	☐	☑	☐
iv) **Pemindahan teknologi/potensi pengkomersialan:** *Technology transfer/commercialization potential*	☐	☐	☑	☐	☐
v) **Kualiti dan usahasama :** *Quality and intensity of collaboration*	☐	☐	☑	☐	☐
vi) **Penilaian kepentingan secara keseluruhan:** *Overall assessment of benefits*	☐	☐	☐	☑	☐

6. Abstrak Penyelidikan

(Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Inggeris**. Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

Abstract of Research

(An abstract of between 100 and 200 words must be prepared in Bahasa Malaysia and in English). This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

Dalam kajian ini, penyelidikan keatas penyediaan bahan penjerap dari sisa-bahan bersilika dilakukan untuk meyingkiran bahan-bahan pencelup dan logam berat. Abu sekam padi (RHA), abu bahan api kelapa sawit (PFA) dan abu terbang arang batu (CFA) dipilih memandangkan tiada kajian dilakukan keatas gabungan sisa-bahan bersilika ini sebagai bahan penjerap dan ia juga didapati dengan sangat banyak di Malaysia. Penghasilan bahan-bahan penjerap novel dihasilkan melalui pelbagai kaedah iaitu kaedah penghidratan, pengaktifan kimia, kaedah magnet dan kaedah sol-gel. Bahan penjerap yang disedikan digunakan untuk menyingkirkan komponen-komponen tunggal seperti zink (Zn^{2+}), nikel (Ni^{2+}), besi (Fe^{2+}), mangan (Mn^{2+}), pencelup Brilliant Green, pencelup Dirict Blue 71 dan pencelup Acid Violet 7 daripada air sisa sintetik. Pelbagai pencirian fizikal dan kimia telah dijalankan keatas bahan penjerap RHA/PFA/CFA terpilih yang disediakan dan digunakan untuk mendapat pemahaman yang lebih baik mengenai proses penjerapan bahan pencelup dan logam berat. Lebih daripada 90% setiap logam pewarna dan berat dapat disingkirkan pada keadaan optimum. Semua parameter ujikaji seperti nisbah abu dalam penyediaan bahan penjerap, masa sentuh, kepekatan awal bahan pencelup atau logam berat, kadar pengadukan dan pH, mempengaruhi penjerapan bahan pencelup dan logam berat. Kajian ini membuktikan bahawa RHA, PFA dan CFA boleh digabungkan dan dijadikan sebagai bahan penjerap alternatif yang sangat baik untuk penyingkiran bahan pencelup dan logam berat melalui proses penjerapan.

In the present study, the preparation of sorbent from waste-derived siliceous materials has been investigated for the removal of dyes and heavy metals. The rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA) were selected, since no work has been carried out to combine these waste-derived siliceous materials as a sorbent, and also it is highly abundant in Malaysia. The novel sorbents were prepared using various methods, namely hydration method, chemical activation, magnetic method and sol-gel method. The prepared sorbents were used to remove single components of zinc (Zn^{2+}), nickel (Ni^{2+}), iron (Fe^{2+}), manganese (Mn^{2+}), brilliant green dye, direct blue 71 dye, and acid violet 7 dye from synthetic wastewater. Various physical and chemical characterizations were carried out for (selected) prepared and spent RHA/PFA/CFA sorbents in order to obtain a better understanding of adsorption process in removing dyes and heavy metals. More than 90% of each dye and heavy metal could be removed during all optimum conditions. All experimental parameters, such as ash ratio in the sorbent preparation, contact time, initial concentration of dye or heavy metal, agitation rate and pH, affecting the adsorption of dye and heavy metal. This study demonstrated that RHA, PFA and CFA could be combined and can be exploited as an excellent alternative sorbent for the removal of dyes and heavy metals by adsorption process.

7. Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini. [Sila gunakan kertas berasingan]

Applicant are required to prepare a Comprehensive Technical Report explaning the project. (This report must be appended separately)

Please refer attachment for Comprehensive Technical Report.

Senaraikan kata kunci yang mencerminkan penyelidikan anda:
List the key words that reflects your research:

Bahasa Malaysia	*Bahasa Inggeris*
Bahan serap	Sorbent
Abu bahan buangan	Waste ash
Pewarna	Dye
Logam berat	Heavy metal

8. Output dan Faedah Projek
Output and Benefits of Project

(a) * **Penerbitan Jurnal**
Publication of Journals
(Sila nyatakan jenis, tajuk, pengarang/editor, tahun terbitan dan di mana telah diterbit/diserahkan)
(State type, title, author/editor, publication year and where it has been published/submitted)

* Sila berikan salinan/*Kindly provide copies*

Refereed Journal

1. Dahlan, I. & Razali, M.H.M (2012). Waste-derived siliceous materials as a novel sorbent for removal of Ni^{2+} from aqueous solutions. ***Water, Air and Soil Pollution*** (Springer). Online First, DOI: 10.1007/s11270-011-1042-z (ISI Impact Factor 2010 : 1.765)
2. Dahlan, I. & Ismail, S. (2012). Physical characterization of prepared and spent CFA/PFA/RHA sorbents in removing heavy metals and dyes. ***Journal of Environmental Science and Technology*** (Asian Network for Scientific Information) 5 (3), 177-183 (Scopus).
3. Dahlan, I. & Noor, A.S.M. (2012). A study on the removal characteristic of acid violet dye from synthetic wastewater using a novel RHA/PFA/CFA sorbent. ***Environmental Engineering and Management Journal*** (Technical University of Iasi, Romania), *Revision*. (ISI Impact Factor 2010 : 1.765).
4. Zwain, H.M. & Dahlan, I. (2012). A review on zinc removal from wastewater using low cost adsorbents. ***Journal of Chemical Technology & Biotechnology*** (Wiley), *Submitted*. (ISI Impact Factor 2010 : 1.818)

Conferences

1. Dahlan, I. & Zwain, H. (2011). Utilization of industrial combustion waste materials as potential sorbent for the removal of zinc (Zn^{2+}) from synthetic wastewater. In ***Proceedings of the 4th International Scientific Conference of Salahaddin University-Erbil***, October 18-20, Erbil, Kurdistan, Iraq, pp. 338-343.
2. Mahdzir, S. & Dahlan, I. (2011). Study of adsorbent prepared from RHA, PFA and CFA using response surface methodology for brilliant green dye removal. In ***Proceedings of the International Engineering for Sustainability Conference (iNESCO)***, October 14-16, Engineering Campus, Universiti Sains Malaysia, Penang, paper N-04.
3. Dahlan, I. & Che Soh, M.N.I. (2011). Manganese (Mn^{2+}) removal from aqueous solutions using sorbent prepared from waste-derived siliceous materials. In ***Proceedings of the Universiti Malaysia Terengganu 10th International Annual Symposium (UMTAS 2011)***, July 11-13, Terengganu, Malaysia, pp. 255.

(b) **Faedah-faedah lain seperti perkembangan produk, pengkomersialan produk/pendaftaran paten atau impak kepada dasar dan masyarakat.**
State other benefits such as product development, product commercialisation/patent registration or impact on source and society.

In the past few years, utilization of industrial waste materials is become more important since these wastes represent unused resources and, in many cases, cause serious disposal problems. Utilization of rice husk ash, palm oil fuel ash and coal fly ash (which come from the burning of rice husk, palm oil fiber/shell, and coal, respectively to generate electricity) will definitely bring benefits to the mill operators in Malaysia. The aim behind using these waste materials (with respect to environmental pollution) is that we could partly reduce the volume of waste materials by converting it into a sorbent that has a high sorption capacity. At the same time, it would be able to partly solve the issues related to wastewater problem by applying this sorbent to remove dye and heavy metal from industrial effluents. On the other hand, utilization of waste material to synthesize sorbent will eventually reduce the cost for preparation of sorbent. Furthermore, from this study we able to establish further understanding on the characteristic of waste-derived siliceous based sorbent in removing dye and heavy metal.

(c) **Latihan Sumber Manusia**
Training in Human Resources

i) Pelajar Sarjana:
Graduates Students
(Perincikan nama, ijazah dan status)
(Provide names, degrees and status)

1. Haider Mohammed Naima (P-WM0022/10), MSc (***Status: Completed***, Viva date: 26 May 2011). Thesis title: Zinc removal from synthetic wastewater by adsorption using rice husk ash, palm oil fuel ash and coal fly ash.
2. Sariyah Mahdzir (P-WM0067/10), MSc (***Status: Completed***, Viva date: 26 May 2011). Thesis title: Study of adsorbent prepared from combination of RHA, PFA and CFA by reflux method for removal of brilliant green dye.
3. Shajaratuldur Ismail (P-WM0069/10), MSc (***Status: Completed***, Viva date: 26 May 2011). Thesis title: Characterization of prepared and spent CFA/POFA/RHA adsorbents in removing heavy metals and dyes.
4. Sariyah Mahdzir (P-WD0191), PhD (***Status: In Progress***). Thesis title: Study of RHA/PFA/CFA adsorbent for removal of dye containing wastewater.
5. Somaia M.O. Tayeh (P-WM0124/11), MSc (***Status: In Progress***). Thesis title: Application of psyllium husks as adsorbent in textile wastewater treatment.
6. Mohsen Vafaei Fard (P-WM0133/11). MSc (***Status: In Progress***). Thesis title: Application of Box Behken design for Preparation of low cost coal bottom ash based sorbent for the removal of Nickel (Ni^{2+})

ii) Lain-lain:
Others

Pelajar Prasiswazah (*Undergraduates Students*)

1. Mohd Hafiz Mohd Razali (96672). BEng (***Status: Completed***, 2011). Thesis title: Utilization of industrial combustion waste materials as potential sorbent for heavy metal ion nickel (II) removal.
2. Mohd Nor Ismilhadi Che Soh (96676). BEng (***Status: Completed***, 2011). Thesis title: Rice husk ash (RHA), coal fly ash (CFA) and palm oil fuel ash (PFA) as a potential sorbent for manganese removal.
3. Mohd Luqman Hakim Mohd Zain (96674). BEng (***Status: Completed***, 2011). Thesis title: Removal of iron (II) from aqueous solutions using sorbent prepared from waste-derived siliceous materials.
4. Ahmad Shahril Mohamed Noor (96630). BEng (***Status: Completed***, 2011). Thesis title: Preparation and characterization of RHA/CFA/PFA sorbent for the removal of acid violet dye.
5. Mohd Aliff Omar Seman (100781). BEng (***Status: In Progress***, 2012). Thesis title: Removal of brilliant green dye and textile wastewater using magnetic sorbents prepared from rice husk ash

9. Peralatan yang Telah Dibeli:
Equipment that has been purchased

None

Dr. Irven Dahlan
Pensyarah
Pusat Pengajian Kejuruteraan Awam
Kampus Kejuruteraan
Universiti Sains Malaysia

15/5/2012

Tandatangan Penyelidik
Signature of Researcher

Tarikh
Date

Komen Jawatankuasa Penyelidikan Pusat Pengajian/Pusat
Comments by the Research Committees of Schools/Centres

Penyelidikan ini telah berjaya menghasilkan
① 4 refereed Journal
② 3 conference papers.
③ 6 orang pelajar Sarjana / 2 orang telah berijazah!
④ 5 orang pelajar Sarjana muda.

Pencapaian yang amat membanggakan dan penyumbang kepada KPI Pusat pengajian.

TANDATANGAN PENGERUSI
JAWATANKUASA PENYELIDIKAN
PUSAT PENGAJIAN/PUSAT
Signature of Chairman
[Research Committee of School/Centre]

Profesor Dr. Badorul Hisham Abu Bakar
Timbalan Dekan
Pengajian Siswazah & Penyelidikan
Pusat Pengajian Kejuruteraan Awam
Kampus Kejuruteraan

16/5/2012
Tarikh
Date

FINAL REPORT

SHORT TERM RESEARCH PROJECT
(304/PAWAM/60310014)

Comprehensive Technical Report On

Development of Waste-Derived Siliceous Materials as a Sorbent for Dye and Heavy Metal Removal.

Research Leader
Dr. Irvan Dahlan

Co-Researchers
Prof. Hamidi Abdul Aziz
Prof. Ismail Abustan
Dr. Syafalni
Mohamad Fared Murshed

ABSTRACT

In the present study, the preparation of sorbent from waste-derived siliceous materials has been investigated for the removal of dyes and heavy metals. The rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA) were selected, since no work has been carried out to combine these waste-derived siliceous materials as a sorbent, and also it is highly abundant in Malaysia. The novel sorbents were prepared using various methods, namely hydration method, chemical activation, magnetic method and sol-gel method. The prepared sorbents were used to remove single components of zinc (Zn^{2+}), nickel (Ni^{2+}), iron (Fe^{2+}), manganese (Mn^{2+}), brilliant green dye, direct blue 71 dye, and acid violet 7 dye from synthetic wastewater. Various physical and chemical characterizations were carried out for (selected) prepared and spent RHA/PFA/CFA sorbents in order to obtain a better understanding of adsorption process in removing dyes and heavy metals. More than 90% of each dye and heavy metal could be removed during all optimum conditions. All experimental parameters, such as ash ratio in the sorbent preparation, contact time, initial concentration of dye or heavy metal, agitation rate and pH, affecting the adsorption of dye and heavy metal. This study demonstrated that RHA, PFA and CFA could be combined and can be exploited as an excellent alternative sorbent for the removal of dyes and heavy metals by adsorption process.

Keywords: Sorbent, Rice husk ash, Palm oil fuel ash, Coal fly ash, Dye, Heavy metal.

CHAPTER 1

INTRODUCTION & LITERATURE REVIEW

The release of huge quantities of dyes wastewater and heavy metals from many industries into water bodies has creates undesirable impact on the environment. Due to strong colour, dyes reduce sunlight transmission into water thus affecting aquatic plants. Typically, untreated dyes wastewaters from dyestuff production and dyeing industries have a great variety of colours and difficult to biodegrade due to complex chemical structures. Furthermore, dyes used in the textile industry may be toxic to aquatic organisms and some of these dyes are suspected carcinogens (Pinheiro et al., 2004; Erdem et al., 2005; Babu et al., 2007; Hameed, 2009). At the same time, unlike other organic pollutants, heavy metals (such as arsenic, cadmium, copper, lead, mercury, and zinc,) are also not easy to biodegrade and tend to accumulate in soil and water reservoirs. The disposal of untreated heavy metal containing effluents into natural water resources causes negative effects to the aquatic environment and in humans some of these metals, even in small amounts can cause severe physiological and health effects (Kadirvelu & Namasivayam, 2003; Rengaraj et al. 2004). As a result, heavy metals are permitted to be discharged only at very low concentrations.

Due to the strong environmental concern and regulation, removal of dyes and heavy metals are necessary before discharging into water streams. Various treatments have been used to treat dyes and heavy metals. Chemical treatment has been used to decolourize dye containing wastewater as well as to remove heavy metal. However, these chemical treatments are too expensive for practical implementation. And also due to low biodegradability of dyes and heavy metals, biological treatments (using activated sludge process, trickling filters and rotary biological contactors) (Spellman, 2003; Wang et al., 2009) cannot effectively remove them from wastewater.

From various treatment technologies exist for dyes and heavy metals removal, adsorption technique using many type of sorbents is still the most favorable method in the removal of these contaminants from wastewaters due to its efficiency; high adsorption capacity and low operational cost method (Demirbas, 2008; Sudet al., 2008; Demirbas, 2009; Gupta & Suhas, 2009). From many type of sorbent, activated carbon (from many sources of raw materials) is currently of great interest for removal of dyes and heavy metals. Although activated carbon is a preferred sorbent, however carbon adsorption remains an expensive process and difficulties associated with regeneration (Bhatnagar & Jain, 2005). Therefore, low-cost (sorbent) alternatives to activated carbons have attracted considerable research interest in recent years.

Attempts have therefore been made to utilize waste materials as alternative sorbents, especially waste-derived siliceous materials, *i.e.* rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA). These ashes are come from the burning of rice husk, palm oil fiber/shell, and coal to generate electricity. The utilization of RHA (Chuah et al., 2005; Foo & Hameed, 2009), oil palm by-product (Issabayeva et al., 2006; Hasnain et al., 2007; Tan et al., 2008a) and CFA (Wang & Wu, 2006) as an adsorbent has been investigated/reviewed in literature. Nevertheless, most of these ashes were converted to activated carbon before utilizing as an adsorbent. Furthermore, no work has been carried out to combine these waste-derived siliceous materials as a sorbent. On the other hand, the role of silica in these waste materials in removing dyes and heavy metals is very scarcely reported.

Therefore, the objective of this study is to synthesize a RHA/PFA/CFA sorbent with good adsorption properties and to understand the role of silica in removing dyes and heavy metals. The rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA) were selected because of it is highly abundant in Malaysia.

The undertaken research project aims to achieve the following objectives:

1. To synthesize and characterize rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA) for the preparation of siliceous-based sorbent
2. To study the sorption of dyes (i.e. brilliant green dye, direct blue 71 dye, and acid violet 7 dye) and heavy metals (i.e. zinc, nickel, iron, and manganese) on RHA/PFA/CFA sorbent in batch process under various operating conditions (effect of initial concentration, effect of temperature, effect of pH solution and effect of sorption time).
3. To study the role of silica (SiO_2) in the preparation of siliceous-based sorbent for the removal dye and heavy metal
4. To study the kinetic and isotherm properties of dyes and heavy metals on RHA/PFA/CFA sorbent

CHAPTER 2

MATERIALS AND METHODS

Figure 2.1 shows the overall flowchart of the present experimental work. This is to give an overview of the research activities that have been performed throughout this study.

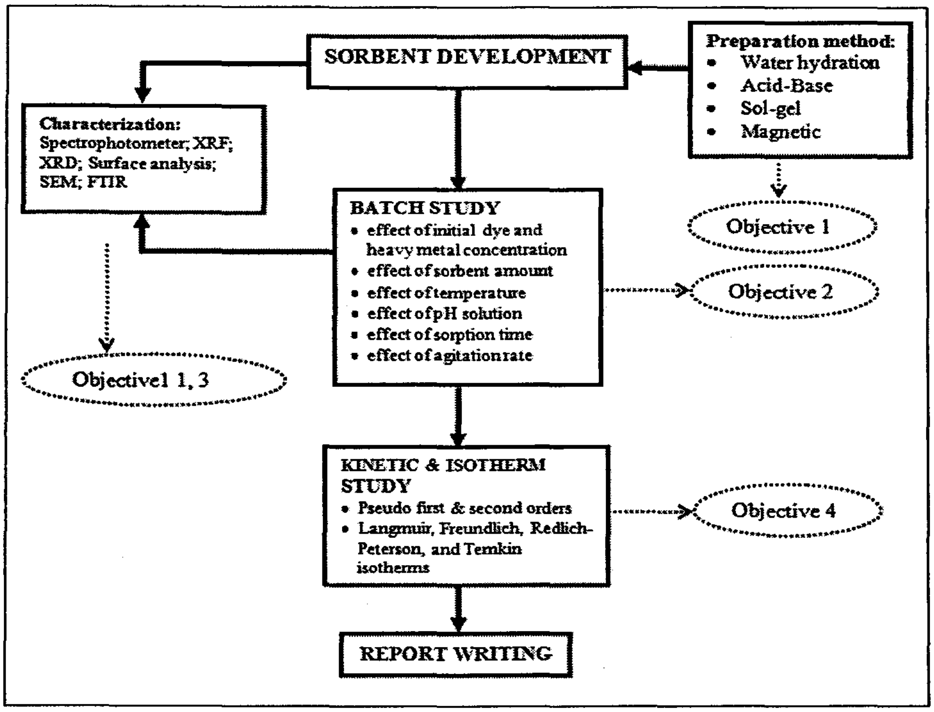


Figure 2.1. Flowchart of overall experimental activities involved in this research.

2.1 Preparation of Sorbent

The sorbents were prepared from rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA). The RHA was obtained from Kilang Beras & Minyak Sin Guan Hup Sdn. Bhd., Penang. The PFA was supplied by United Oil Palm Mill, Penang. While CFA was collected from Stesen Janakuasa Sultan Azlan Shah, Manjung, Perak. Prior to use, all three type of ashes were sieved to obtain less than 63 μm fine particle size and oven dried overnight at 110°C. The dyes (i.e. brilliant green dye, direct blue 71 dye, and acid violet 7 dye) were obtained from Sigma-Aldrich Sdn. Bhd. Other chemicals were supplied by local suppliers.

In this present study, different preparation methods were used in order to synthesize RHA/PFA/CFA sorbent.

(1). Preparation of hydrated RHA/PFA/CFA sorbent

A specific amount of RHA, PFA and CFA was added into 100 ml deionized water in the conical flask. Then the conical flask was inserted into a water bath shaker with a rotating stirring rate of 150 rpm and temperature of 65°C for 3 h. After that, the slurry was filtered and dried in the oven at 110°C for 3 h before used as sorbent.

(2). Preparation of NaOH-treated RHA/PFA/CFA sorbent

Modified RHA/PFA/CFA sorbent was prepared by mixing a specific amount of RHA, PFA and CFA into 500 ml NaOH 3 M. The mixture was stirred (constantly) using hot plate for 5 h. Then, the product was washed with warm distilled water and ethanol, filtered and then dried in the oven at 110°C for 3 h before used as sorbent.

(3). Preparation of HCl-treated RHA/PFA/CFA sorbent

For the modification of HCl-treated RHA/PFA/CFA sorbent, a specific amount of each ash (RHA, PFA, CFA) was refluxed with 500 ml of 3 M HCl at 80°C in a round-bottom flask for 3 h. The mixture was then air-cooled, filtered and repeatedly washed with deionized water until the filtrate was neutral. It was then dried in an oven at 110°C before use.

(4). Preparation of HCl-NaOH treated RHA/PFA/CFA sorbent

The prepared sorbent (Method No. 3) was further treated with 3M NaOH solution according to the preparation of Method No. 2.

(5). Preparation of RHA/PFA/CFA sorbent by sol-gel method

A specific amount of each ash (RHA, PFA, CFA) was mixed and stirred in nitric acid (HNO_3 65%) for 24 h. This removes almost all metals to negligible levels. It was then filtered and rinsed with deionized water until the pH of the rinse became constant. The mixture was subsequently dried in an oven at 110°C for one day. A specific amount of the acidified RHA/PFA/CFA sorbent was dissolved in 250 ml of 6 M NaOH, stirred for 12 h, and filtered to remove undissolved particles. The filtrant was titrated with 3 M nitric acid which contained 10% (w/w) Al^{3+} [$Al(NO_3)_3.9H_2O$ in HNO_3]. A black suspension was observed when the pH reached 11.5. Titration was carried out until the pH ~ 5. The sample was then aged for 6 days. The soft gel formed was filtered and dried at 110°C for 24 h. This sorbent was then calcined at 700°C for 5 h.

(6). Preparation of magnetic RHA/PFA/CFA sorbent

A specific amount of RHA was suspended in distilled water (500 mL). A ferric chloride solution was freshly prepared by adding 18 g $FeCl_3$ to distilled water (150 mL). A ferrous sulfate solution was prepared by adding 20 g FeSO4 to distilled water (150 mL). Both solutions were combined and vigorously stirred at 60-70 °C. The suspension formed was then added into suspension of RHA at room temperature and slowly stirred for 30 min. After mixing, 10 M NaOH (aqueous) was added drop wise into the suspension until the PH raised to 10–11. During NaOH addition, the suspension became dark brown at pH ~6 and then black at pH ~ 10. After mixing for 60 min, the suspension was aged at room temperature for 24 h and then repeatedly washed with distilled water followed by ethanol. The sorbent was vacuum filtered and dried overnight at 50 °C in a hot air oven.

2.2 Batch Adsorption Studies

Batch adsorption studies were carried out at ambient temperature by varying contact time, initial concentration of dye/heavy metal, temperature, sorbent amount, shaking rate, and pH. All experiments were carried out in 250 ml conical flasks and the total volume of the synthetic wastewater was kept at 100 ml. The pH of solution was maintained at a desired value by adding 0.1 M NaOH or $HNCO_3$. The conical flasks were shaken at a certain speed in a SK-600 horizontal shaker or Certomat S-II horizontal shaker (Sartorius AG). Samples were withdrawn at appropriate time intervals, filtered through fiber filter paper and filtrate was analyzed using DR2800 Spectrophotometer. The percentage removal of dye/heavy metal was calculated using the following relationship:

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \, x \, 100 \tag{2.1}$$

where C_o and C_e are the initial and equilibrium concentration of dye/heavy metal solution (mg/l), respectively. All experiments were duplicated to increase the precision of the results, and only the average value was reported throughout this research. In some part of this research, removal efficiency data were presented in term of normalized data. Before plotting the graph, the data were normalized in the range of 0 ($new\,x_{\min}$) to 1 ($new\,x_{\max}$) to obtain a new removal efficiency scale value data (x_{i-n}) by the following Equation (2.2),

$$x_{i-n} = \frac{x_i - x_{\min}}{x_{\max} - x_{\min}}(new\,x_{\max} - new\,x_{\min}) + new\,x_{\min} \tag{2.2}$$

2.3 Isothern and Kinetic Studies

The experimental data from the effect of initial dye and heavy metal concentrations was used in equilibrium and kinetic studies. At time t = 0 and equilibrium, the dye and heavy metal concentrations was measured and the amount of adsorption at equilibrium, qe (mg/g), was calculated by,

$$q_e = \frac{(C_o - C_e).V}{W} \tag{2.3}$$

where C_o and C_e (mg/l) are the liquid-phase concentrations of sample at initial and equilibrium, respectively. W (g) is the mass of sorbent used and V (l) is the volume of the solution.

Adsorption isotherm is fundamentally essential to explain how solutes interact with sorbents, and is critical in optimizing the use of sorbents. In the present study, the equilibrium isotherms were analyzed using the Langmuir, Freundlich, Redlich-Peterson, and Temkin isotherms. The linear form of Langmuir, Freundlich, Redlich-Peterson, and Temkin isotherms are given in Eqs (2.4), (2.5), (2.6) and (2.7), respectively.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \tag{2.4}$$

$$\ln q_e = \ln K_F + \frac{1}{n}\ln C_e \tag{2.5}$$

$$\ln(K_R \frac{C_e}{q_e} - 1) = \ln a_R + \beta \ln C_e \tag{2.6}$$

$$q_e = B_1 \ln K_t + B_1 \ln C_e \tag{2.7}$$

where the constant Q_0 signifies the adsorption capacity (mg/g) and b is related with the energy of the adsorption (l/mg), K_F and n are Freundlich constants, K_R is the R–P isotherm constant (l/g), a_R is the R–P isotherm constant (l/mg), β is the exponent which lies between 1 and 0, and K_t and B_1 are Temkin isotherms which is related to maximum binding energy and heat of adsorption, respectively.

2.4 Chemical and Physical Analysis

The concentration of the dye and heavy metal in the solution before and after sorption treatment was analyzed using DR2800 Spectrophotometer. Apart from that, selected RHA/PFA/CFA sorbents, before and after the adsorption process, was characterized based on its physical and chemical properties using various analytical instruments. For example, the chemical composition of each raw RHA, PFA, CFA as well as the prepared RHA/PFA/CFA sorbents was determined using X-ray Fluorescence (XRF) spectrometer. The specific surface area of the prepared sorbents and raw materials were determined using Mastersizer 2000 and/or BET (Brunner-Emmett-Teller) methods on an Autosorb-1 Quantachrome analyzer. Scanning electron microscope (SEM) was used to examine the sorbent surface morphologies and X-ray diffraction (XRD) spectrum was recorded using X-ray diffractometer to investigate the various phases present in the sorbent. The specific surface functional groups in the sorbent were determined using Fourier Transform Infrared (FTIR) spectroscopy.

CHAPTER 3

RESULTS AND DISCUSSION

The chemical composition of rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA), which was analyzed using Rigaku RIX 3000 X-ray Fluorescence (XRF) spectrometer, is shown in Table 3.1. It was shown that the silica (SiO_2) was the significant component inside these ashes besides other metals.

Table 3.1 Chemical composition of RHA, PFA and CFA.

Composition (Oxides)	Percentage (wt%)		
	RHA	PFA	CFA
SiO_2	63.31	34.00	31.00
C	18.63	25.00	24.00
K_2O	2.23	2.90	0.68
P_2O_5	0.58	2.00	0.12
CaO	0.43	5.00	6.60
MgO	0.42	3.10	3.50
Fe_2O_3	0.26	5.30	10.00
SO_3	0.20	0.26	0.33
TiO_2	0.09	0.25	0.48
Cl_2O	0.18	0.03	trace
Al_2O_3	0.11	5.50	11.00
Others	0.01	0.24	0.29
LOI	13.54	16.42	12.00

3.1 A Study on the Removal Characteristic of Zinc ion (Zn^{2+}) from Synthetic Wastewater Using a Novel Waste-Derived Siliceous Sorbent

In this study, the removal of zinc (Zn^{2+}) from synthetic wastewater was investigated by adsorption method using RHA/PFA/CFA sorbent prepared by sol-gel method (Adam & Chua, 2004; Adam et al., 2006).

3.1.1 Effect of Sorbent Amount

The amount of sorbent is one of the important parameters to obtain the quantitative adsorption of Zn^{2+} from synthetic wastewater. The dependence of Zn^{2+} adsorption on amount was studied by varying the amount of RHA/PFA/CFA sorbent from 0.25 to 4 g while keeping other parameters (contact time, shaking rate, pH and initial Zn^{2+} concentration) constant. Figure 3.1 shows the effect of sorbent amount on removal efficiency of Zn^{2+}. It can be observed that removal efficiency of Zn^{2+} increases with increase in sorbent amount. Zn^{2+} removal efficiency significantly increased from 93.3% to 98.5% when the amount of RHA/PFA/CFA sorbent was increased from 0.25 to 1 g. An increase in the adsorption with the amount of sorbent might be attributed to greater surface area and the availability of more exchangeable sites for metal ions. At the sorbent amount of greater than 1 g, the Zn^{2+} removal efficiencies are almost similar, hence no additional adsorption of Zn^{2+} to adsorption sites of the sorbent. Although, there is a slightly decrease in Zn^{2+} removal efficiency from 2 to 4 g, this might be due to desorption effect, however, the effect is not significant.

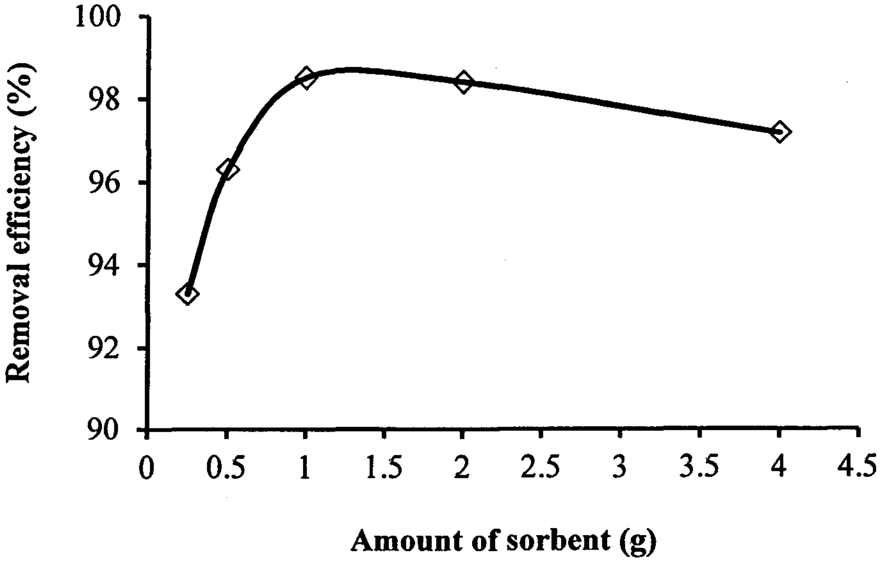


Figure 3.1 Effect of sorbent amount on the removal of Zn^{2+}.

3.1.2 Effect of Contact Time

Equilibrium time is another main important parameters for an economical wastewater treatment process. To establish a suitable contact time between the RHA/PFA/CFA sorbent and Zn^{2+} solution, the removal efficiency of Zn^{2+} were studied as a function of time over 0.5 to 2.5 h. Figure 3.2 shows the effect of contact time on removal efficiency of Zn^{2+}. The results showed that a half-hour (0.5 h) equilibrium time for the RHA/PFA/CFA sorbent is enough to remove more than 95% of Zn^{2+}. This shows that adsorption site are well exposed, thus quick reaction is occurred. As the contact time increase to 1 h, about 97.2% Zn^{2+} removal efficiency was achieved. Above 1 h of contact time, there were no significant Zn^{2+} removal efficiency was observed, therefore equilibrium time was reached in 1 h. Thus, to make sure that equilibrium was reached, it was decided to use the equilibrium time of 1 h in the rest of this study.

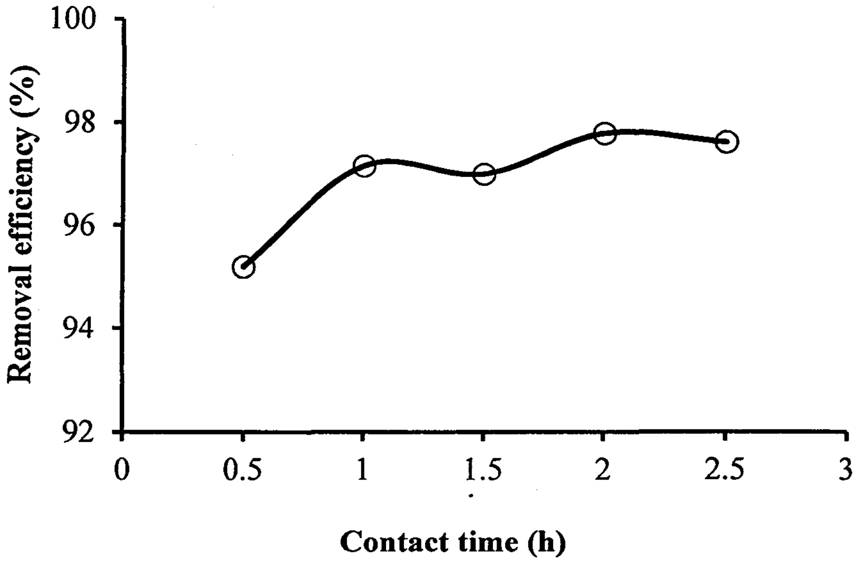


Figure 3.2 Effect of contact time on the removal of Zn^{2+}.

3.1.3 Effect of Shaking Rate

The effect of shaking rate was studied by varying the shaking rate from 50 to 250 rpm while keeping other parameters constant. Results shown in Figure 3.3 indicate that removal efficiency of RHA/PFA/CFA sorbent increased from 92.8% to 97.5% when shaking rate increased from 50 to 100 rpm. An enhanced adsorption rate at higher shaking rate is probably due to an increase in the mobility of sorbing species (Raji & Anirudhan, 1996). Apart from that, the increase of the shaking rate might improve the diffusion of the zinc ions towards the surface of the RHA/PFA/CFA sorbents. For shaking rate greater than 100 rpm, the removal efficiency of Zn^{2+} remained constant, thus a shaking rate of 100 rpm is sufficient to assure the surface binding for zinc uptake.

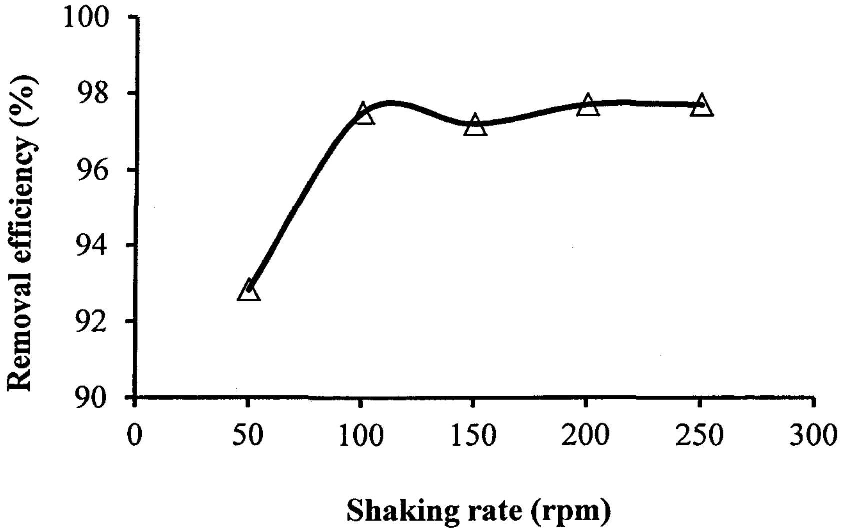


Figure 3.3 Effect of shaking rate on the removal of Zn^{2+}.

3.1.4 Effect of pH

The behavior of metal ions in aqueous solutions (synthetic wastewater) is influenced by pH of the solution. The pH does not only determine the speciation of metal ions in the solution but also determines the surface charge of the sorbent (Cho et al., 2005). Thus, the role of pH was examined in the pH range 2 – 10 on the Zn^{2+} removal. The effect of pH on the Zn^{2+} removal is presented in Figure 3.4. It was shown that increasing pH of the solution from 2 to 8 caused the Zn^{2+} removal efficiency increased from 87% to 97%. The low adsorption removal of Zn^{2+} by RHA/PFA/CFA sorbents at low pH values can be attributed to the fact that at low pH values, the H^+ ion concentration is high, therefore protons can compete with the zinc cations for surface adsorption sites of the sorbent, since at low pH zinc are present in solution as Zn^{2+} free cations. Furthermore when pH increases, there is a decrease in positive surface charge, which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of RHA/PFA/CFA sorbent's active site which favor adsorption process to occur.

From Figure 3.4, it was also found that there was a reduction in Zn^{2+} removal efficiency to 94%, when equilibrium pH was increased to 10. Therefore, in this study pH 8 was considered as an optimum condition for adsorption process. Different observations were reported by other researchers for Zn^{2+} adsorption. Study by Abdel Salam et al. (2011) reported that the optimum pH of 6 was obtained for Zn^{2+} adsorption using peanut husk charcoal and natural zeolite. Similar to that, Amuda et al. (2007) also found the optimum pH of 6 for the removal of Zn^{2+} using composite sorbents (chitosan-coated acid treated coconut shell carbon). The different results obtained in this study are probably caused by structural changes being effected in the Zn^{2+} molecules and the surface adsorption characteristics of RHA/PFA/CFA sorbent. Therefore, this study shows that the pH of the solutions plays an important role in the whole Zn^{2+} adsorption process and on the adsorption capacity of RHA/PFA/CFA sorbents.

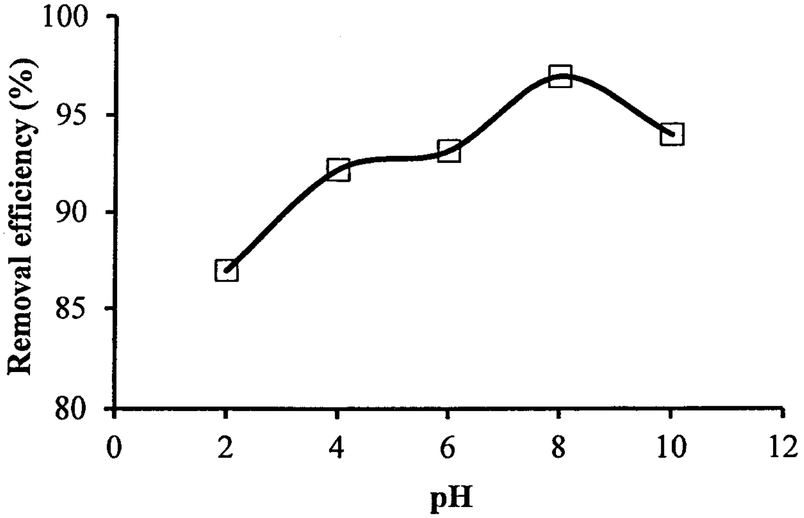
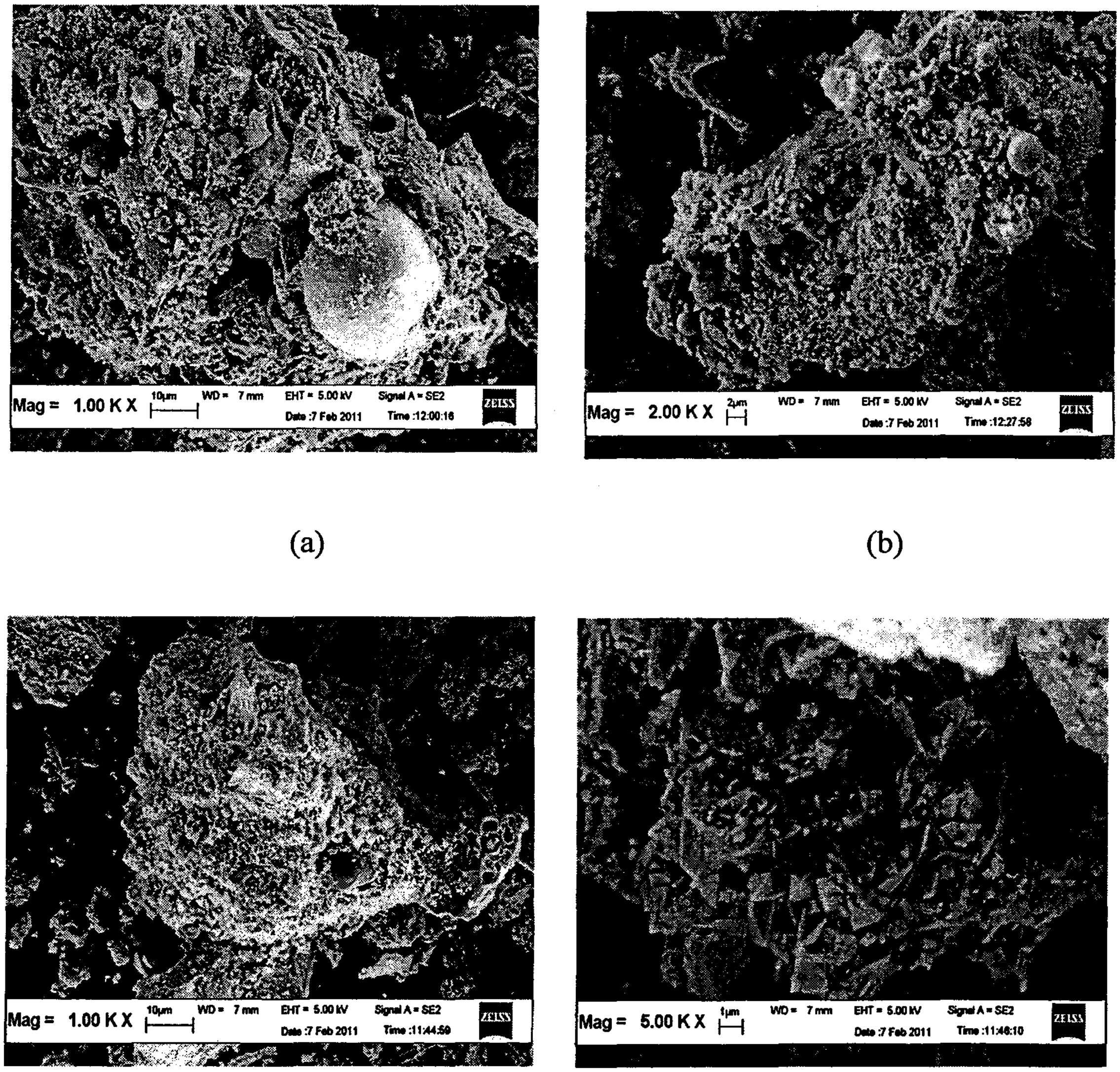


Figure 3.4 Effect of pH on the removal of Zn^{2+}.

3.1.5 Characterization of RHA/PFA/CFA Sorbents

The surface morphology of the selected RHA/PFA/CFA sorbents was examined using scanning electron microscopy (SEM). Figure 3.5 shows the image of the selected RHA/PFA/CFA sorbents before and after treatment with Zn^{2+}. It was observed (Figure 3.5a & b) that RHA, PFA and CFA are combined to each other to form larger or complex particles with compact structures during the preparation of sorbent using sol-gel method. From previous studies, raw RHA was reported to have uniform structure with a dome-shaped and/or a skeletal structure (Dahlan et al., 2008). While raw PFA usually has the shape of flat plate layers with small particles deposited on its surface (Zainudin et al., 2005) and raw CFA typically consists of smooth sphere particles/structures (Lee et al., 2006). After the adsorption of Zn^{2+}, the surface of the RHA/PFA/CFA sorbents was found to have more compact structures covered by lumps of smaller particles (Figure 3.5c), which is most probably the zinc ions. Closer view at higher magnification (5000X) shows that the sorbent surface consists of a tetrahedron and/or octahedron-like structures with other small granular particles (Figure 3.5d), and this might be caused by zinc sorption which covered the external surface of RHA/PFA/CFA sorbents.



(a) (b)

(c) (d)

Figure 3.5 Scanning electron micrograph of prepared RHA/PFA/CFA sorbents at (a) 1000X, (b) 2000X and spent RHA/PFA/CFA sorbents at (c) 1000X and (d) 5000X magnifications.

To further strengthen this study, selected RHA/PFA/CFA sorbents was also characterized for particle size distribution before and after Zn^{2+} removal. The particle size distribution of selected RHA/PFA/CFA sorbents is shown in Figure 3.6. It was shown that RHA/PFA/CFA sorbent before and after treated with Zn^{2+} has bimodal-type particle size distribution, with two (nearly) similar range. The bimodal-type particle size distribution of the prepared and spent RHA/PFA/CFA sorbents might be resulted from a process involving breakup of multiple sources of particles or variable growth mechanisms during the preparation method and as well as from a process involving the agglomerating of smaller particles (which is most probably the zinc ions that cover the surface of the sorbent) during the adsorption process.

The results also showed that the volume of the first particle size distribution range (*i.e.* RHA/PFA/CFA sorbent after treated with Zn^{2+}) is reduced as compared to RHA/PFA/CFA sorbent before treated with Zn^{2+}. Meanwhile, the volume of the second particle size distribution range of RHA/PFA/CFA sorbent after treated with Zn^{2+} is increased, which means that higher particle size distributions range are available after Zn^{2+} ion adsorption on the RHA/PFA/CFA sorbent surface.

It was also found that the specific surface area of RHA/PFA/CFA sorbent before treated with Zn^{2+} was much higher (0.774 m^2/g) than that of the RHA/PFA/CFA sorbent after treated with Zn^{2+} (0.666 m^2/g). The lower specific surface area of RHA/PFA/CFA sorbent after treated with Zn^{2+} could be due to the agglomerating of smaller particles (which is most probably the zinc ions that cover the surface of the sorbent) during the adsorption process. Apart from that, the average surface weighted mean and average volume weighted mean are dramatically increased (from 7.753 μm and 65.005 μm, respectively) to 15.984 μm and 353.178 μm, respectively, after the RHA/PFA/CFA sorbent was treated with Zn^{2+}.

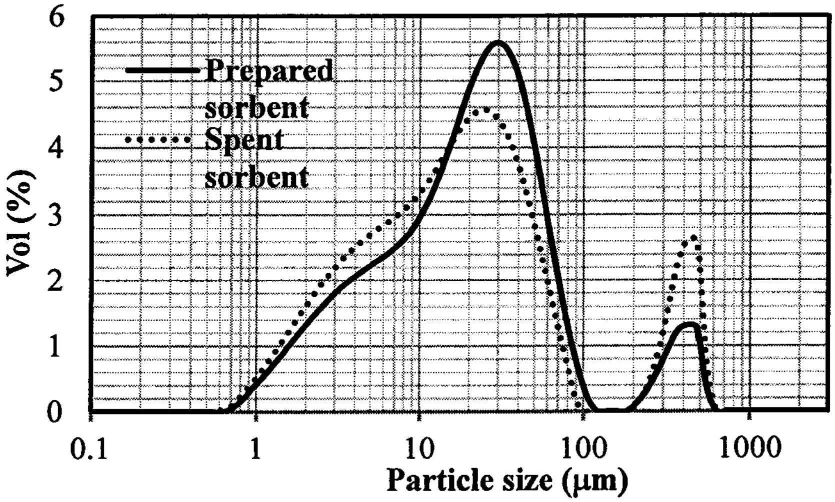


Figure 3.6 Particle size distribution of RHA/PFA/CFA sorbents.

From the results of this study, it can be concluded that waste-derived siliceous materials, *i.e.* rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA), can be prepared and used as an effective sorbent for the removal of zinc ion (Zn^{2+}) from synthetic wastewater. All experimental parameters, such as amount of sorbent, contact time, shaking rate, and pH affecting the adsorption of Zn^{2+}. During all optimum conditions tested, it was found that RHA/PFA/CFA sorbent was able to remove more than 95% of Zn^{2+} from synthetic wastewater.

3.2 Manganese (Mn^{2+}) Removal From Aqueous Solutions Using RHA/PFA/CFA Sorbent.

In this study, water hydration and reflux methods were used to prepare RHA/PFA/CFA sorbent in order to select the best method for sorbent preparation. Different prepared RHA/PFA/CFA sorbents were resulted from this preparation, i.e. hydrated RHA/PFA/CFA sorbent, hydrated RHA/PFA/CFA sorbent with $Ca(OH)_2$ addition, NaOH-treated RHA/PFA/CFA sorbent, HCl-treated RHA/PFA/CFA sorbent, and HCl-NaOH treated RHA/PFA/CFA sorbent and these sorbents were labeled as sorbent S1-A, S1-B, S2, S3 and S4, respectively.

Table 3.2 shows the result of manganese removal using different prepared RHA/PFA/CFA sorbents. It was shown that S- 1(B) sorbent (hydrated RHA/PFA/CFA sorbent with $Ca(OH)_2$ addition) was found to have highest manganese removal. Therefore, S- 1(B) sorbent prepared using water hydration method with $Ca(OH)_2$ addition was used for the next study.

Table 3.2 Manganese removal based on different preparation methods

Method	Sorbent label	Removal efficiency (%)
Water hydration	S- 1(A)	96
	S- 1(B)	99
Reflux	S- 2	92
	S-3	79
	S-4	98

After selecting the sorbent based on preparation method, the water hydration method with $Ca(OH)_2$ addition was used to prepare the sorbents with various RHA/PFA/CFA ratio. It was found out from Table 3.3 that sorbent prepared with RHA/PFA/CFA ratio of 0:6:3 gave the highest manganese removal. Thus, it was decided to prepare hydrated PFA/CFA sorbent with $Ca(OH)_2$ addition (with PFA/CFA ratio of 6:3) in the rest of this study.

Table 3.3 Manganese removal based on ratio

RHA/PFA/CFA ratio			Manganese removal (%)
RHA	PFA	CFA	
3	3	3	97
0	3	3	97
3	0	3	97
3	3	0	98
0	3	6	97
6	3	0	96
3	0	6	97
6	0	3	98
3	6	0	96
0	6	3	99

3.2.1 Effect of Contact Time

Figure 3.7 shows manganese removal efficiency as function of contact time. It is shown that increase in shaking time increased removal efficiency until equilibrium adsorption was established. It is obvious that increase in contact time from 5 to 60 minutes enhanced the percent removal of manganese significantly. The initial rapid adsorption gives away a very slow approach to equilibrium. The nature of sorbent and its available sorption sites affected the time needed to reach the equilibrium. In the beginning fast adsorption, may be explained due to the availability of more number of adsorption sites. After initial adsorption of adsorbate, the available sites in the adsorbent reduced and thus rate of adsorption further decreased, which attained a limiting value at equilibrium

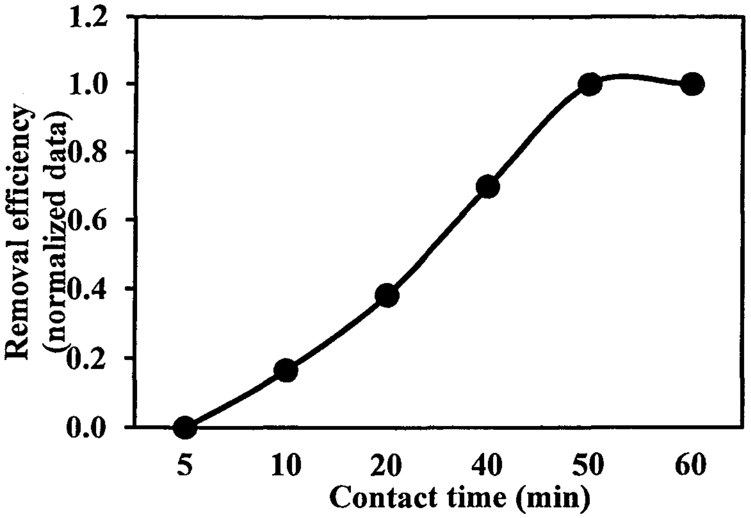
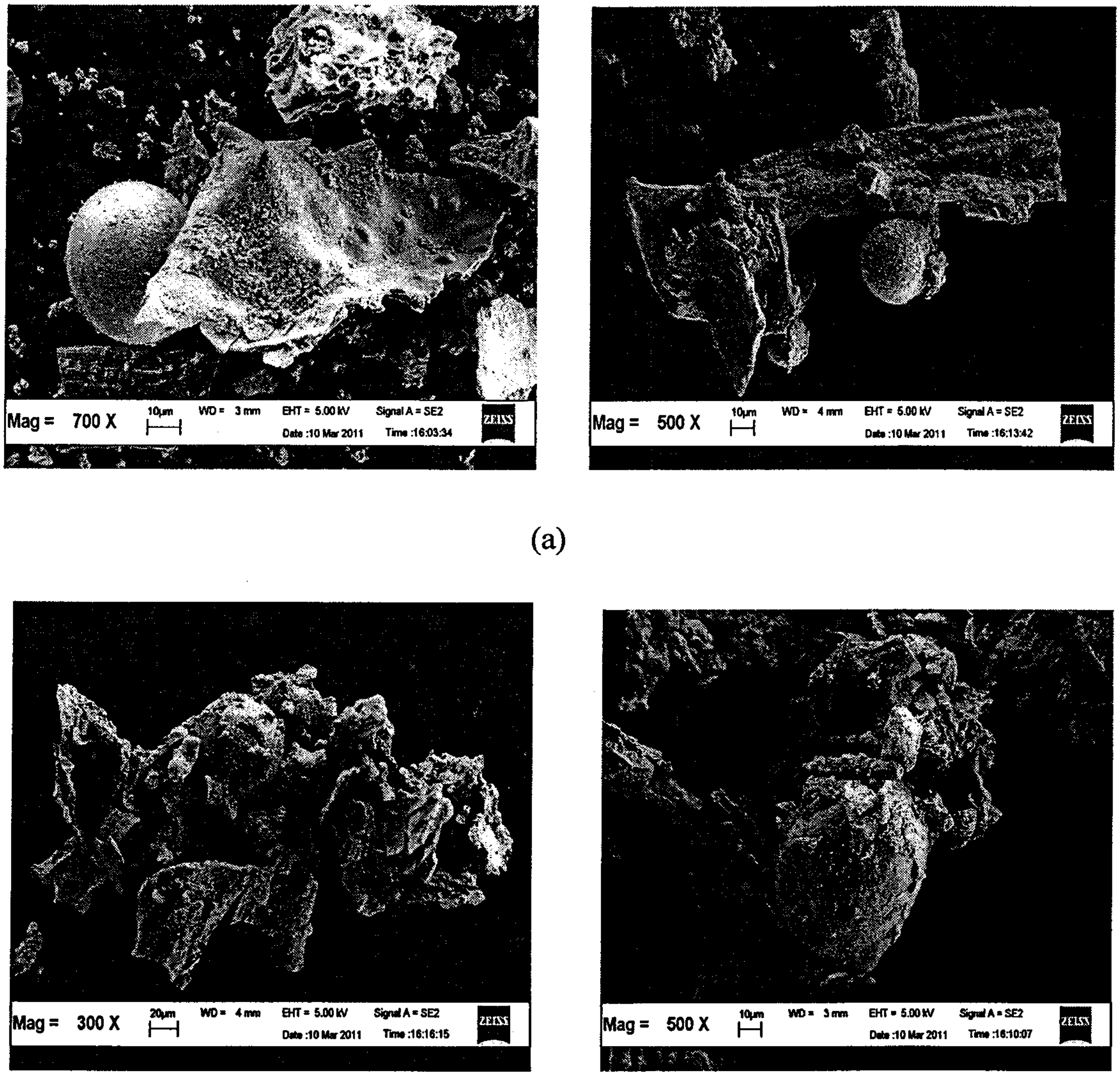


Figure 3.7 Effect of contact time on the adsorption of Mn^{2+} using PFA/CFA sorbent.

3.2.2 Scanning Electron Microscopy (SEM) Analysis

Figure 3.8 shows the image of the PFA/CFA sorbent before and after treatment with manganese. SEM photographs shown in Figure 3.8(a) revealed that PFA and CFA are combined to each other to form larger or complex particles during the preparation. From previous studies, raw PFA usually has the shape of flat plate layers with small particles deposited on its surface and raw CFA typically consists of smooth sphere particles/ structures. After the adsorption of manganese, the surface of the PFA/CFA sorbent was found to have more compact structures. The rough irregular-shaped particles are attached on the surface and inside of the PFA/CFA sorbent and this might be caused by manganese sorption which covered the external surface of PFA/CFA sorbent as shown in Figure 3.8(b).



(a)

(b)

Figure 3.8 Scanning electron micrograph of (a) prepared PFA/CFA sorbent and (b) PFA/CFA sorbent after treated with manganese.

3.3 RHA/PFA/CFA Sorbent for Removal of Ni^{2+} From Aqueous Solutions

In the present study, the preparation of sorbent from waste-derived siliceous materials was investigated for the removal of nickel ion (Ni^{2+}) from aqueous solutions. The sorbents were prepared using the water hydration method (Dahlan et al., 2008). In the preliminary study, the sorbents were prepared from RHA, PFA and CFA in order to select the best ratio between the ashes. In this study, all removal efficiency data were presented in term of normalized data.

The amount of ash is one of the important parameters in the preparation of sorbent using hydration method, therefore it is necessary to choose the best ratio between RHA, CFA and PFA; but not all three types of ashes have to be used to synthesize the sorbent. In this study, the sorbent was only prepared by combination of two ashes with the aim to reduce complexity of the prepared sorbent. Figure 3.9 shows the effect of various ratios in the preparation of waste-derived siliceous materials as a sorbent in removing Ni^{2+}. The ratios shown in Figure 3.9 represent the actual mass (g) of ashes used in the sorbent preparation. It can be observed that amount of each ash (in sorbent preparation) was found to have effect on resulting sorbent in removing Ni^{2+} from synthetic wastewater. Although the effect was not too significant, however for RHA/CFA sorbent with ratio of 6:3 (ratio number six), the removal efficiency significantly dropped as compared to other ratios. At this moment, the influential factor for various ratios in synthesizing sorbents from waste-derived siliceous materials that provide a high Ni^{2+} removal efficiency is still unclear. From all the ratios, it can be observed that sorbent contains RHA and PFA (with ratio of 3:3) gave the highest Ni^{2+} removal efficiency. Therefore, to further investigate the effect of these waste-derived siliceous materials as a sorbent in removing Ni^{2+}, it was decided to prepare hydrated RHA/PFA sorbent (with ratio of 3:3) in the rest of this study.

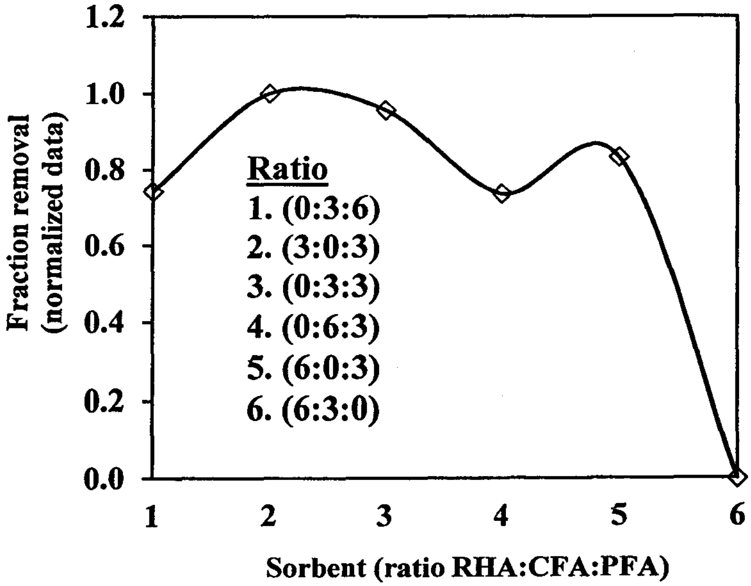


Figure 3.9 Effect of ash ratio in the preparation of waste-derived siliceous sorbent on the removal of Ni^{2+}. (Experimental conditions: initial concentration, 25 mg/L; contact time, 2 h; shaking rate, 130 rpm; sorbent dosage, 0.3 g; room temperature).

3.3.1 Effect of Contact Time

To establish a suitable contact time between the RHA/PFA sorbent and synthetic wastewater, the removal efficiency of Ni^{2+} were studied as a function of time from 5 to 60 minutes. The removal efficiency of Ni^{2+} increased with the increase in shaking time until equilibrium adsorption was established at 30 minutes (Figure 3.10). This shows that adsorption sites are well exposed, thus quick reaction occurred. The results also show that at 30 minutes equilibrium time, the RHA/PFA sorbent is enough to remove more than 90% of Ni^{2+}. The nature of sorbent and its available sorption sites affect the time needed to reach equilibrium (Bhattacharya et al., 2008). In the beginning, fast adsorption may be explained due to the availability of more number of adsorption sites. After initial adsorption of adsorbate, the available sites in the adsorbent reduced and thus, the rate of adsorption further decreased, which attained a limiting value at equilibrium. Above 30 minutes of equilibrium time, there no further significant Ni^{2+} removal. Thus, it was decided to adopt the equilibrium time as 30 minutes for the rest of this study.

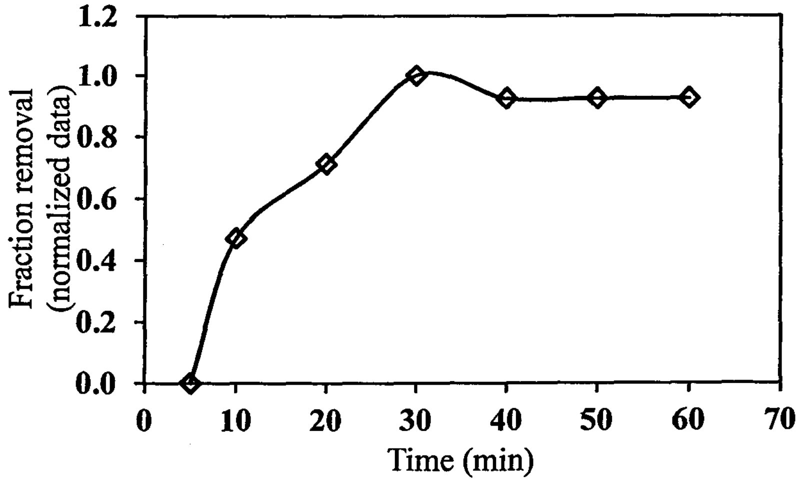


Figure 3.10 Effect of contact time on the removal of Ni^{2+} using RHA/PFA sorbent (Experimental conditions: initial concentration, 130 mg/L; shaking rate, 130 rpm; sorbent dosage, 0.3 g; room temperature)

3.3.2 Effect of Nickel Concentration

The effect of initial concentrations on metal ion uptake was investigated by varying the nickel concentration from 25 to 200 mg/L. In this study, the RHA/PFA sorbent efficiency follows a bell shaped curve (Figure 3.11). It can be seen from Fig. 3, the Ni^{2+} removal efficiencies were markedly increased with the initial Ni^{2+} concentration up to 100 mg/L and remained constant up to 130 mg/L. The rapid increase of nickel removal at low initial concentration might be due the surface area and the availability of adsorption sites of RHA/PFA sorbent were relatively high and the nickel ions were easily adsorbed. As the Ni^{2+} concentration increased (above 130 mg/L) the total available adsorption sites became limited and/or saturated and the RHA/PFA sorbent could no longer bind further Ni^{2+}, resulting in a decrease in the Ni^{2+} removal efficiencies.

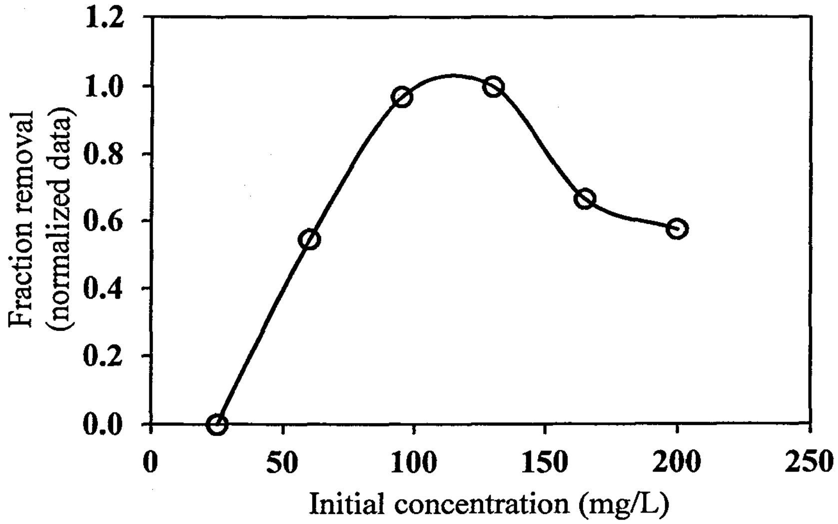


Figure 3.11 Effect of nickel concentration on the removal of Ni^{2+} using RHA/PFA sorbent (Experimental conditions: contact time, 2 h; shaking rate, 130 rpm; sorbent dosage, 0.3 g; room temperature)

3.3.3 Effect of Agitation Rate

The effect of agitation rate was investigated by varying the agitation rate from 100 to 210 rpm while keeping other parameters constant. The effect of agitation rate on removal efficiency of Ni^{2+} is shown in Figure 3.12. As can be seen in Figure 3.12, the removal efficiency of RHA/PFA sorbent increased when shaking rate increased from 100 to 130 rpm. More than 90% of Ni^{2+} is removed from the synthetic wastewater at agitation rate of 130 rpm. An enhanced of Ni^{2+} removal efficiency at higher agitation rate is probably due to an increase in the mobility of adsorbing species (Raji & Anirudhan, 1996). Apart from that, the increase of the agitation rate might improve the diffusion of nickel ions towards the surface of the RHA/PFA sorbents. For agitation rate greater than 130 rpm, the removal efficiency of Ni^{2+} was found to decrease. This might be due to higher boundary layer resistance to mass transfer in the bulk. Thus, it is concluded that agitation rate above 130 rpm is not suitable to ensure the surface binding of Ni^{2+}.

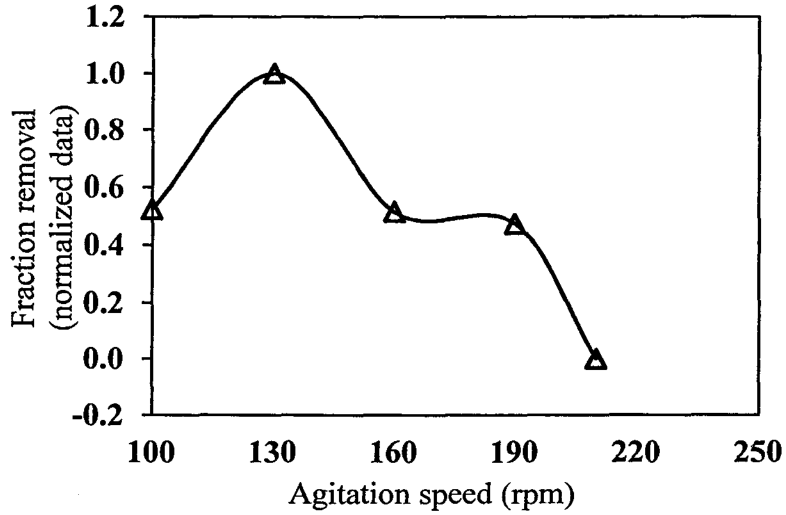


Figure 3.12 Effect of shaking rate on the removal of Ni^{2+} using RHA/PFA sorbent (Experimental conditions: initial concentration, 130 mg/L; contact time, 2 h; sorbent dosage, 0.3 g; room temperature)

3.3.4 Effect of pH

The hydrogen ion concentration (pH) of the aqueous solutions (synthetic wastewater) is an important parameter since it effects not only the surface charge of sorbent, but also the degree of ionization and speciation of sorbent during adsorption (Cho et al., 2005). The behavior of Ni^{2+} ions in aqueous solutions was examined in the pH range 2 – 10. The effect of pH on the Ni^{2+} removal is presented in Figure 3.13. It was shown that increasing pH solution from 2 to 4 caused the Ni^{2+} removal efficiency to increase. The low adsorption removal of Ni^{2+} by RHA/PFA sorbents at low pH values can be attributed to the fact that at low pH values, the H^+ ion concentration is high, therefore protons can compete with the nickel cations for surface adsorption sites of the sorbent, since at low pH nickel are present in solution as Ni^{2+} free cations. Furthermore when pH increases, there is a decrease in positive surface charge, which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of RHA/PFA sorbent's active site which favor adsorption process to occur.

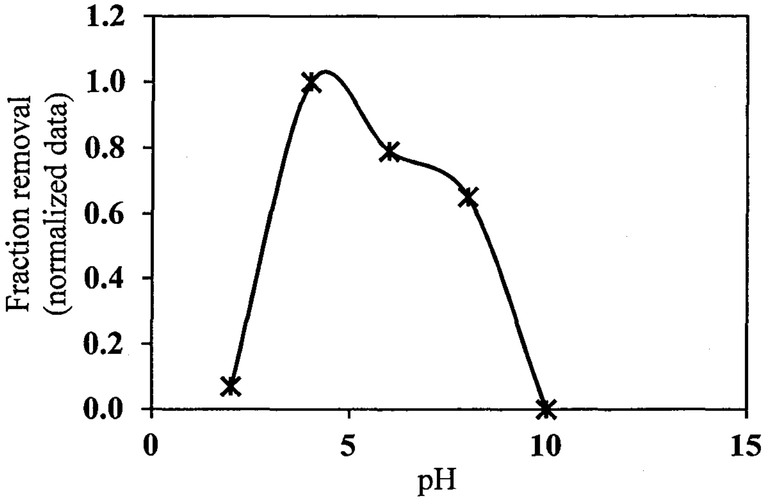


Figure 3.13 Effect of pH on the removal of Ni^{2+} using RHA/PFA sorbent (Experimental conditions: initial concentration, 130 mg/L; contact time, 2 h; shaking rate, 130 rpm; sorbent dosage, 0.3 g; room temperature)

Other than that, there was a reduction in Ni^{2+} removal efficiency at pH above 4. The reduction of nickel removal at pH above 4 might be due to the fact that the covalent bonds between Ni^{2+} and the surface functional group of RHA/PFA sorbents are very weak. Therefore, in this study pH 4 was considered as the optimum condition for adsorption process. Similar result was reported by Liu et al. (2009) for Ni^{2+} removal from synthetic wastewater using chemically modified and raw brown algae sorbents. They found that the optimal Ni^{2+} removal efficiencies were observed in the pH range of 4.3–6.5. However, different observations were reported by other researchers for NI^{2+} adsorption. Study by Kehinde et al. (2009) reported that higher Ni^{2+} adsorption was obtained at pH 7-8 using sorbent prepared from coconut husk and teak tree bark. In another study, Srivastava et al. (2006) found that maximum Ni^{2+} removal efficiency occurred at pH 6 using sorbent prepared from rice husk ash. The different results obtained in this study are probably caused by structural changes being effected in the Ni^{2+} molecules and the surface adsorption characteristics of RHA/PFA sorbent. Therefore, this study shows that the pH of the solutions plays an important role in the whole Ni^{2+} adsorption process and on the adsorption capacity of RHA/PFA sorbents.

3.3.5 Characterization of RHA/PFA Sorbents

The particle size distribution of the selected RHA/PFA sorbent was examined and the result is shown in Figure 3.14. It was shown that RHA/PFA sorbent before treated with Ni^{2+} (prepared sorbent) has a wider range of particle size distributions as compared to RHA/PFA sorbent after treated with Ni^{2+} (spent sorbent). The average volume of the particle size distribution range of spent RHA/PFA sorbents is higher than the prepared RHA/PFA sorbents, which means that higher particle size distributions range are formed after Ni^{2+} adsorption on the RHA/PFA sorbent. It was also found that the specific surface area of the prepared RHA/PFA sorbent was much higher (0.576 m^2/g) than that of the spent RHA/PFA sorbents (0.153 and 0.203 m^2/g for spent sorbent 1 and 2, respectively). The lower specific surface area of spent RHA/PFA sorbents could be due to the agglomerating of smaller particles (which is most probably the nickel ions that cover the surface of the sorbent) during the adsorption process. Apart from that, the surface weighted mean and volume weighted mean are dramatically increased (from 10.417 μm and 67.855 μm, respectively) to 39.118 μm and 142.156 μm, respectively, after the RHA/PFA sorbent was treated with Ni^{2+} (spent sorbent 2).

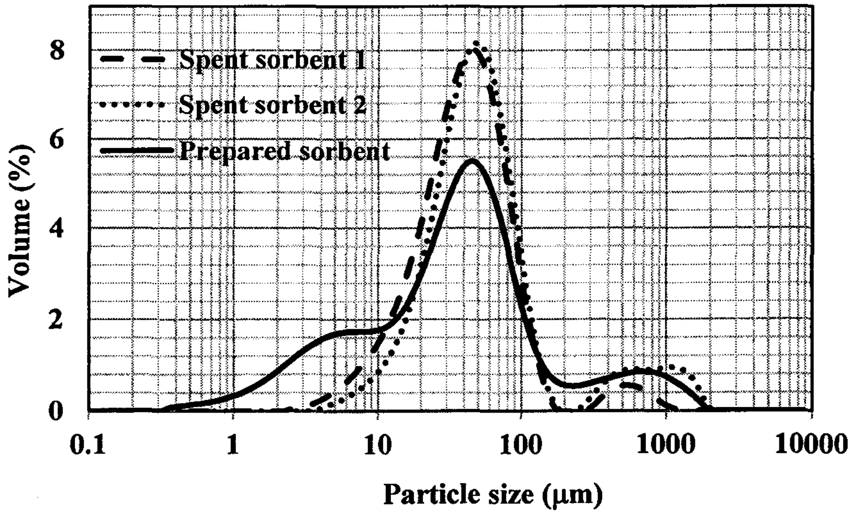
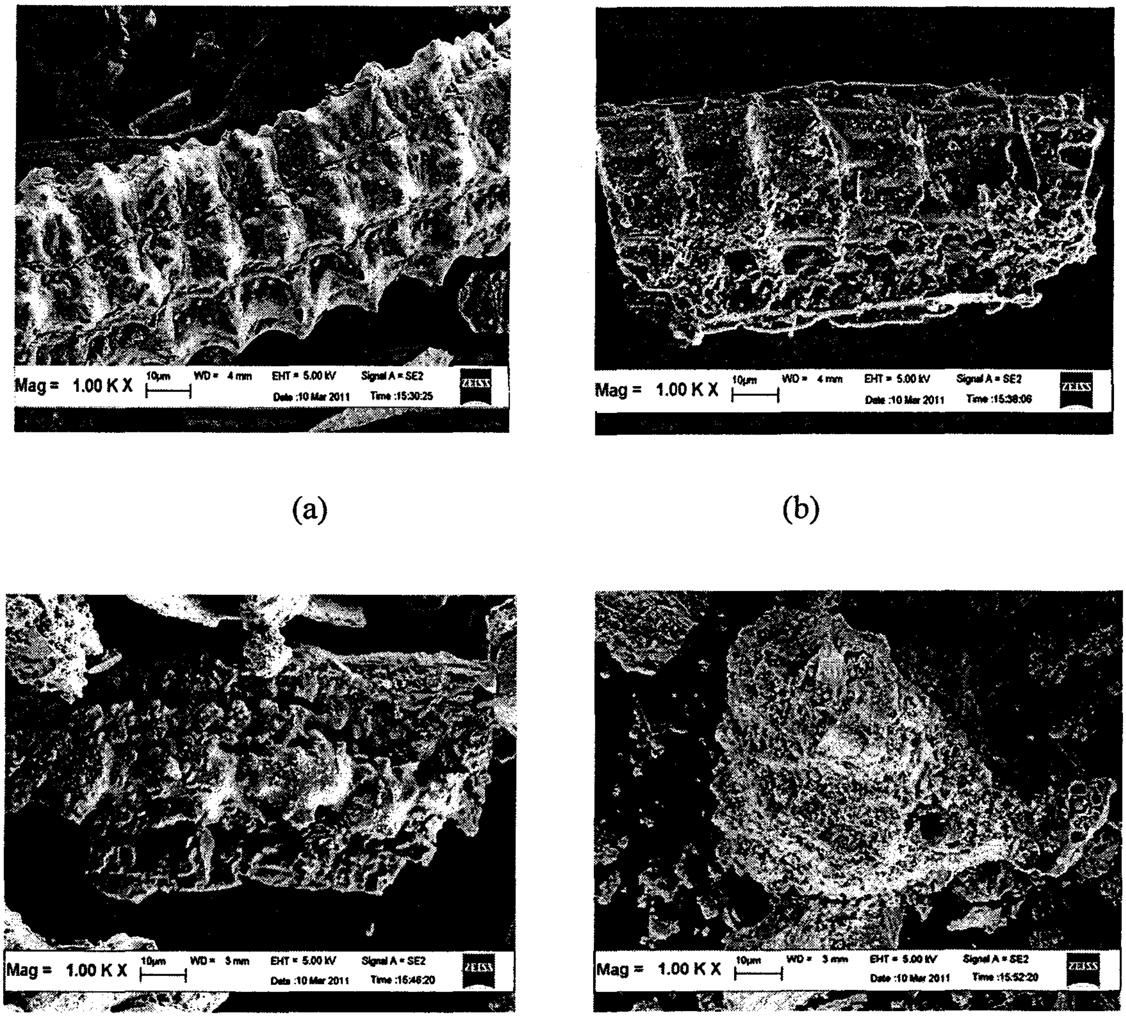


Figure 3.14 Particle size distribution of RHA/PFA sorbents

To further strengthen this study, selected RHA/PFA sorbent was also characterized for surface morphology using scanning electron microscopy (SEM). The surface morphology of the raw RHA, PFA, prepared RHA/PFA sorbent and spent RHA/PFA sorbent is shown in Figure 3.15. It can be observed from Figure 3.15(a), the surface of raw RHA has a dome-shaped (or a skeletal) structure. Raw PFA (Figure 3.15b) has the shape of flat plate layers with small particles deposited on its surface. After the sorbent was prepared by water hydration method, RHA and PFA are combined to each other to form larger or complex particles with compact structures (Figure 3.15c). After the adsorption of Ni^{2+}, the surface of the RHA/PFA sorbents was found to have more compact structures covered by lumps of smaller particles (Figure 3.15d) which is most probably the nickel ions that covered the external surface of RHA/PFA sorbent.



(a) (b)

(c) (d)

Figure 3.15 Scanning electron micrograph of (a) raw RHA, (b) PFA, (c) prepared RHA/PFA sorbent and (d) RHA/PFA sorbent after treated with nickel.

It is evident from batch adsorption studies that sorbent prepared from waste-derived siliceous materials especially the one prepared from RHA and PFA, could be used as an effective sorbent for the removal of nickel ions (Ni^{2+}) from synthetic wastewater. More than 90% of Ni^{2+} could be removed under optimum conditions.

3.4 Novel Waste-Derived Sorbent for Fe^{2+} Removal of From Aqueous Solutions

In this study, water hydration method (Dahlan et al., 2008) was used to prepare RHA/PFA/CFA sorbent. Various effects on the removal efficiency of iron was investigated. In this study, all removal efficiency data were presented in term of normalized data. Before plotting the graph, the data were normalized in the range of 0 to 1 to obtain a new removal efficiency scale value data.

3.4.1 Effect of Initial Concentration on Fe^{2+} Removal

The effect of initial concentration on removal of Fe^{2+} was investigated by varying the iron concentration in the range of 25 to 200 mg/l as illustrated in Figure 3.16. It was found that the fraction removals of iron obviously increased with increasing of initial iron concentration up to 60 mg/L. This rapid increment can be explained by the surface area and the availability of adsorption sites of RHA/PFA/CFA sorbent were relatively high and the iron metal were easily adsorbed. This result also reflects that the uptake of iron from aqueous solution was concentration dependent. This might be due to the increase in driving force of the iron concentration gradient (Uddin et al., 2009). As the concentration reached 95 mg/L, the fraction removal started to decrease with increasing of concentration due to total available adsorption sites or active sites became limited and/or saturated. Therefore, the RHA/PFA/CFA sorbent could no longer bind further Fe^{2+}. In can be concluded that iron can only be removed until it reach the equilibrium stage, and then no more iron were removed from the solution.

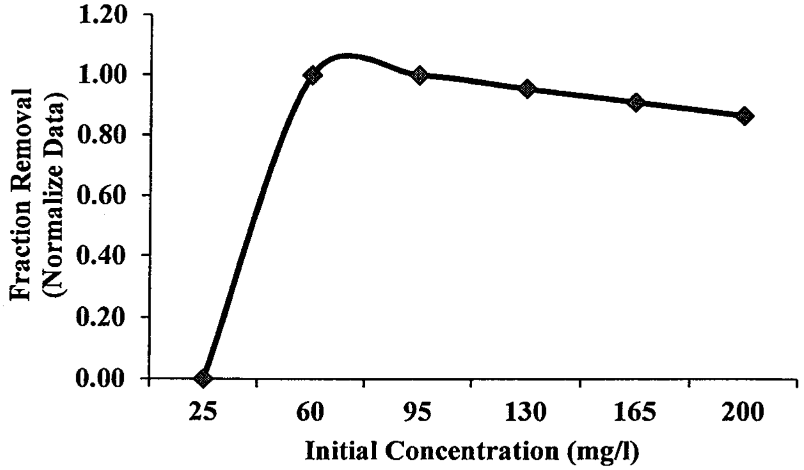


Figure 3.16 Effect of initial Fe^{2+} concentration on the removal of Fe^{2+} by RHA/PFA/CFA sorbents

3.4.2 Effect of Agitation Time on Fe^{2+} Removal

To ascertain a suitable agitation time between the RHA/PFA/CFA sorbent and aqueous solution, the fraction removal of Fe^{2+} were studied as a function of time from 10 to 70 minutes while keeping other parameters constant. Figure 3.17 depicts Fe^{2+} fraction removal as function of agitation time. It shown that fraction removal significantly increases as the time increased until equilibrium adsorption was established at 40 minutes (Figure 3.17). This can be explained by the fact that adsorption sites are well exposed, thus quick reaction occurred. It can be seen on Figure 3.17 which shows that RHA/PFA/CFA sorbent is enough to remove more than 90% of Fe^{2+} at 40 minutes equilibrium time. This theory is supported by Bhattacharya et al., (2008) which suggested that the nature of the sorbent and its available sorption sites affect the time needed to reach equilibrium. In the beginning, fast adsorption may be explained due to the availability of more number of adsorption sites. After initial adsorption of adsorbate, the available sites in the adsorbent reduced and thus, the rate of adsorption further decreased, which attained a limiting value at equilibrium. Beyond 40 minutes of equilibrium time, there is no further significant Fe^{2+} removal observed. Thus, it was decided to assume the equilibrium time reached in 40 minutes for the rest of this study. Similar trend results were reported by Uddin et.al (2009) and Sivaraj et.al (2001).

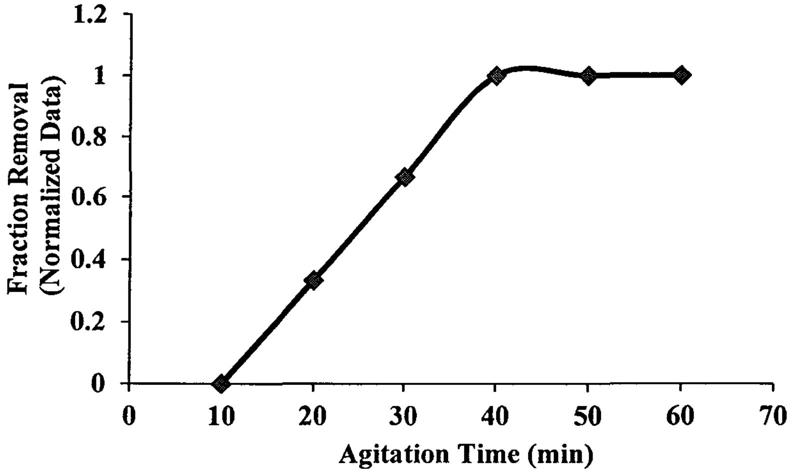
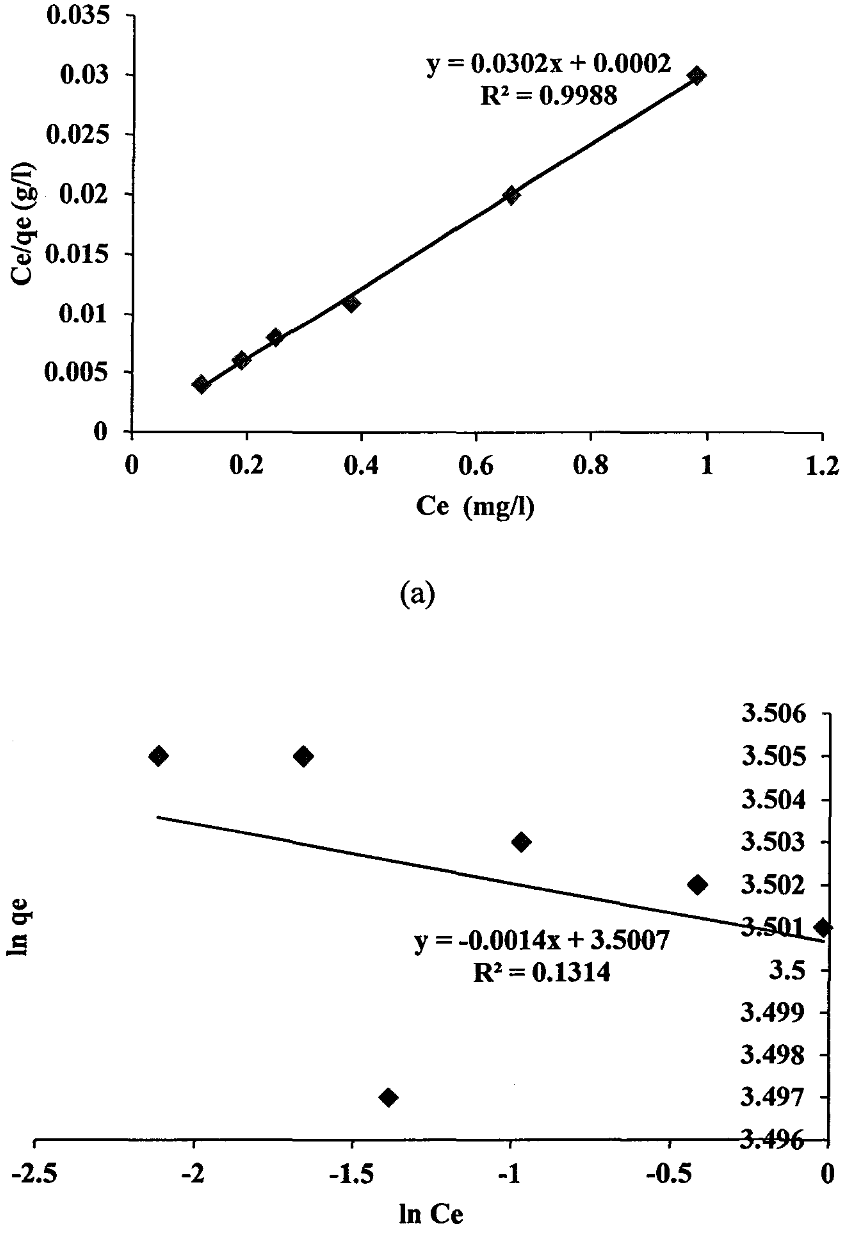


Figure 3.17 Effect of agitation time on the removal of Fe^{2+} by RHA/PFA/CFA sorbents

3.4.3 Sorption Isotherms

The distribution of the sorbate species among liquid and sorbent can be describing using sorption isotherm. Sorption isotherms can be generated based on numerous theoretical models where Langmuir and Freundlich isotherms model are commonly used. The Langmuir model assumes that uptake of metal ions occurs on a homogenous surface by monolayer sorption without any interaction between sorbed ions. The applicability of the isotherm model was evaluated by the coefficient of correlation value (R^2). The adsorption data for iron metal on RHA/PFA/CFA sorbents were analyzed by a regression analysis to fit the above Langmuir and Freundlich isotherm models, and the results are shown in Figure 3.18. The calculated Langmuir and Freundlich isotherm constants and the corresponding coefficient of correlation are listed in Table 3.4. Langmuir isotherm was based on assumption that adsorption occurs at specific homogeneous sites within the sorbent. Figure 3.18(a) shows the linear Langmuir isotherm plot which indicates that iron metal adsorption on RHA/PFA/CFA sorbent follows the Langmuir model with R^2 value of 0.9988. Conclusion can be made that Langmuir regression models agrees reasonably well with the experimental data of the iron metal adsorption on RHA/PFA/CFA sorbent.

For Freundlich isotherm, it assumed heterogeneous surface energies. Langmuir isotherm plots in Figure 3.18 (b) shows that iron metal adsorption on RHA/PFA/CFA sorbent do not follows the Freudlich model with R^2 value of only 0.1314. The results indicated that the Freudlich isotherm model do not agrees reasonably well with the experimental data of the iron metal adsorption on RHA/PFA/CFA sorbent.



(a)

(b)

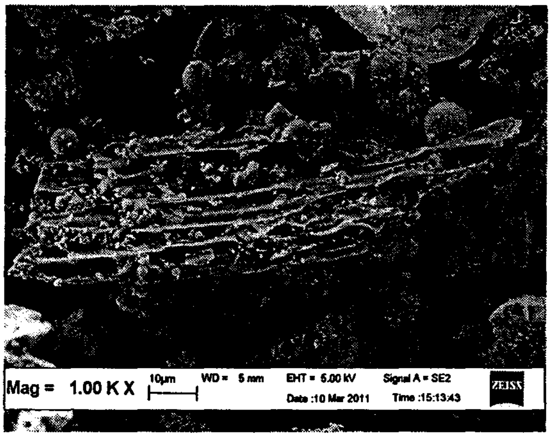
Figure 3.18 (a) Langmuir isotherm plot and (b) Freundlich isotherm for iron adsorption on RHA/PFA/CFA sorbents

Table 3.4 Isotherm parameter for iron adsorption on RHA/PFA/CFA sorbents.

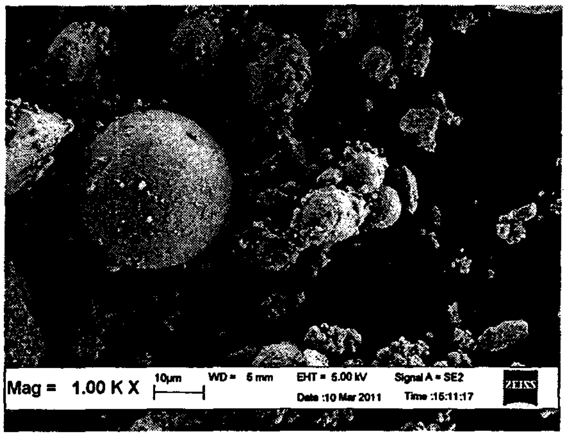
Langmuir Models			**Freundlich model**		
Q_o (mg/g)	b (l/mg)	R^2	K_F (mg/g)	1/n	R^2
33.11	151.01	0.9988	3.5008	-0.0014	0.1314

3.4.4 Scanning Electron Microscope (SEM)

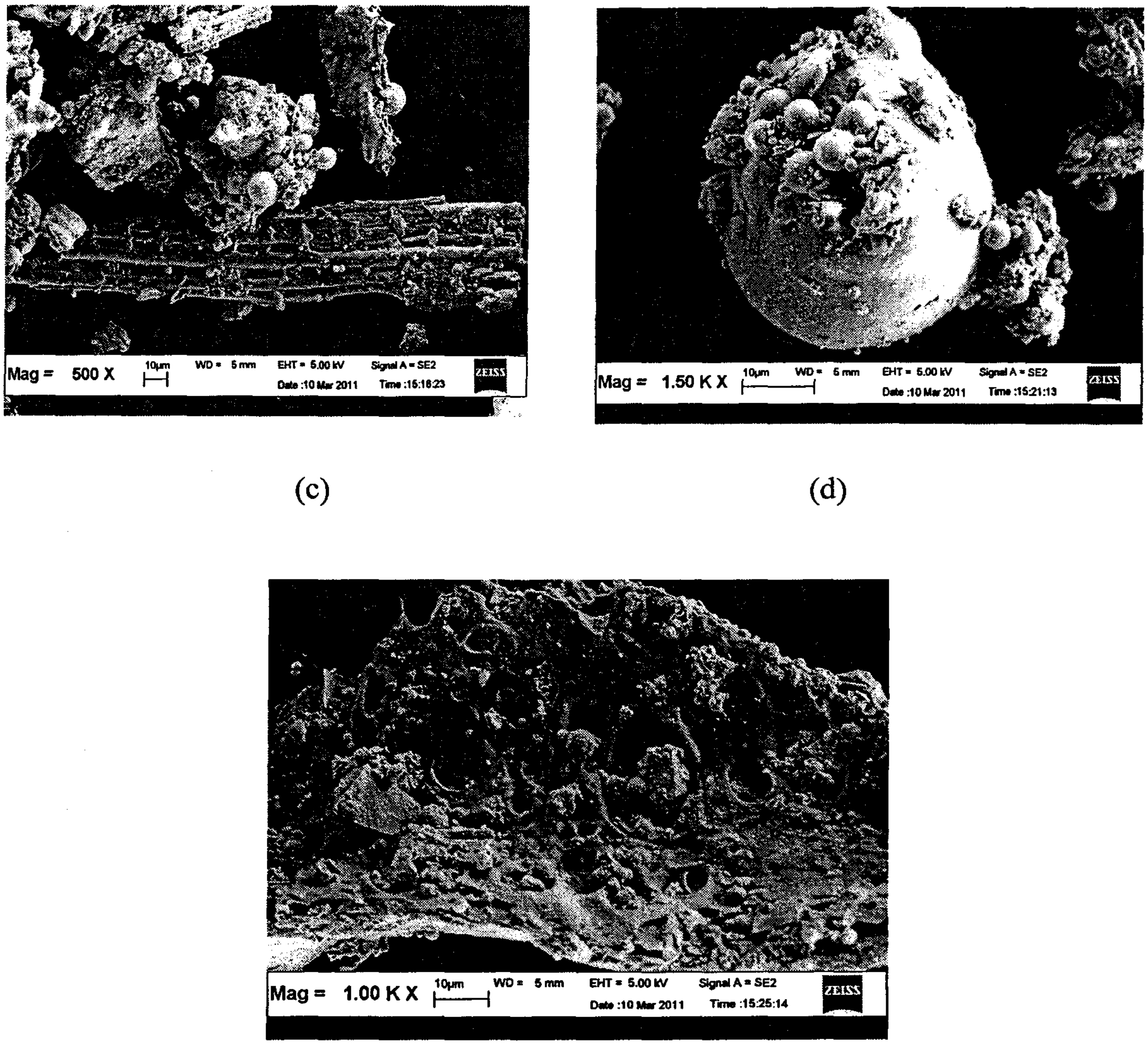
Surface morphology of the untreated, high efficiency and low efficiency RHA/PFA/CFA sorbents were shown in Figure 3.19. The figure illustrates SEM images of the selected RHA/PFA/CFA sorbents before and after treatment with iron metal. It can be clearly observed (Figure 3.19 a and b) that the rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA) are combined to each other to form complex particles during the preparation of sorbent using hydration method. A dome-shaped or a skeletal structure of untreated RHA and a shape of flat irregular layers of raw PFA were noticed side by side (back and front, respectively) with small smooth sphere particles of raw CFA deposited on its surface of the sorbent. After the sorbent was prepared by water hydration method, RHA, PFA and CFA are combined to each other to form larger or complex particles with compact structures (Figure 3.19c). After the adsorption of Fe^{2+}, the surface of the RHA/PFA/CFA sorbents was found to have more compact structures covered by lumps of smaller particles (Figure 3.19d) which are most probably the nickel ions that covered the external surface of RHA/PFA sorbent.



(a)



(b)



(c) (d)

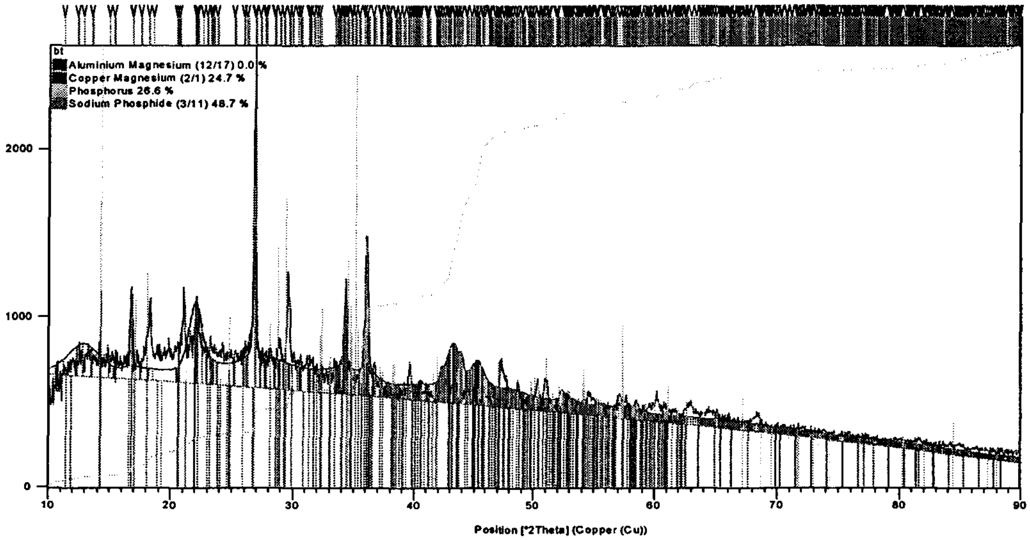
(e)

Figure 3.19 Scanning electron micrograph photo of (a) untreated sorbent 1, (b) untreated sorbent 2, (c) sorbent at high efficiency 3, (d) sorbent at high efficiency 3 and (e) sorbent at low efficiency

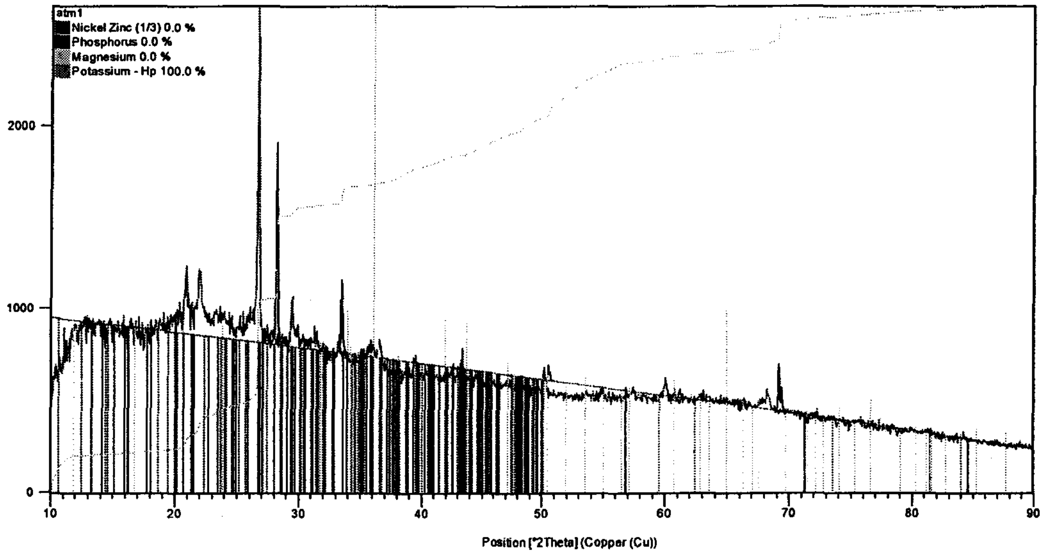
After the adsorption of iron metal, the surface of the RHA/PFA/CFA sorbents was found to have more compact structures covered by irregular rough particles. It was also observed that the specific structure of raw RHA, PFA, and CFA were no longer visible after the adsorption of iron metals towards the surface the RHA/PFA/CFA sorbents.

3.4.5 X-Ray Diffraction (XRD)

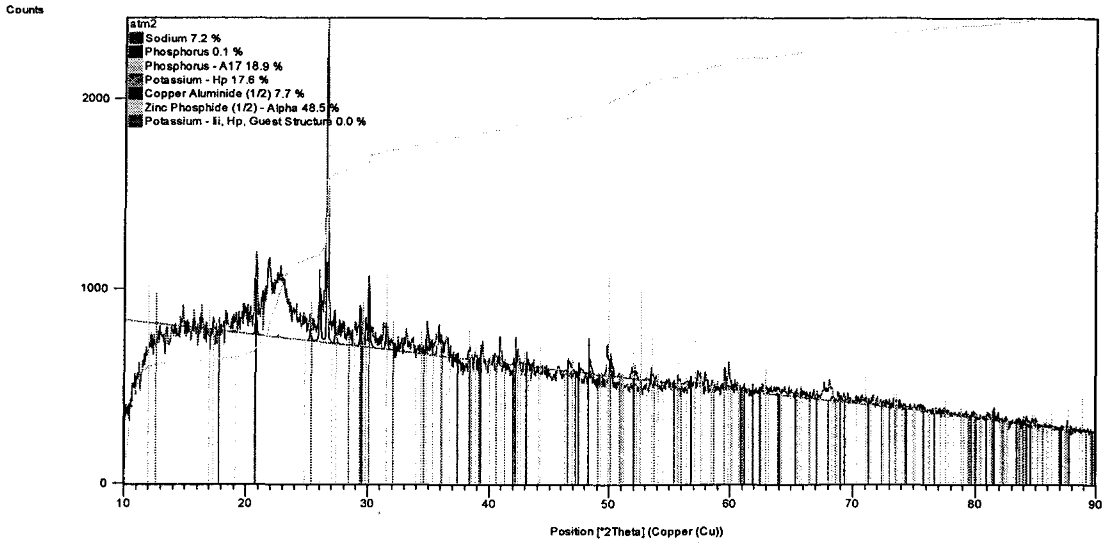
Due to small amount of these crystal phases, therefore no significant peak was detected by XRD analysis. Figure 3.20(a) shows XRD analysis of untreated sorbent. It demonstrates the predominant elements in this sample. The compositions of the elements are copper magnesium (24.7%), phosphorus (26.6%) and sodium phosphide (48.7%).The data was analyzed using Expert High score Plus. Figure 3.20(b) demonstrates similar behaviour as Figure 3.20(a) where no significant peak was detected by the XRD analysis. The predominant element in low removal efficiency of Fe^{2+} is 100% potassium. Figure 3.20(c) shows the analysis of XRD for the high efficiency removal sample. The predominant elements are sodium (7.2%), phosphorus (20%), potassium (17.6%), copper aluminide (7.7%), and zinc phosphide (48.5%).



(a)



(b)



(c)

Figure 3.20 XRD of (a) Untreated sorbent, (b) sorbent with low efficiency and (c) sorbent with high efficiency

3.4.6 Surface Analysis

Figure 3.21 illustrates that both untreated and treated RHA/PFA/CFA sorbents has bimodal particle size distribution that might be due to breakup of multiple sources of particles or variable growth mechanisms during the preparation method. The untreated RHA/PFA/CFA sorbent has a wider range of particle size distributions as compared to both low and high efficiency RHA/PFA/CFA sorbent after treated with Fe^{2+}, which have similar range of particle size distributions. However, average volume of the particle size distribution range of treated RHA/PFA/CFA sorbents is higher than the untreated RHA/PFA/CFA sorbents, which means that higher particle size distributions range are formed after Fe^{2+} adsorption on the RHA/PFA/CFA sorbent. The first particle size distribution range for untreated with Fe^{2+} sorbent is reduced, meanwhile, the volume of the second particle size distribution range of RHA/PFA/CFA sorbents after treated with Fe^{2+} is increased, which mean that higher particle size distributions range are available after Fe^{2+} ion adsorption occurs on the sorbent surface. It was also found that the specific surface area of the untreated RHA/PFA/CFA sorbent was higher ($0.698 m^2/g$) than that of the treated RHA/PFA/CFA sorbents (0.221 and $0.0859 m^2/g$ for low efficiency and high efficiency sorbent, respectively). The lower specific surface area of treated RHA/PFA/CFA sorbents might be results from the agglomerating of smaller particles (which is most probably the iron ion that cover the specific site of the surface of the sorbent) during the adsorption process. Apart from that, the volume weighted mean and surface weighted mean are dramatically increased (from 56.180 µm and 8.595 µm, respectively) to 101.591 µm and 27.200 µm, for low efficiency and 101.591 µm and 27.200 µm for high efficiency, respectively, after the RHA/PFA/CFA sorbent was treated with iron.

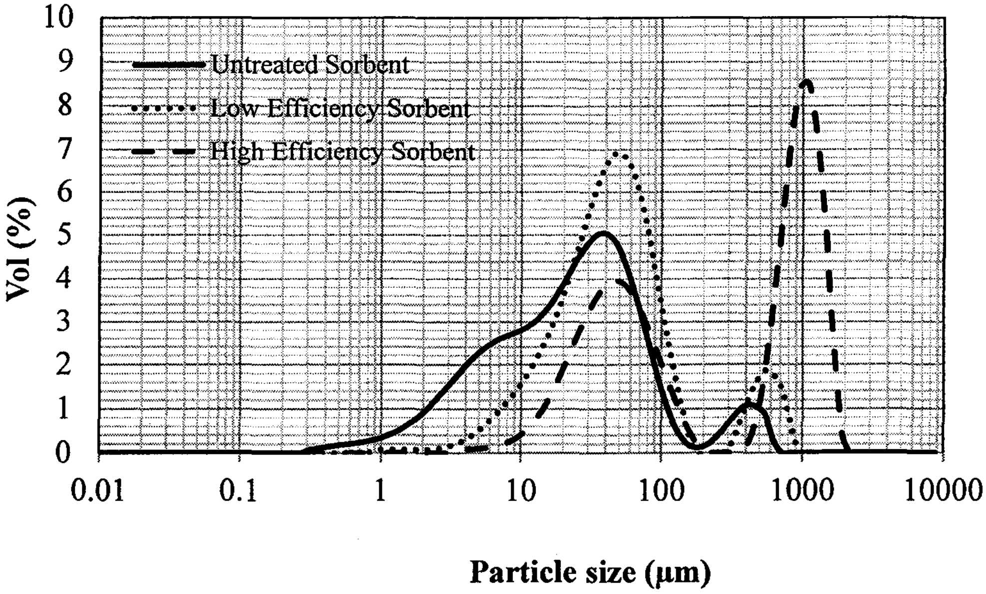


Figure 3.21 Surface analysis of untreated, low efficiency and high efficiency sorbent

This study has shown that the combination of three siliceous waste material, RHA, PFA and CFA could be used as an alternative effective sorbent for the removal of iron ions (Fe^{2+}) from aqueous solution. More than 90% of Fe^{2+} could be removed under optimum conditions.

3.5 A Study on the Removal Characteristic of Acid Violet Dye from Synthetic Wastewater Using RHA/PFA/CFA Sorbent

In this study, a novel RHA/PFA/CFA sorbent was developed by sol-gel method (Adam and Chua, 2004; Adam et al., 2006). Batch studies were performed to evaluate the effect of various experimental parameters.

3.5.1 Effect of dye concentrations and contact time

Figure 3.22 shows the effect of concentration and contact time on acid violet dye uptake at equilibrium time by RHA/PFA/CFA sorbent. It was observed at 120 minutes of equilibrium time, the amount of dye adsorbed was increased (7.1 mg/g to 24.1 mg/g) as the initial concentration of dye increased from 50 mg/l to 350 mg/l. Since other variables such as shaking rate and pH were constant, this result reflects that the uptake of dye from synthetic wastewater was concentration dependent. This might be due to the increase in driving force of the dye concentration gradient (Uddin et al., 2009).

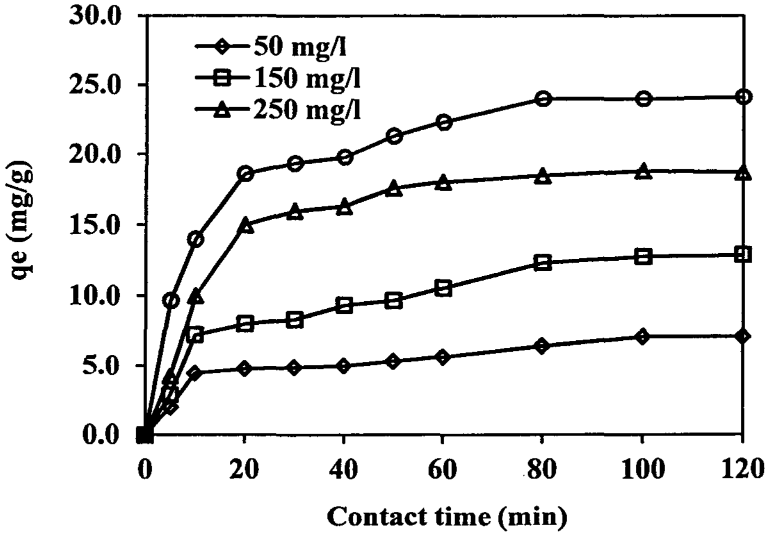


Figure 3.22 Effect of contact time on the adsorption of various acid violet dye concentrations by RHA/PFA/CFA sorbents

The results also showed that increase in contact time from 5 to 80 minutes enhanced the amount of dye adsorbed at equilibrium time. This shows that adsorption site are well exposed, thus quick reaction is occurred. The nature of sorbent and its available sorption sites affected the time needed to reach the equilibrium (Bhatnagar and Jain, 2005). In the beginning, fast adsorption may be explained due to the availability of more number of adsorption sites. After initial adsorption of dye, the available sites in the RHA/PFA/CFA sorbent reduced and thus, rate of adsorption further decreased, which attained a limiting value at equilibrium. Above 80 minutes of contact time, there was no significant uptake of dye were observed, especially for dye concentrations of 150 mg/l and above, therefore it was assumed that the equilibrium time reached in 80 minutes. Similar trend results were reported by Uddin et.al (2009) and Sivaraj et.al (2001) in removing methylene blue and acid violet dyes using jackfruit leaf and orange peel as a sorbent, respectively.

3.5.2 Effect of shaking rate and contact time

In batch adsorption studies, shaking rate is among the important parameters related to diffusion or mobility of the pollutants towards the surface of the sorbents. Figure 3.23 shows the plot between acid violet dye uptakes at equilibrium time by RHA/PFA/CFA sorbent versus contact time at different shaking rate (130, 170 and 210 rpm). It was observed that the amount of dye adsorbed was increased as the contact time increased from 5 to 80 minutes. This result was similar to previous findings. Results shown in Figure 3.23 also indicate that the amount of dye adsorbed was slightly increased when shaking rate increased. At 80 minutes of equilibrium time, the amount of dye adsorbed was slightly increased (6.4 mg/g to 7.4 mg/g) as the shaking rate increased from 130 to 170 rpm. A slightly enhanced adsorption rate at higher shaking rate is probably due to an increase in the mobility of sorbing species (Raji and Anirudhan, 1996). Apart from that, the increase of the shaking rate might improve the diffusion of the acid violet dye towards the surface of the RHA/PFA/CFA sorbents. Nevertheless, in this study, the effect of shaking rate on acid violet dye uptakes by RHA/PFA/CFA sorbent was not too significant. Thus, a lower shaking rate is sufficient to assure the surface binding for acid violet dye uptake.

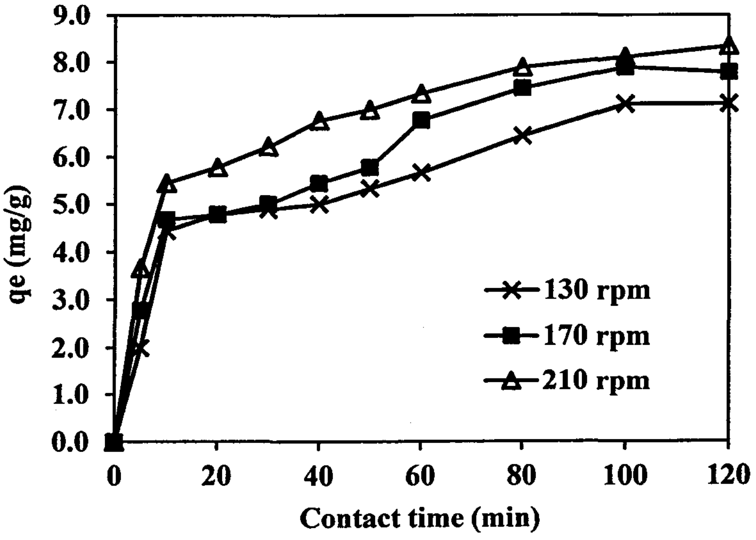
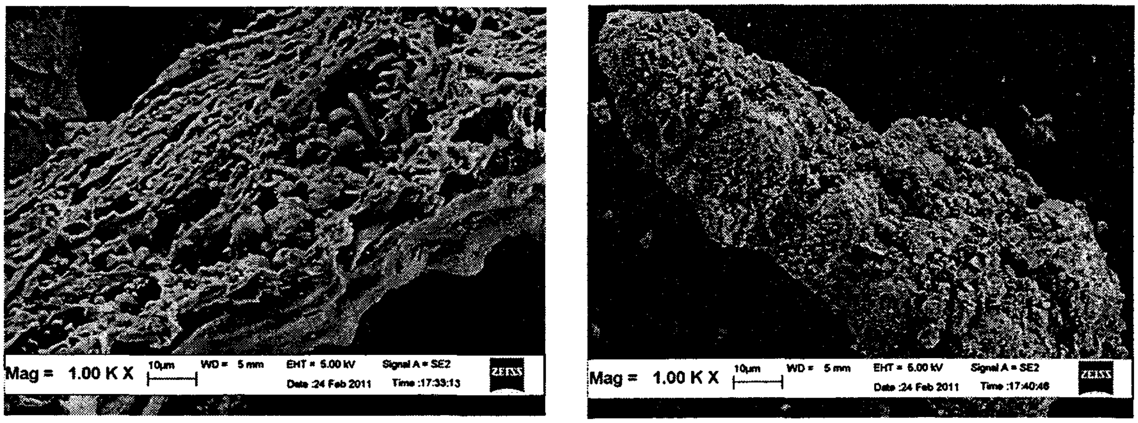


Figure 3.23 Effect of contact time on the adsorption of acid violet dye by RHA/PFA/CFA sorbents at various shaking rate

3.5.3 Characterization of RHA/PFA/CFA sorbents

Figure 3.24 illustrates SEM images of the selected RHA/PFA/CFA sorbents before and after treatment with acid violet dye. It can be clearly observed (Fig. 1a) that the rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA) are combined to each other to form complex particles during the preparation of sorbent using sol-gel method. A dome-shaped or a skeletal structure of raw RHA and a shape of flat irregular layers of raw PFA were noticed side by side (back and front, respectively) with small smooth sphere particles of raw CFA deposited on its surface of the sorbent. After the adsorption of acid violet dye, the surface of the RHA/PFA/CFA sorbents was found to have more compact structures covered by irregular rough particles. It was also observed that the specific structure of raw RHA, PFA, and CFA were no longer visible after the adsorption of acid violet dye towards the surface the RHA/PFA/CFA sorbents.

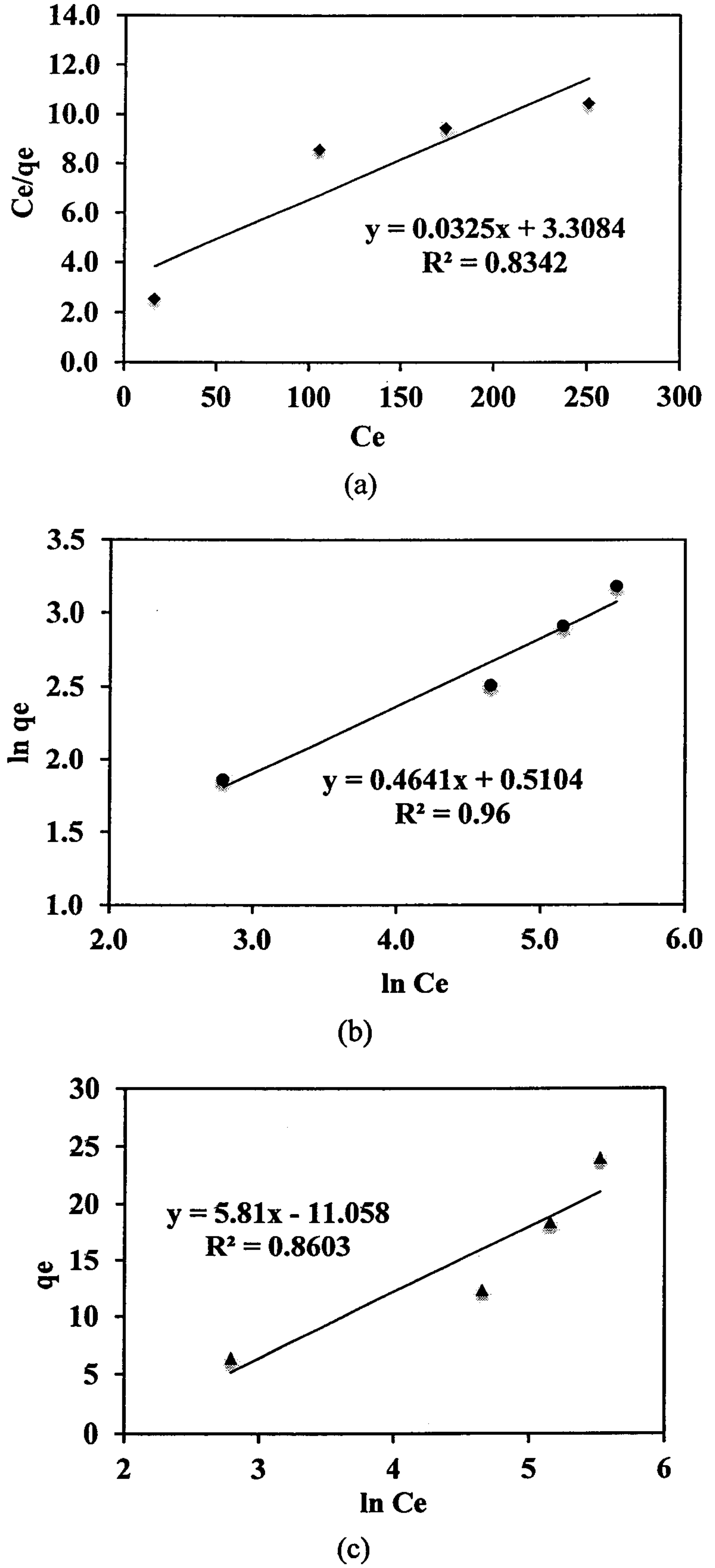


(a) (b)

Figure 3.24 Scanning electron micrograph of (a) prepared and (b) spent RHA/PFA/CFA sorbents

3.5.4 Adsorption isotherms

The adsorption data for acid violet dye adsorption on RHA/PFA/CFA sorbents were analyzed by a regression analysis to fit the Langmuir, Freundlich and Temkin isotherm models, and the results are shown in Figure 3.25. The calculated Langmuir, Freundlich and Temkin isotherm constants and the corresponding coefficient of correlations are listed in Table 3.5.



(a)

(b)

(c)

Figure 3.25 (a) Langmuir isotherm plot, (b) Freundlich isotherm plot and (c) Temkin isotherm plot for acid violet dye adsorption on RHA/PFA/CFA sorbents

Table 3.5 Isotherm parameters for acid violet dye adsorption on RHA/PFA/CFA sorbents.

Langmuir model			***Freundlich model***			***Temkin model***		
Q_o (mg/g)	b (l/mg)	**R^2**	K_F (mg/g)	1/n	**R^2**	K_T (l/mg)	B_1	**R^2**
30.74	0.0098	**0.83**	1.65	0.46	**0.96**	1.47	5.81	**0.86**

The linear Langmuir isotherm plot (Figure 3.25a) shows that the acid violet dye adsorption on RHA/PFA/CFA sorbent follows the Langmuir model. Other isotherm plots (Freundlich and Temkin) were also follows the similar results as shown in Figure 3.25b & c. In addition, the coefficient of correlation for all the isotherm plots were considered high (R^2 above 0.8) which showing a good linearity of the specific isotherm model. The results indicated that all the isotherm models agrees reasonably well with the experimental data of the acid violet dye adsorption on RHA/PFA/CFA sorbent.

Nevertheless, from all the data fitted to the isotherm models, the Freundlich isotherm model was found to have the best fit to the experimental data since this isotherm exhibited the highest value of correlation coefficient (R^2 = 0.96). This model predicts that the acid violet dye concentration in the RHA/PFA/CFA sorbent increased with the increase in its initial concentration of acid violet dye in synthetic wastewater. This result indicates that the adsorption of acid violet dye on RHA/PFA/CFA sorbent is not only limited to the monolayer formation but also describes the heterogeneous and reversible adsorptions (Chatterjee et al., 2007; Ng and Cheung, 2003). This might confirm the complexity of the surface of RHA/PFA/CFA sorbent as mentioned earlier in the characterization of this sorbents. In addition, the 1/n value (0.46) is smaller than 1, indicating that the RHA/PFA/CFA sorbent favourably adsorbed acid violet dye.

Different results were reported by other researchers for acid dye adsorption. Study by Thinakaran et al. (2008) reported that the adsorption of acid violet 17 (AV17) on activated carbon (prepared from sunflower seed hull) was found to follow Langmuir isotherm model. In another study, Sivaraj et al. (2001) found that the adsorption of acid violet from aqueous solutions on sorbent (prepared from waste orange peel) follows both the Langmuir and Freundlich isotherms. Similar to that, Anjaneya et al. (2009) reported the same adsorption isotherms for the process of acid violet dye uptake using biosorbent (*Penicillium* sp). The different results obtained in this study are probably due to the characteristic nature of the RHA/PFA/CFA sorbent and the adsorption mechanism of acid violet dye, which suggests the possibility of structural changes or alterations in the acid violet dye–RHA/PFA/CFA complex.

3.6 Removal of Brilliant Green Dye Using Sorbent Prepared From Combination of RHA, PFA and CFA By Responce Surface Methodology (RSM)

The main purpose of this work is to study the removal of synthetic brilliant green dye by adsorption batch process using RHA/PFA/CFA sorbent. Other objectives were to determine the optimum condition for adsorbent preparation from RHA, PFA, and CFA using response surface methodology. The sorbent was prepared through reflux method. In the preliminary study was conducted to select the best additives for further experimental analysis. The additives used include LiCl, NaOH, $CaCl_2$, $FeCl_3$ and $NaHCO_3$.

In this experiment, preparation of the sorbent was designed using a standard response surface methodology (RSM) which is called a central composite design (CCD). Five variables were studied which include reflux time, amount of RHA, amount of PFA, amount of CFA, and concentration of chemical. Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used in developing mathematical model that correlates the sorbent preparation variables with its adsorption capacity based on the data obtained. The data were utilized to develop a correlation between the sorbent preparation variables with its adsorption capacity by fitting it to the second-degree polynomial equation (Montgomery, 2001).

3.6.1 Preliminary study

Preliminary study was carried out using five different additives to activate the RHA/PFA/CFA in order to find the best additive for adsorbent preparation. NaOH gives highest dyes adsorption percentage with 91.58% followed by $NaHCO_3$, LiCl, $CaCl_2$ and $FeCl_2$. Thus, for further analysis, NaOH was used to find optimum condition of dyes adsorption. Figure 3.26 shows the comparison of the treated dyes by adsorbent prepared with different additives while the percentage of the dyes removal is shown in the Table 3.6.

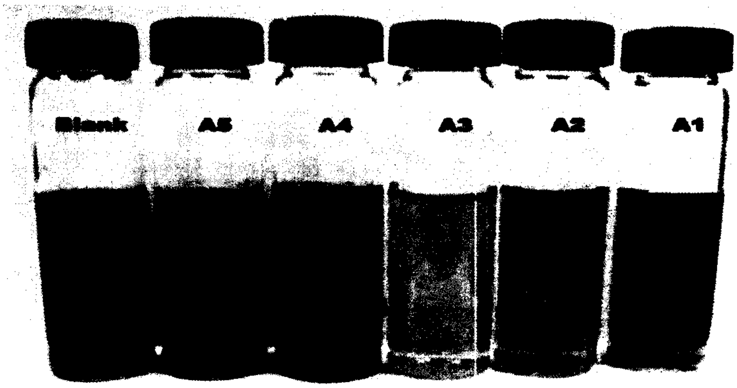


Figure 3.26 Comparison of dyes removal for different additives; A1 (LiCl), A2 ($NaHCO_3$), A3 (NaOH), A4 ($CaCl_2$) and A5 ($FeCl_2$)

Table 3.6 Percentage of dye removal for different additives used

Sample Code	**Additives**	**Percentage of dye removal (%)**
A1	LiCl	80.79
A2	NaHCO3	86.84
A3	NaOH	91.58
A4	CaCl2	69.74
A5	FeCl3	5.79

3.6.2 Development of regression model equation

CCD was used to develop correlation between preparations of adsorbents with its adsorption capacity (%). From the preliminary study, NaOH gave highest adsorption value and it was used as an additive in batch analysis. The adsorption percentage of dye at various sorbent preparation conditions are shown in Table 3.7. From the analysis, the adsorption percentage is in the range of 67.51 to 90.96%. The fitness of the model was checked with analysis of variance (ANOVA) as shown in Table 3.8.The significance of the empirical model can be evaluated from the Prob. > F values. Prob.> F values less than 0.500 for 95% confident interval shows that the model is significant. In this experiment, the overall quadratic model generated is significant with the Prob. > F value of 0.0102. The data were utilized to develop a correlation between the adsorbent preparation variables with its adsorption capacity by fitting it to the second-degree polynomial equation and the equation was given below in terms of coded factor.

$$\text{Dye adsorbed (\%)} = 84.30 + 2.11x_1 + 4.23x_2 - 2.17x_3 - 0.12x_4 + 1.26x_5 - 0.78x_1^2 - 1.42x_2^2 - 0.94x_3^2 - 0.98\,x_4^2 + 0.40\,x_5^2 - 0.19x_1x_2 - 1.26x_1x_3 - 1.96x_1x_4 - 0.43x_1x_5 + 1.34x_2x_3 - 1.38x_2x_4 - 0.33x_2x_5 - 1.17x_3x_4 + 0.16x_3x_5 - 0.83x_4x_5$$

Positive sign indicates synergistic effect, whereas negative sign indicates antagonistic effect (Tan et al., 2008b).

Table 3.7 Experimental design matrix and results for RHA/PFA/CFA sorbents.

Run	x_1	x_2	x_3	x_4	x_5	**Adsorption Efficiency (%)**	
						Experimental	**Predicted**
R1	120.00	10.00	10.00	10.00	2.00	73.01	74.58
R2	240.00	10.00	10.00	10.00	1.00	79.38	81.11
R3	120.00	20.00	10.00	10.00	1.00	76.62	78.80
R4	240.00	20.00	10.00	10.00	2.00	88.53	92.29
R5	120.00	10.00	20.00	10.00	1.00	67.51	66.73
R6	240.00	10.00	20.00	10.00	2.00	77.11	77.91
R7	120.00	20.00	20.00	10.00	2.00	85.14	86.39
R8	240.00	20.00	20.00	10.00	1.00	86.35	87.76
R9	120.00	10.00	10.00	20.00	1.00	80.66	79.67
R10	240.00	10.00	10.00	20.00	2.00	83.47	84.05
R11	120.00	20.00	10.00	20.00	2.00	83.42	84.46
R12	240.00	20.00	10.00	20.00	1.00	85.80	86.99
R13	120.00	10.00	20.00	20.00	2.00	77.13	75.21
R14	240.00	10.00	20.00	20.00	1.00	73.30	71.53
R15	120.00	20.00	20.00	20.00	1.00	83.25	81.94
R16	240.00	20.00	20.00	20.00	2.00	79.58	79.84
R17	60.00	15.00	15.00	15.00	1.50	76.37	76.97
R18	300.00	15.00	15.00	15.00	1.50	88.25	85.40
R19	180.00	5.00	15.00	15.00	1.50	68.65	70.17
R20	180.00	25.00	15.00	15.00	1.50	90.85	87.09
R21	180.00	15.00	5.00	15.00	1.50	89.29	84.88
R22	180.00	15.00	25.00	15.00	1.50	74.06	76.22
R23	180.00	15.00	15.00	5.00	1.50	85.43	80.60
R24	180.00	15.00	15.00	25.00	1.50	77.54	80.13
R25	180.00	15.00	15.00	15.00	0.50	83.07	83.37
R26	180.00	15.00	15.00	15.00	2.50	90.96	88.42
R27	180.00	15.00	15.00	15.00	1.50	82.46	84.30
R28	180.00	15.00	15.00	15.00	1.50	83.95	84.30
R29	180.00	15.00	15.00	15.00	1.50	83.16	84.30
R30	180.00	15.00	15.00	15.00	1.50	85.53	84.30
R31	180.00	15.00	15.00	15.00	1.50	84.47	84.30
R32	180.00	15.00	15.00	15.00	1.50	83.95	84.30

x_1 (reflux time), x_2 (amount of RHA), x_3 (amount of PFA), x_4 (amount of CFA), and x_5 (concentration of chemical).

Table 3.8 Analysis of variance (ANOVA) for percentage of dye removal

Source	**Sum of Square**	**DF**	**Mean Squares**	**F Value**	**Prob > F**	
Model	991.99	20	49.60	4.08	0.0102	Significant
x_1	106.43	1	106.43	8.75	0.0130	
x_2	429.43	1	429.43	35.33	< 0.0001	
x_3	112.58	1	112.58	9.26	0.0112	
x_4	0.33	1	0.33	0.027	0.8719	
x_5	38.25	1	38.25	3.15	0.1037	
x_1^2	17.73	1	17.73	1.46	0.2525	
x_2^2	58.94	1	58.94	4.85	0.0499	
x_3^2	25.71	1	25.71	2.12	0.1738	
x_4^2	28.39	1	28.39	2.34	0.1547	
x_5^2	4.66	1	4.66	0.38	0.5483	
x_1x_2	0.61	1	0.61	0.050	0.8271	
x_1x_3	25.40	1	25.40	2.09	0.1762	
x_1x_4	61.62	1	61.62	5.07	0.0458	
x_1x_5	2.89	1	2.89	0.24	0.6354	
x_2x_3	28.68	1	28.68	2.36	0.1528	
x_2x_4	30.64	1	30.64	2.52	0.1407	
x_2x_5	1.70	1	1.70	0.14	0.7153	
x_3x_4	21.76	1	21.76	1.79	0.2079	
x_3x_5	0.42	1	0.42	0.034	0.8566	
x_4x_5	11.12	1	11.12	0.91	0.3594	
Residual	133.72	11	12.16			
Pure Error	5.61	5	1.12			
Cor Total	1125.71	31				

The R^2 value that fit this model is 0.8812. R^2 is a coefficient of determination which gives the proportion of the variance of one variable that is predictable from the other variable. High R^2 value represents the correlation between the predicted and experimental dye adsorption. Figure 3.27 shows the predicted value versus the experimental value for sorption capacity of prepared adsorbent.

Based on the Pred.>F values (Table 3.8), time of reflux (x_1), amount of RHA (x_2) and amount of PFA (x_3) were found to have significant effects on the adsorption capacity. Figure 3.29 shows the correlation between reflux time (x_1) and amount of CFA (x_4). From the figure, it can be seen that at constant time of refluxing process during adsorbent preparation, the adsorption capacity of adsorbent increased at lower amount of CFA but gradually decreasing after certain amount of CFA was used. This shows that the amount of CFA give the effect on dyes adsorption and least amount of CFA is needed for high optimum adsorption. However, by keeping the amount of CFA low and constant, while increasing time of reflux, the adsorption of prepared adsorbent on dyes material is increase.

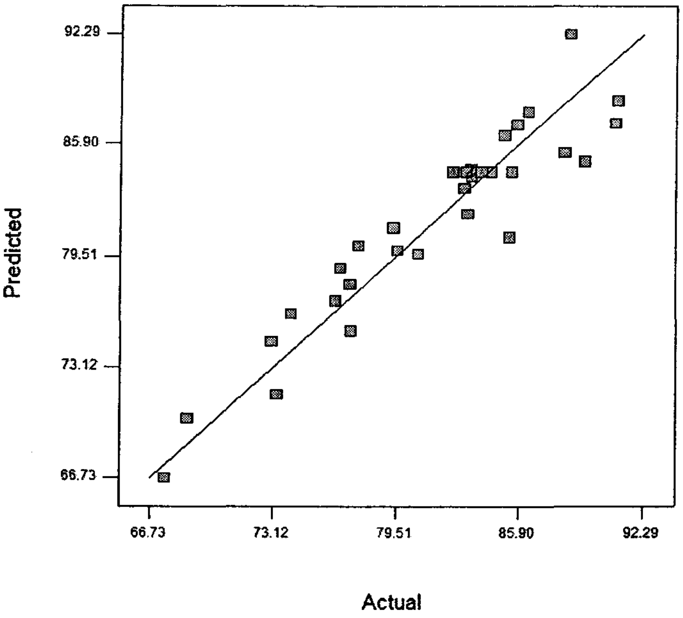


Figure 3.27 Predicted vs actual dye adsorption

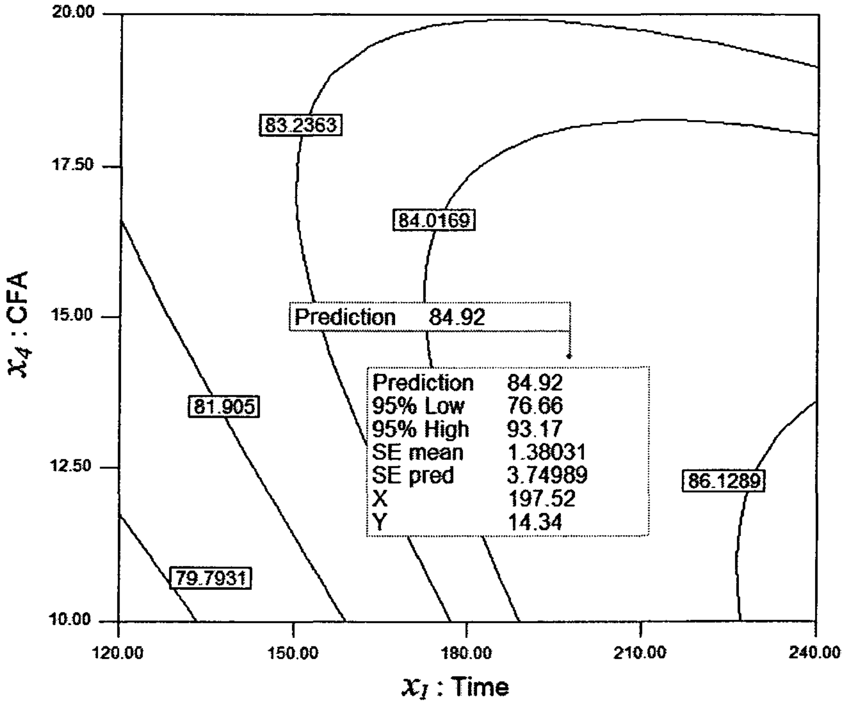


Figure 3.29 Contour plot of adsorption capacity

3.6.3 Optimization of Dye Adsorption

The optimization condition for dyes adsorption was determined by entering the desired values or condition of variables into the software to generate the prediction adsorption values. As the chemical reagents are usually costly and give difficulties in handling, lower concentration of the chemical is more desired. Thus, the optimum adsorption with low concentration of chemical should be found. The reflux time and amount of RHA, PFA and CFA are set to be in range because time should not be too long and no limitation of the usage of these three waste materials. Ten possible desired optimum data was greeted by the software which the highest adsorption capacity is 90.1% with desirability of 0.981 as shown in Table 3.9. From this table, the optimum adsorption values was obtained by refluxing 20.0g, 12.3g and 10.0g of RHA, PFA and CFA respectively in 1 mol/L of NaOH for 240 minutes.

Table 3.9 Predicted optimization values for dyes adsorptions

No	**Time**	**RHA**	**PFA**	**CFA**	**NaOH conc.**	**Dye absorbed**	**Desirability**
1	240.00	20.00	12.30	10.00	1.00	90.0863	0.981
2	240.00	20.00	11.63	10.77	1.00	90.0743	0.981
3	239.97	20.00	10.00	12.28	1.00	89.9440	0.978
4	240.00	20.00	10.51	11.04	1.01	90.0336	0.975
5	239.96	19.06	12.09	15.04	1.00	88.9135	0.955
6	240.00	17.02	10.04	14.33	1.00	88.8853	0.955
7	240.00	15.83	10.00	19.14	1.01	87.3458	0.914
8	239.71	13.26	10.00	18.39	1.00	86.4256	0.898
9	169.28	20.00	13.11	17.67	1.00	86.0684	0.890
10	240.00	10.00	10.60	18.93	1.00	83.3205	0.821

3.6.4 Characterization

Figure 3.30 shows the SEM images of the prepared sorbent and spent sorbents that reveal its surface texture and porosity. From the images, the presence of RHA, PFA and CFA in the adsorbent can be seen. RHA, PFA and CFA might combine to each other to form larger or complex particles during preparation of sorbent (reflux) process. However, for the prepared sorbent, combined compounds might lower the total surface area hence decrease the adsorption capacity of the adsorbent.

Figure 3.30(a) shows the present of micro-size particles attached on the spherical CFA compound and on the internal surface of porous RHA. The particles might be forming during refluxing process. From Figure 3.30(b), the agglomeration of particles was seen on the RHA, PFA and CFA surfaces. The agglomerate seen is the dyes compound that attached on the adsorbent surfaces.

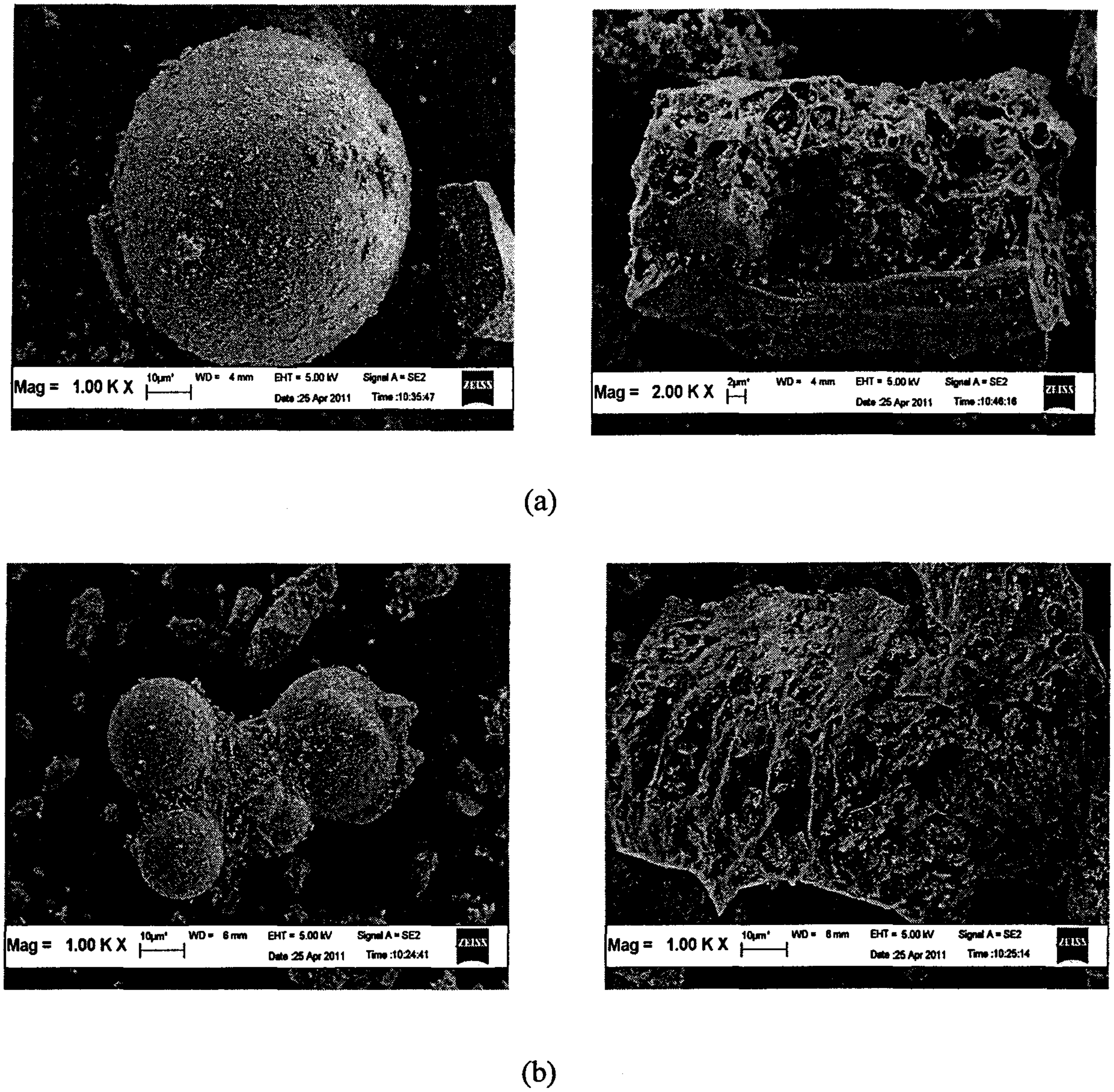


Figure 3.30 Scanning electron micrograph of (a) prepared and (b) spent RHA/PFA/CFA sorbents.

3.6.5 Fourier Transform Infrared

The outer functional group of adsorbents was examined using FTIR. The FTIR spectra of prepared and spent sorbent are shown in Figure 3.31 and 3.32. Figure 3.31 shows the presence of broad vibration between 2800 and 3700 cm^{-1} which indicate the presence of both free and hydrogen bonded O-H groups. This stretching might be due to presence of both the silanol groups (Si-OH) and adsorbed water at peak of 3435 cm^{-1} on the surface (Colthup et al., 1990).

The band between frequency of 2200 to 2400 cm^{-1} shows the present of silane group (Si-H). It might also show the presence of P-H phosphine for prepared adsorbent and anhydrous sulphuric acid (-SO2-OH) for spent sorbent. The band range within 1550-1650 cm^{-1} indicates the present of amine functional group or may also indicate the presence of carboxyl salt, nitro group or aromatic ring. 1424 cm^{-1} band shows the presence of nitrate or carbonate ion functional groups (Colthup et al., 1990).

The stretching band at frequency 1084 cm^{-1} shows the presence of Si-OR or may also referred to carbonyl functional group (aldehyde and ketone) as it lies in the range of 1260-1000 cm^{-1}. The band fron 675 to 870 cm^{-1} shows the presence of either alkene or phenyl ring substitution band while peak around 619 shows the present of Cl functional group (Colthup et al., 1990). The spectrum that higher than 3400 cm^{-1} in Figure 3.32 shows that the absent of some O-H group after reaction of adsorbent with Brilliant Green dye.

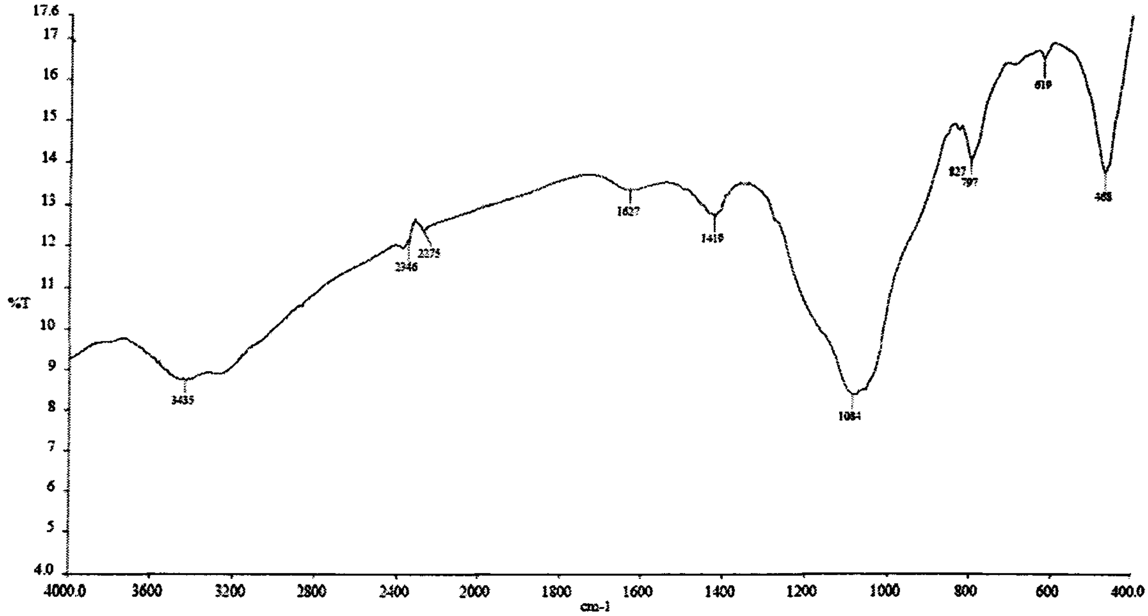


Figure 3.31 FTIR spectrum for prepared sorbent

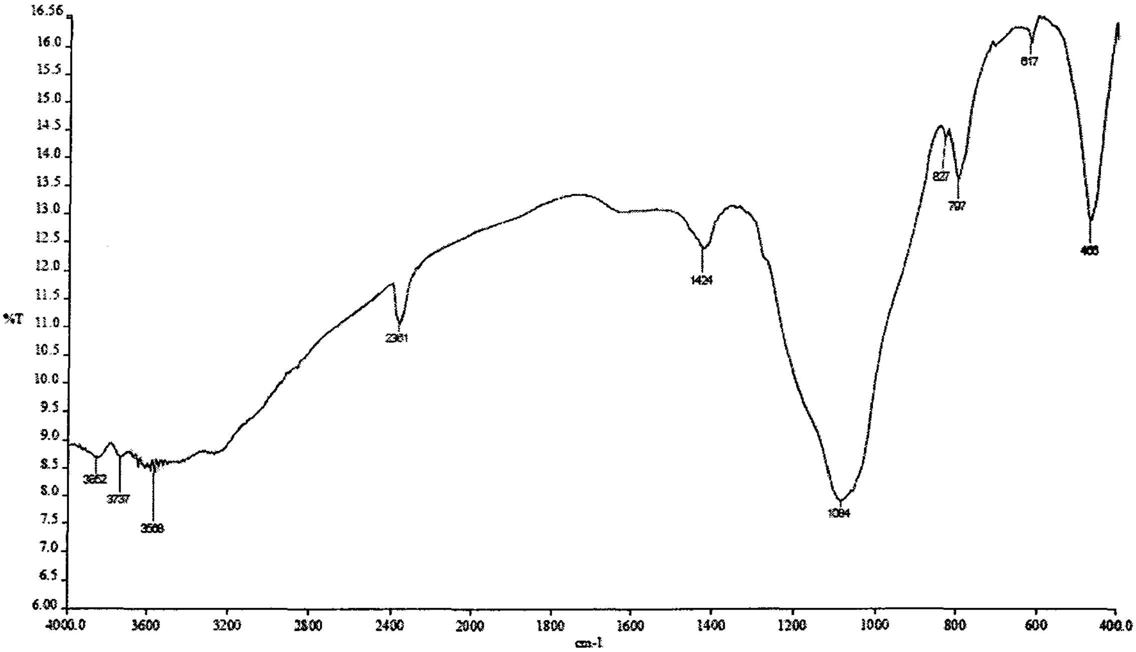


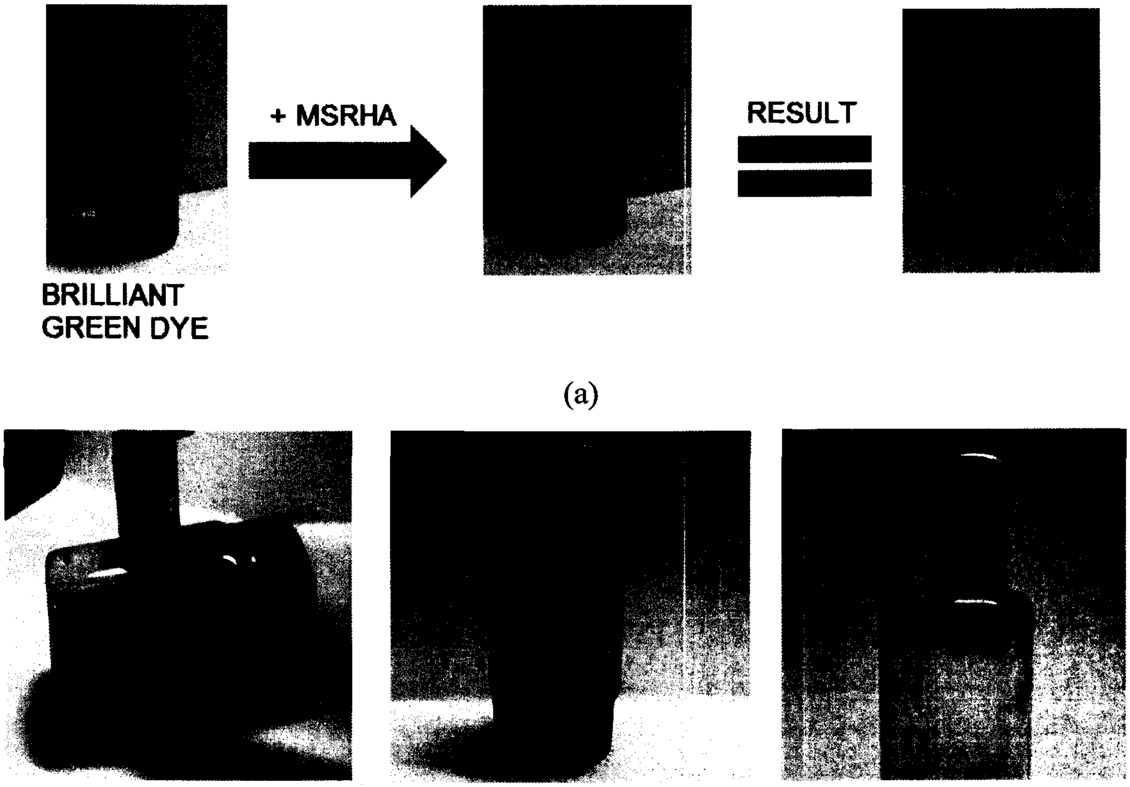
Figure 3.32 FTIR spectrum for spent sorbent

3.7 Magnetic RHA-Based Sorbent For Brilliant Green Dye Removal

This study was focused on the removal of brilliant green dye from synthetic wastewater using mangetic sorbent prepared from rice husk ash (MSRHA). MSRHA sorbent was prepared according to the method given by Nakahira et al. (2006) with some modifications. Batch experiments were carried out by adsorbing brilliant green dye from aqueous solution. Figure 3.33 shows the photographs of the MSRHA adsorption process. MSRHA sorbent were dispersed in the dye solution and after shaking at certain condition, a clear solution was obtained (Figure 3.33a). Then by magnetic separation under an external magnetic field, the solution had been mostly purified (Figure 3.33b).

3.7.1 Effect of MSRHA sorbent

Figure 3.34 shows the result for the effect of MSRHA sorbent amount on adsorption of dye. As can be seen, the dye removal percentage increases from 38.88% to 95.42% as increasing in the MSRHA sorbent amount. The increasing of removal percentages of dye concentrations as increasing of MSRHA sorbent amount can be explained with the increasing amount of surface area of MSRHA sorbent which enabled the MSRHA sorbent to supporting the large amount of absorbate on its surface area.



(a)

(b)

Figure 3.33 Photographs of MSRHA sorbent (a) before and after brilliant green dye sorption and (b) magnetic separation under an external magnetic field can obtain a clear solution.

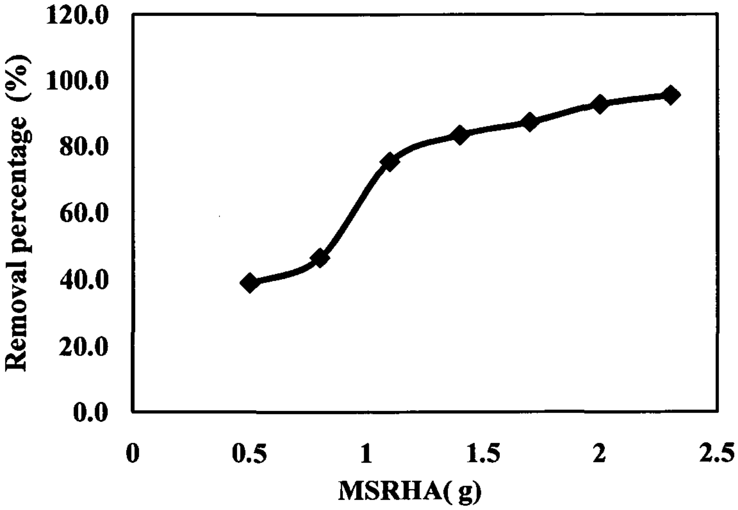


Figure 3.34 Graph of dye concentration removal percentage versus MSRHA sorbent

3.7.2 Effect of temperature

Figure 3.35 shows the result for the effect of temperature on adsorption of dye onto MSRHA sorbent. As can be seen, the dye removal percentage increases from 92.74% to 96.65% as increasing temperature interval from 27 – 50°C. After that, for the temperature interval from 50 – 60°C, the percentage removal has become slightly dropped because the MSRHA sorbent has reached its maximum temperature for the Adsorption process of the dye. For this experiment, it's had been observed that the optimum temperature for increasing the adsorption process of dye is 50°C.

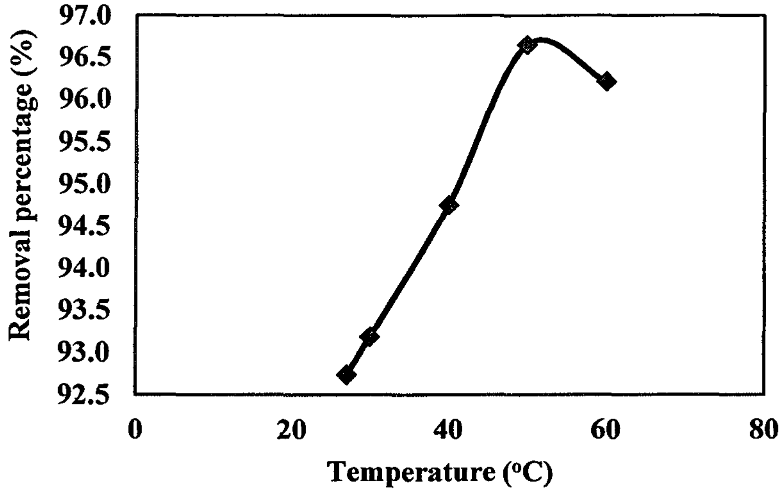


Figure 3.35 Graph of dye concentration removal percentage versus temperature

3.8 Characterization of Prepared and Spent CFA/PFA/RHA Sorbents in Removing Heavy Metal and Dye

In this study, physical characterization of CFA/PFA/RHA sorbent was investigated to obtain a better understanding of adsorption process in removing heavy metals and dye. The sorbents from CFA, PFA and RHA were prepared using water hydration method, sol-gel method and activation by NaOH method. The prepared sorbents were used to remove single components of zinc (Zn^{2+}), nickel (Ni^{2+}), iron (Fe^{2+}), and brilliant green dye from synthetic wastewater.

Based on the adsorption studies, the adsorption efficiency for different methods of preparation was tabulated in the Table 3.10. Based on the results obtained (Table 3.10), sol-gel method showed the highest percentage of adsorption efficiency meanwhile activation by NaOH method showed the lowest percentage of adsorption efficiency. The percentage of adsorption efficiency for different methods was observed in order to know the effectiveness of the CFA, PFA, and RHA combination as a sorbent and to identify the appropriate method for adsorbent preparation.

Table 3.10 Adsorption efficiency of CFA/PFA/RHA sorbents prepared from various methods

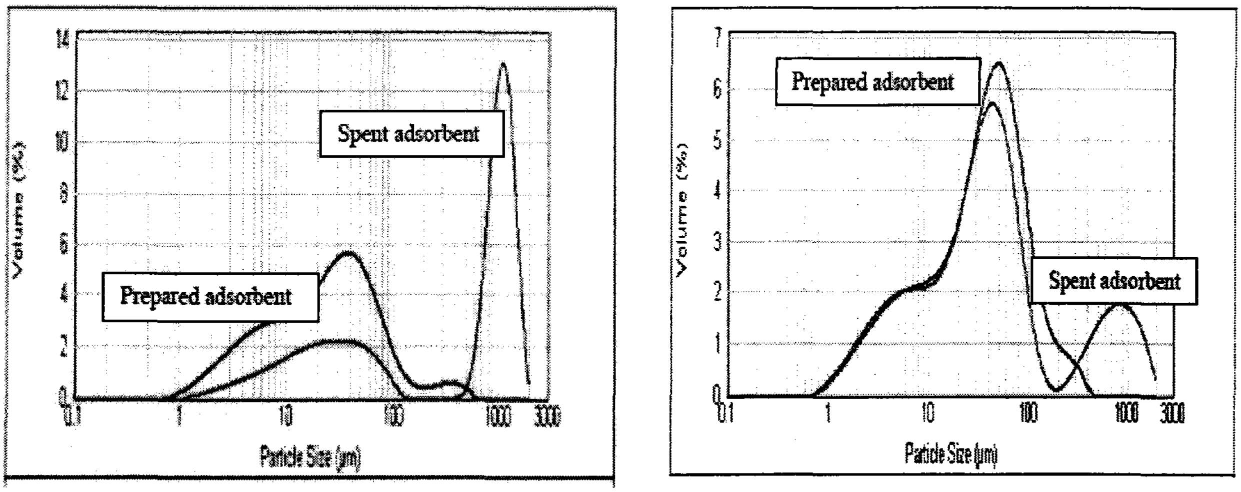
Preparation method	**Sorbent efficiency**	**Pollutant to be removed**
Water hydration (WH) WH1	>90%	iron (Fe^{2+})
WH2		nickel (Ni^{2+})
Sol gel (SG1)	96 – 98%	zinc (Zn^{2+})
Activation by NaOH (AN)	68 – 91%	brilliant green dye

The adsorption efficiency was affected by several factors such as sorbent preparation variables and chemical used. The main variables affecting the sorbent performance were amount of solid wastes, shaking rate and pH. These variables were important in order to obtain sorbent with high pollutant removal efficiency. Optimum amount of solid wastes and shaking rate will ensure that all of the solid wastes mix together accordingly. Based on the result obtain, sol gel method showed the highest adsorption efficiency compare with the other two methods. Observation on steps used in the sorbent preparation, sol-gel method involves a series of complicated steps and using with more than one chemical component. Treatment with concentrated HNO_3 helps to reduce the impurities and leach out the metal oxides by forming nitrates which were easily dissolved in water. After that, sodium silicate solution was produced when dissolved in NaOH. The sodium silicate solution was neutralized using HNO_3 containing the metal to produce silica gel with the metal ion chemically incorporated into the silica matrix.

3.8.1 Sorbent Characterization

A number of characterization techniques were used to characterize the physical properties of selected CFA/PFA/RHA sorbents before and after treated with heavy metals and dye.

Particle Size Distribution. Selected CFA/PFA/RHA sorbents was characterized for particle size distribution before and after treated with heavy metals and dye. In this analysis, eight samples of prepared and spent CFA/PFA/RHA sorbents were chosen to undergo the analysis. Four samples were taken from water hydration method (WH1 and WH2), two samples were taken from sol-gel method (SG1) and the remaining two were taken from activation by NaOH method (AN). The particle size distribution of the selected CFA/PFA/RHA sorbents was examined and the results are shown in Figures 3.36-3.38.



(a) (b)

Figure 3.36 Particle size distribution of prepared and spent CFA/PFA/RHA sorbent from water hydration method (high efficiency) in removing (a) iron (Fe^{2+}) and (b) nickel (Ni^{2+}).

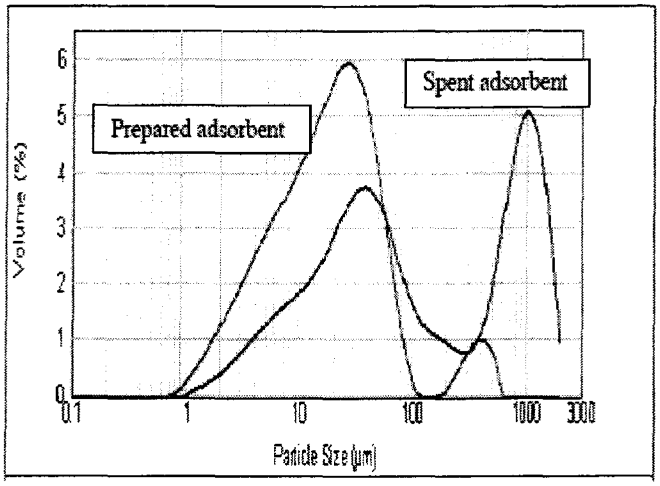


Figure 3.37 Particle size distribution of prepared and spent CFA/PFA/RHA sorbent from sol gel method (high efficiency) in removing zinc (Zn^{2+}).

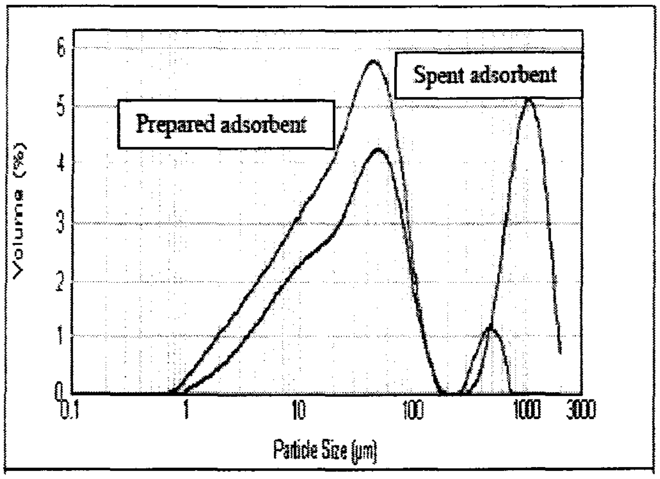


Figure 3.38 Particle size distribution of prepared and spent CFA/PFA/RHA sorbent from activation by NaOH method (low efficiency) in removing brilliant green dye.

It was shown that both prepared CFA/PFA/RHA sorbents (WH1 and WH2) (Figure 3.36) has unimodal particle size distribution. While the spent CFA/PFA/RHA sorbents shows bimodal particle size distribution, which might be resulted from a process involving the agglomerating of smaller particles (which is most probably the iron and nickel ions that cover the surface of the sorbent) during the adsorption process. Although the adsorption efficiency of the CFA/PFA/RHA sorbents prepared from water hydration method was almost the same (> 90%), however the analysis with the particle size distribution showed different results. This could be due to different affinity of metal ions towards the surface of CFA/PFA/RHA sorbent and as well as the present of impurities. Whereas the CFA/PFA/RHA sorbents prepared from sol gel method and activation by NaOH method, as well as their spent sorbents were shown to have bimodal particle size distribution (Figures 3.37-3.38). The bimodal particle size distribution of the prepared CFA/PFA/RHA sorbents might be resulted from a process involving breakup of multiple sources of particles or variable growth mechanisms during the preparation method which is more complex than water hydration method.

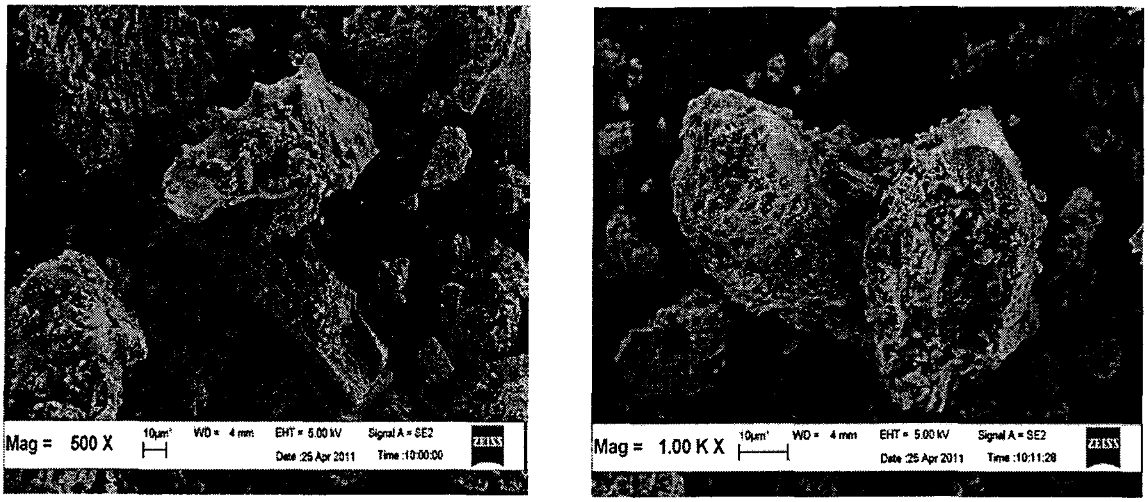
Specific surface area. The CFA/PFA/RHA sorbent prepared from water hydration method (WH2) and activation by NaOH method (AN) was selected for determination of specific surface area. The BET specific surface area obtained was tabulated in the Table 2.11.

Table 2.11 BET specific surface area of selected CFA/PFA/RHA sorbent

CFA/PFA/RHA sorbent	**BET specific surface area (m^2/g)**
WH2	16.11
AN	7.71

Based on the observation in Table 2.11, the BET specific surface area for prepared WH2 sorbent and prepared AN sorbent was 16.11 m^2/g and 7.71 m^2/g respectively. Prepared WH2 sorbent showed the higher BET specific surface area. The BET specific surface area of the sorbent might be affected by the reaction between CFA/PFA/RHA and chemical used during the sorbent preparation and contact time.

Surface morphology. SEM was used to observe the surface morphology of the prepared and spent CFA/PFA/RHA sorbents. Using this analysis, the structural of the particles made up of the sorbent was clearly observed. In this analysis, three samples were chosen, *i.e.* two sample of sorbent prepared from activation by NaOH method (before and after treated with brilliant green dye) and one sample of spent sorbent (from sol-gel method) after treated with zinc (Zn^{2+}). Figures 3.39-3.40 show the surface morphology of the (selected) prepared and spent CFA/PFA/RHA sorbents.



(a) (b)

Figure 3.39 Scanning electron micrograph of (a) prepared CFA/PFA/RHA sorbent and (b) spent CFA/PFA/RHA after treated with brilliant green dye.

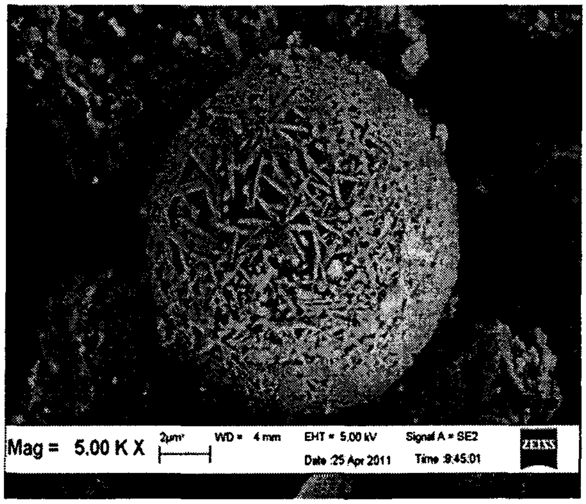


Figure 3.40 Scanning electron micrograph of spent CFA/PFA/RHA after treated with zinc (Zn^{2+}).

Based on the observation of Figure 3.39a, the surface of CFA/PFA/RHA sorbent (prepared from activation by NaOH method) has an irregular-shaped particle that unevenly scattered. After the adsorption of brilliant green dye, the sorbent was found to have more compact structures covered by rough irregular-shaped particles on the surface and inside the sorbent (Figure 3.39b). On the other observation of spent CFA/PFA/RHA sorbent (which was initially prepared from sol-gel method), it was observed from Figure 3.40 that the surface of coal fly ash particle was covered by needle-like structures which is most probably the zinc ions that covered the external surface of sorbent. The present of those structures showed that the adsorption was actually occurred and the sorbent was able to adsorb heavy metals and dye. Through this analysis, it showed that the adsorption process was affected by the physical characteristics of CFA/PFA/RHA sorbents.

CHAPTER 4

CONCLUSIONS

This study showed that waste-derived siliceous materials, *i.e.* rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA) could be combined and used as an effective sorbent for the removal of heavy metals and dyes from synthetic wastewater. All experimental parameters, such as amount of sorbent, initial concentration of synthetic wastewater, contact time, shaking rate, temperature, and pH affecting the adsorption of heavy metals and dyes. During all optimum conditions tested, it was found that RHA/PFA/CFA sorbent was able to remove more than 90% of pollutants from synthetic wastewater. Langmuir, Freundlich, Redlich-Peterson and Temkin isotherm equations were used to describe the adsorption of heavy metals and dyes.

From characterization studies, it was shown that the particle size distribution of the sorbents have a variation as a result of the reaction during the preparation of sorbent and as well as after treated with heavy metals and dye. The surface morphology of the sorbents revealed the structure of the prepared and spent RHA/PFA/CFA sorbents. Through this analysis, it showed that the adsorption process was affected by the physical characteristics of RHA/PFA/CFA sorbents. The specific functional group of the RHA/PFA/CFA sorbents showed the present of hydrocarbon, hydroxyl and silicon groups. The chemical compositions of the adsorbent showed that it consists of some complex compounds as the results of combination reaction of different basic compounds existed in RHA/PFA/CFA sorbents. It can be concluded that RHA/PFA/CFA sorbent used in this study can be exploited as an excellent alternative for the removal of acid violet dye by adsorption process.

Acknowledgements

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APPENDIX

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Waste-Derived Siliceous Materials as a Novel Sorbent for Removal of Ni^{2+} from Aqueous Solutions

Irvan Dahlan · Mohd Hafiz Mohd Razali

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Abstract In the present study, the preparation of sorbent from waste-derived siliceous materials has been investigated for the removal of nickel ion (Ni^{2+}) from aqueous solutions. Three types of ashes, i.e., rice husk ash (RHA), palm oil fuel ash (PFA), and coal fly ash (CFA), were used in the preparation of sorbent. Batch studies were carried out to examine the effect of various experimental parameters, i.e., RHA/CFA/PFA ratio in the sorbent preparation, contact time, initial concentration of Ni^{2+}, agitation rate, and pH. Among all the ratios of the prepared sorbent, it was found that sorbent containing RHA and PFA gave the highest Ni^{2+} removal efficiency. The optimum conditions for Ni^{2+} removal using RHA/PFA sorbent were obtained at contact time of 30 min, Ni^{2+} concentration of 100 mg/L, agitation rate of 130 rpm, and pH 4. During the optimum condition, more than 90% of Ni^{2+} could be removed in all experiment studies. It was also found that the spent RHA/PFA sorbents had a narrow range of particle size distributions as compared to prepared RHA/PFA sorbent. In addition, the surface morphology of the spent RHA/PFA sorbents had more compact structures.

Keywords Nickel ion (Ni^{2+}) · Synthetic wastewater · Sorbent · Siliceous wastes · Adsorption

1 Introduction

Heavy metals are generally established in water and wastewater generated from industrial activities, such as electroplating, chemical manufacturing, leather tanning, mining, and mineral processing. They are natural components of the earth's crust. Heavy metals do not biodegrade and tend to accumulate in living organisms, causing various health problems to animals and human beings (Chuah et al. 2005). Nickel ion (Ni^{2+}) is one of the heavy metal which is often present in our environment. Nickel ions are non-biodegradable toxic heavy metal and may cause dermatitis and allergic sensitization (Kandah and Meunier 2006). The removal of heavy metals, especially Ni^{2+} from water and wastewater is an issue of major concern. In Malaysia, the threshold limit (parameter limits of standard B) of nickel-containing liquid from sewage and industrial effluents has been set to 1 mg/L (DOE 1979). Heavy metals are permitted to be discharged only at very low concentrations.

Numerous methods have been investigated for the removal of heavy metals (including Ni^{2+}) such as chemical precipitation, chemical coagulation, chemical oxidation, and biological techniques. From the many treatment technologies that exist, adsorption using many types of solid materials is one of the most studied,

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I. Dahlan (✉) · M. H. M. Razali
School of Civil Engineering, Universiti Sains Malaysia,
Engineering Campus, Seri Ampangan,
14300 Nibong Tebal, Penang, Malaysia
e-mail: ceirvan@eng.usm.my

mainly due to its efficiency, high adsorption capacity, and low operational cost (Demirbas 2009; Gupta and Suhas 2009; Sud et al. 2008; Demirbas 2008). Recently, the use of cheap waste-derived material from industrial and agricultural sectors has been highlighted in the literatures for heavy metal removal from wastewater. These waste materials include rice husk ash (RHA), palm oil fuel ash (PFA), and coal fly ash (CFA). These ashes come from the burning of rice husk, palm oil fiber/shell, and coal to generate heat or electricity. These waste materials are available abundantly in Malaysia. The utilization of RHA (Chuah et al. 2005; Foo and Hameed 2009), palm oil by-product (Isa et al. 2007; Tan et al. 2008; Issabayeva et al. 2006), and CFA (Wang and Wu 2006) as sorbents has been studied and reviewed in literature. Nevertheless, most of these ashes were converted to activated carbon before utilizing as a sorbent. In addition, no work has been carried out to combine these waste-derived siliceous materials as a sorbent. Therefore, the aim of this study is to synthesize a sorbent from RHA, PFA, and CFA with good adsorption properties to remove nickel ion (Ni^{2+}) from aqueous solution.

2 Materials and Methods

2.1 Materials

The raw rice husk ash (RHA) was taken directly from Kilang Beras & Minyak Sin Guan Hup Sdn. Bhd., Penang. Palm oil fuel ash (PFA) was collected from United Oil Palm Mill, Penang. While coal fly ash (CFA) was given by Sultan Azlan Shah power plant, Manjung, Perak. Prior to use, all three types of ashes were sieved to obtain less than 63 μm fine particle size and oven-dried overnight at 110°C. The chemical composition of these raw materials is listed in Table 1. Synthetic wastewater (which contain Ni^{2+}) was prepared from $Ni(NO_3)_2.6H_2O$ (Fisher Scientific, 99%).

Table 1 Chemical composition of raw materials

Composition	Percentage (wt.%)		
	RHA	PFA	CFA
SiO_2	63.31	34.00	31.00
C	18.63	25.00	24.00
K_2O	2.23	2.90	0.68
P_2O_5	0.58	2.00	0.12
CaO	0.43	5.00	6.60
MgO	0.42	3.10	3.50
Fe_2O_3	0.26	5.30	10.00
SO_3	0.20	0.26	0.33
TiO_2	0.09	0.25	0.48
Cl_2O	0.18	0.03	trace
Al_2O_3	0.11	5.50	11.00
Others	0.01	0.24	0.29
LOI	13.54	16.42	12.00

2.2 Sorbent Preparation

The sorbents were prepared using the water hydration method (Dahlan et al. 2008). In the preliminary study, the sorbents were prepared from RHA, PFA, and CFA in order to select the best ratio between the ashes. The preparation of sorbents is described as follows. A specific amount (grams) of RHA, PFA, and CFA was added into 100 ml deionized water in the conical flask. Then, the conical flask was inserted into a water bath shaker with a stirring rate of 150 rpm and temperature of 65°C for 3 h. After that, the slurry was filtered and dried in the oven at 110°C for 3 h before used as sorbent.

2.3 Batch Adsorption Studies

Batch adsorption studies were carried out at ambient temperature by varying contact time, initial concentration of Ni^{2+}, shaking rate, and pH. All experiments were carried out in 250 ml conical flasks and the volume of the synthetic wastewater was kept as 100 ml. The pH of solution was maintained at a desired value by adding 0.1 M NaOH or HNO_3. The conical flasks were shaken at a certain speed in a SK-600 horizontal shaker. Samples were withdrawn at appropriate time intervals, filtered through glass fiber filter (Advantec) and filtrate was analyzed using DR2800 Spectrophotometer. The percentage removal of Ni^{2+} was calculated using the following relationship:

$$\% \text{ Removal} = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

where C_o and C_e are the initial and equilibrium concentration of Ni^{2+} in solution (milligrams per liter), respectively. All experiments were duplicated to increase the precision of the results, and only the average values were reported throughout this study. In this study, all removal efficiency data were presented in term of normalized data. Before plotting the graph, the data were normalized in the range of 0 (new $x_{\min}$) to 1 (new $x_{\max}$) to obtain a new removal efficiency scale value data (x_{i-n}) by the following Eq. 2,

$$x_{i-n} = \frac{x_i - x_{\min}}{x_{\max} - x_{\min}}(\text{new}\,x_{\max} - \text{new}\,x_{\min}) + \text{new}\,x_{\min} \qquad (2)$$

2.4 Analysis and Characterization

The chemical composition of each raw waste-derived siliceous material was determined using X-ray fluorescence spectrometer. The scanning electron microscopy (SEM) examinations were performed through Leo Supra 35 VP Scanning Electron Microscope to obtain the surface morphologies of sorbents. Surface analysis of the selected sorbents was conducted using Mastersizer 2000.

3 Results and Discussion

The amount of ash is one of the important parameters in the preparation of sorbent using hydration method; therefore, it is necessary to choose the best ratio between RHA, CFA, and PFA, but not all three types of ashes have to be used to synthesize the sorbent. In this study, the sorbent was only prepared by combination of two ashes with the aim to reduce complexity of the prepared sorbent. Figure 1 shows the effect of various ratios in the preparation of waste-derived siliceous materials as a sorbent in removing Ni^{2+}. The ratios shown in Fig. 1 represent the actual mass (grams) of ashes used in the sorbent preparation. It can be observed that amount of each ash (in sorbent preparation) was found to have effect on resulting sorbent in removing Ni^{2+} from synthetic wastewater. Although the effect was not too significant, however for RHA/CFA sorbent with ratio of 6:3 (ratio number six), the removal efficiency significantly dropped as compared to other ratios. At this moment, the influential factor for various ratios in synthesizing sorbents from waste-derived siliceous materials that provide a high Ni^{2+} removal efficiency is still unclear. From all the ratios, it can be observed that sorbent contains RHA and PFA (with ratio of 3:3) gave the highest Ni^{2+} removal efficiency. Therefore, to further investigate the effect of these waste-derived siliceous materials as a sorbent in removing Ni^{2+}, it was decided to prepare hydrated RHA/PFA sorbent (with ratio of 3:3) in the rest of this study.

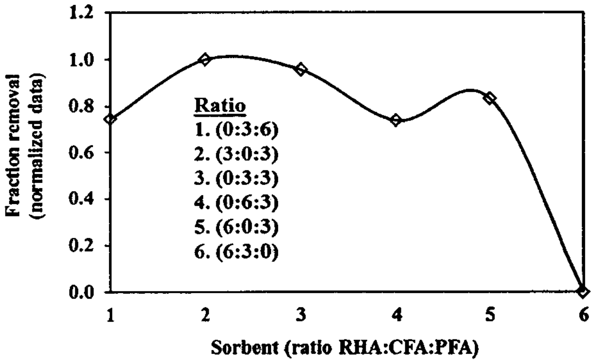

Fig. 1 Effect of ash ratio in the preparation of waste-derived siliceous sorbent on the removal of Ni^{2+}

3.1 Effect of Contact Time

Knowledge of the equilibrium time is very important for an economical wastewater treatment process. To establish a suitable contact time between the RHA/PFA sorbent and synthetic wastewater, the removal efficiency of Ni^{2+} were studied as a function of time from 5 to 60 min. The removal efficiency of Ni^{2+} increased with the increase in shaking time until equilibrium adsorption was established at 30 min (Fig. 2). This shows that adsorption sites are well exposed, thus quick reaction occurred. The results also show that at 30 min equilibrium time, the RHA/PFA sorbent is enough to remove more than 90% of Ni^{2+}. The nature of sorbent and its available sorption sites affect the time needed to reach equilibrium (Bhattacharya et al. 2008). In the beginning, fast adsorption may be explained due to the availability of more number of adsorption sites. After initial adsorption of adsorbate, the available sites in the adsorbent reduced and thus, the rate of adsorption further decreased, which attained a limiting value at equilibrium. Above 30 min of equilibrium time, there was no further significant Ni^{2+} removal. Thus, it was decided to adopt the equilibrium time as 30 min for the rest of this study.

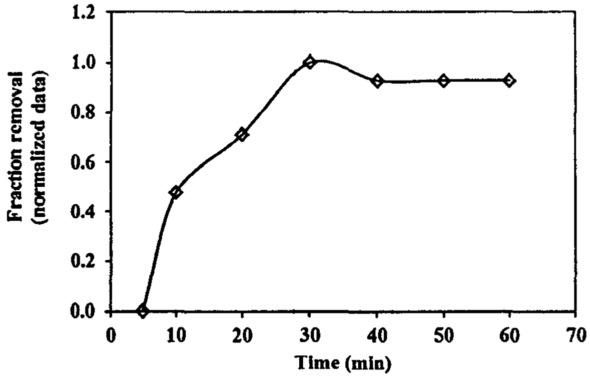

Fig. 2 Effect of contact time on the removal of Ni^{2+} using RHA/PFA sorbent

3.2 Effect of Nickel Concentration

The effect of initial concentrations on metal ion uptake was investigated by varying the nickel concentration from 25 to 200 mg/L. In this study, the RHA/PFA sorbent efficiency follows a bell-shaped curve (Fig. 3). It can be seen from Fig. 3, the Ni^{2+} removal efficiencies were markedly increased with the initial Ni^{2+} concentration up to 100 mg/L and remained constant up to 130 mg/L. The rapid increase of nickel removal at low initial concentration might be due the surface area and the availability of adsorption sites of RHA/PFA sorbent were relatively high and the nickel ions were easily adsorbed. As the Ni^{2+} concentration increased (above 130 mg/L), the total available adsorption sites became limited and/or saturated and the RHA/PFA sorbent could no longer bind further Ni^{2+}, resulting in a decrease in the Ni^{2+} removal efficiencies.

3.3 Effect of Agitation Rate

The effect of agitation rate was investigated by varying the agitation rate from 100 to 210 rpm while keeping other parameters constant. The effect of agitation rate on removal efficiency of Ni^{2+} is shown in Fig. 4. As can be seen in Fig. 4, the removal efficiency of RHA/PFA sorbent increased when shaking rate increased from 100 to 130 rpm. More than 90% of Ni^{2+} is removed from the synthetic wastewater at agitation rate of 130 rpm. An enhanced of Ni^{2+} removal efficiency at higher agitation rate is probably due to an increase in the mobility of adsorbing species (Raji and Anirudhan 1996). Apart from that, the increase of the agitation rate might improve the diffusion of nickel ions towards the surface of the RHA/PFA sorbents. For agitation rate greater than 130 rpm, the removal efficiency of Ni^{2+} was found to decrease. This might be due to higher boundary layer resistance to mass transfer in the bulk. Thus, it is concluded that agitation rate above 130 rpm is not suitable to ensure the surface binding of Ni^{2+}.

3.4 Effect of pH

The hydrogen ion concentration (pH) of the aqueous solutions (synthetic wastewater) is an important parameter since it affects not only the surface charge of sorbent, but also the degree of ionization and speciation of sorbent during adsorption (Cho et al. 2005). The behavior of Ni^2+ ions in aqueous solutions was examined in the pH range 2–10. The effect of pH on the Ni^{2+} removal is presented in Fig. 5. It was shown

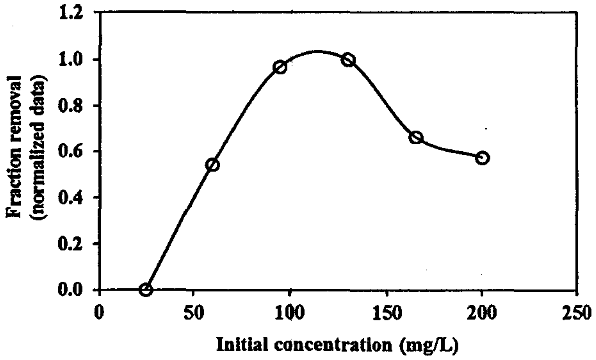

Fig. 3 Effect of nickel concentration on the removal of Ni^{2+} using RHA/PFA sorbent

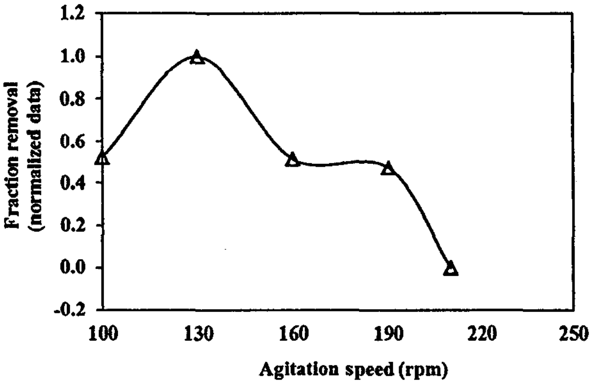

Fig. 4 Effect of shaking rate on the removal of Ni^{2+} using RHA/PFA sorbent

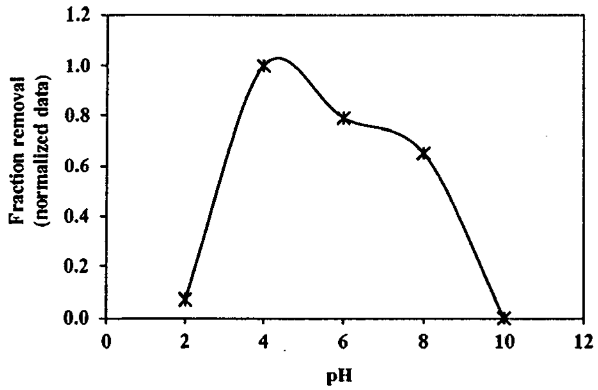

Fig. 5 Effect of pH on the removal of Ni^{2+} using RHA/PFA sorbent

that increasing pH solution from 2 to 4 caused the Ni^{2+} removal efficiency to increase. The low adsorption removal of Ni^{2+} by RHA/PFA sorbents at low pH values can be attributed to the fact that at low pH values, the H^+ ion concentration is high, therefore protons can compete with the nickel cations for surface adsorption sites of the sorbent, since at low pH, nickel are present in solution as Ni^{2+} free cations. Furthermore, when pH increases, there is a decrease in positive surface charge, which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of RHA/PFA sorbent's active site which favor adsorption process to occur.

Other than that, there was a reduction in Ni^{2+} removal efficiency at pH above 4. The reduction of nickel removal at pH above 4 might be due to the fact that the covalent bonds between Ni^2+ and the surface functional group of RHA/PFA sorbents are very weak. Therefore, in this study, pH 4 was considered as the optimum condition for adsorption process. Similar result was reported by Liu et al. (2009) for Ni^{2+} removal from synthetic wastewater using chemically modified and raw brown algae sorbents. They found that the optimal Ni^{2+} removal efficiencies were observed in the pH range of 4.3–6.5. However, different observations were reported by other researchers for Ni^{2+} adsorption. Study by Kehinde et al. (2009) reported that higher Ni^{2+} adsorption was obtained at pH 7–8 using sorbent prepared from coconut husk and teak tree bark. In another study, Srivastava et al. (2006) found that maximum Ni^{2+} removal efficiency occurred at pH 6 using sorbent prepared from rice husk ash. The different results obtained in this study are probably caused by structural changes being effected in the Ni^{2+} molecules and the surface adsorption characteristics of RHA/PFA sorbent. Therefore, this study shows that the pH of the solutions plays an important role in the whole Ni^{2+} adsorption process and on the adsorption capacity of RHA/PFA sorbents.

3.5 Characterization of RHA/PFA Sorbents

The particle size distribution of the selected RHA/PFA sorbent was examined and the result is shown in Fig. 6. It was shown that RHA/PFA sorbent before treated with Ni^{2+} (prepared sorbent) has a wider range of particle size distributions as compared to RHA/PFA sorbent after treated with Ni^{2+} (spent sorbent). The average volume of the particle size distribution range of spent RHA/PFA sorbents is higher than the prepared RHA/PFA sorbents, which means that higher particle size distributions range are formed after Ni^{2+} adsorption on the RHA/PFA sorbent. It was also found that the specific surface area of the prepared RHA/PFA sorbent was much higher (0.576 m^2/g) than that of the spent RHA/PFA sorbents (0.153 and 0.203 m^2/g for spent sorbents 1 and 2, respectively). The lower specific surface area of spent RHA/PFA sorbents could be due to the agglomerating of smaller particles (which is most probably the nickel ions that cover the surface of the sorbent) during the adsorption process. Apart from that, the surface-weighted mean and volume-weighted mean are dramatically increased (from 10.417 and 67.855 μm, respectively) to 39.118 and 142.156 μm, respectively, after the RHA/PFA sorbent was treated with Ni^{2+} (spent sorbent 2).

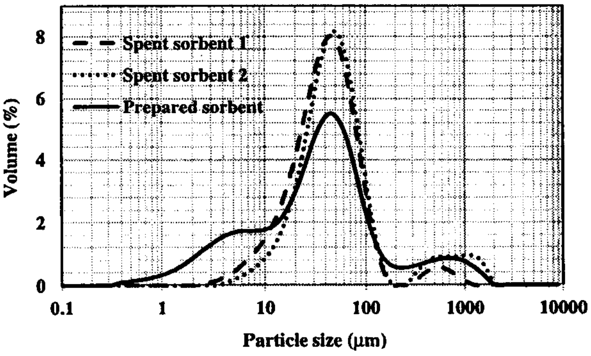

Fig. 6 Particle size distribution of RHA/PFA sorbents

To further strengthen this study, selected RHA/PFA sorbent was also characterized for surface morphology using SEM. The surface morphology of the raw RHA, PFA, prepared RHA/PFA sorbent and spent RHA/PFA sorbent is shown in Fig. 7. It can be observed from Fig. 7a, the surface of raw RHA has a dome-shaped (or a skeletal) structure. Similar surface morphology of this raw RHA was also reported in the literature (Dahlan et al. 2008; Vlaev et al. 2003; Krishnarao et al. 2001). Raw PFA (Fig. 7b) has the shape of flat plate layers with small particles deposited on its surface, same as reported by Zainudin et al. (2005). After the sorbent was prepared by water hydration method, RHA and PFA are combined to each other to form larger or complex particles with compact structures (Fig. 7c). After the adsorption of Ni^{2+}, the surface of the RHA/PFA sorbents was found to have more compact structures covered by lumps of smaller particles (Fig. 7d) which is most probably the nickel ions that covered the external surface of RHA/PFA sorbent.

4 Conclusions

It is evident from batch adsorption studies that sorbent prepared from waste-derived siliceous materials, especially the one prepared from RHA and PFA, could be used as an effective sorbent for the removal of nickel ions (Ni^{2+}) from synthetic wastewater. More than 90% of Ni^{2+} could be removed under optimum conditions. All experimental parameters, such as RHA/CFA/PFA ratio in the sorbent preparation, contact time, initial concentration of Ni^{2+}, agitation rate, and pH, affected the adsorption of Ni^{2+}.

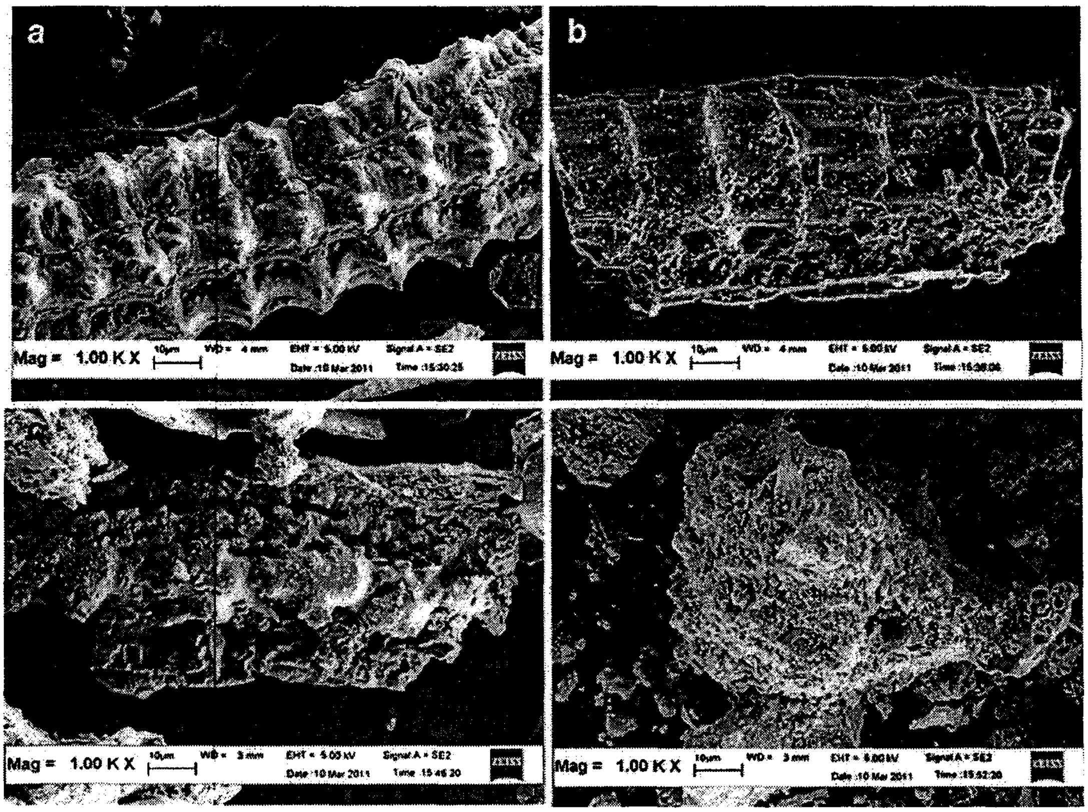

Fig. 7 Scanning electron micrograph of **a** raw RHA, **b** PFA, **c** prepared RHA/PFA sorbent, and **d** RHA/PFA sorbent after treated with nickel

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Physical Characterization of Prepared and Spent CFA/PFA/RHA Sorbents in Removing Heavy Metals and Dyes

I. Dahlan and S. Ismail
School of Civil Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia

Corresponding Author: I. Dahlan, School of Civil Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia Tel: +604-5996255 Fax: +604-5941009

ABSTRACT

High concentration of heavy metals and dyes creates health and environmental problems. Different types of treatment have been applied to remove these pollutants. In this study, physical characterization of CFA/PFA/RHA sorbent has been investigated to obtain a better understanding of adsorption process in removing heavy metals and dye. The sorbents from Coal Fly Ash (CFA), Palm oil Fuel Ash (PFA) and Rice Husk Ash (RHA) were prepared using water hydration method, sol-gel method and activation by NaOH method. The prepared sorbents were used to remove single components of zinc (Zn^{2+}), nickel (Ni^{2+}), iron (Fe^{2+}) and brilliant green dye from synthetic wastewater. The CFA/PFA/RHA sorbent prepared from sol-gel method showed high adsorption efficiency. From the particle size distribution analysis it was shown that the sorbents have a variation as a result of the reaction during the preparation of sorbent and treatment processes. Higher BET specific surface area was obtained for sorbent prepared from water hydration method. The surface morphology of the sorbents revealed the structure of CFA/PFA/RHA sorbent before and after the adsorption processes. This study shows that physical characteristics of CFA/PFA/RHA sorbent affecting the adsorption of heavy metals and dye.

Key words: Sorbent, solid ash, characterization, heavy metal, dye

INTRODUCTION

Now a days, Malaysia has been facing with pollution problems especially from the wastewater. Compare to 20 to 30 years ago, pollution towards water source is considering a norm. However, when Malaysia had become more develop throughout the years, this problem is started to pose back effects. Industrial sector has become one of the major economies in Malaysia. Existence of various factories had contributed to increase contaminants and concentration in wastewater discharge. The main concern is heavy metals and dyes. Heavy metals contamination is common in water and wastewater. Heavy metals are generally present in the wastewaters of various industries such as electroplating, metal finishing, leather tanning, paint manufacturing, steel fabrication and battery manufacturing. Heavy metals can cause serious water pollution and threaten the environment (Al-Madhoun *et al.*, 2005). There are many types of heavy metals such as Fe,Ni, Zn and Mn. A number of metal ions are essential for biological systems such as sodium (Na), potassium (K), calcium (Ca), manganese (Mn), iron (Fe) and zinc (Zn). Metals ions such as Ni is essential for living organism in small quantities. However, those heavy metals may pose toxicity when the concentration above the permissible limit. The presence of heavy metals in aquatic environments is known to cause severe damage to aquatic life (Mohammadi *et al.*, 2005) besides the fact that these metals kill microorganisms during biological treatment of waste water with a consequent delay of the process of water purification (Antunes *et al.*, 2003).

Apart from heavy metals, wastewater containing dye is also another major environmental problem. Due to chemical structure, dyes are resistant to fading on exposure to light, water and many chemicals (Robinson *et al.*, 2001). Many dyes are difficult to be decolorized and decomposed biologically due to dye's complex structure and synthetic origin. There are many structure varieties of dyes such as acidic, basic, disperse, azo, diazo, anthraquinone based and metal complex dyes (Ahmad *et al.*, 2002).

Therefore, many researches have been carried out to find a solution for wastewater treatment in removing the heavy metals and dyes. As the advance technology had been invented many researches have been carried out in order to find an ideal method for removal of heavy metals and dyes. One of the methods that been applied is adsorption. Adsorption process has been found becoming a prominent method of treating aqueous effluent in industrial processes for a variety of separation and purification purpose (Benkli *et al.*, 2005). This technique also found to be highly efficient for the removal of heavy metals and dyes in terms of initial cost, simplicity of design, ease of operation and insensitivity to toxic substances (Garg *et al.*, 2004).

The most recent research is utilization solid wastes as a sorbent. Malaysia is well known in agricultural sector. From those agricultural plants, palm oil industry and rice milling industry have generated a huge amount of biomass wastes annually, i.e., Palm oil Fuel Ash (PFA) and Rice Husk Ash (RHA). Apart from these agricultural wastes, Malaysia also produce voluminous Coal Fly Ash (CFA) generated from burning coal to generate electricity. Even though, the utilization of RHA, PFA and CFA have been studied as a sorbent to remove pollutants, but all studies only use one type of ash (with or without modification) and most of these ashes were converted into activated carbon before utilizing as a sorbent. In addition, no work has been carried out to combine these waste-derived siliceous materials as a sorbent. Therefore, the adsorption characteristics of these waste-derived siliceous materials (CFA/PFA/RHA) towards removing heavy metals and dyes are still unclear. Thus, in this research, characterization of CFA/PFA/RHA sorbent was investigated to obtain a better understanding of adsorption process in removing heavy metals and dyes.

MATERIALS AND METHODS

The sorbents were obtained from previous study (Naima, 2011; Mahdzir, 2011; Mohd Zain, 2011; Mohd Razali, 2011) and it was prepared from Coal Fly Ash (CFA), Palm oil Fuel Ash (PFA) and Rice Husk Ash (RHA) using various methods. CFA/PFA/RHA sorbents were prepared by water hydration method, sol-gel method and activation by NaOH method. These prepared sorbents were tested (in batch experiment) to remove zinc (Zn^{2+}), nickel (Ni^{2+}), iron (Fe^{2+}) and brilliant green dye from aqueous solutions (synthetic waste water).

The concentration of heavy metals and dyes in aqueous solutions before and after adsorption was determined using a DR 2500 spectrophotometer (Shimadzu, Japan). The Scanning Electron Microscopy (SEM) examinations were performed through Leo Supra 35 VP Scanning Electron Microscope to obtain the surface morphologies of selected CFA/PFA/RHA sorbents and to verify the presence of porosity. Surface analysis of the selected sorbents was examined using Mastersizer 2000. BET specific surface area was analyzed using Autosorb-1 Quantachrome analyzer.

RESULTS AND DISCUSSION

Sorbent efficiency: The collected sorbents were prepared from three different methods and were tested with different types of heavy metals and dye. Based on the adsorption studies, the adsorption efficiency for different methods of preparation was tabulated in the Table 1. Based on the results obtained (Table 1) sol-gel method showed the highest percentage of adsorption efficiency meanwhile activation by NaOH method showed the lowest percentage of adsorption efficiency. The percentage of adsorption efficiency for different methods was observed in order to know the effectiveness of the CFA, PFA and RHA combination as a sorbent and to identify the appropriate method for adsorbent preparation.

The adsorption efficiency was affected by several factors such as sorbent preparation variables and chemical used. The main variables affecting the sorbent performance were amount of solid wastes, shaking rate and pH. These variables were important in order to obtain sorbent with high pollutant removal efficiency. Optimum amount of solid wastes and shaking rate will ensure that all of the solid wastes mix together accordingly. Based on the result obtain, sol gel method showed the highest adsorption efficiency compare with the other two methods. Observation on steps used in the sorbent preparation, sol-gel method involves a series of complicated steps and using with more than one chemical component. Treatment with concentrated HNO_3 helps to reduce the impurities and leach out the metal oxides by forming nitrates which were easily dissolved in water. After that, sodium silicate solution was produced when dissolved in NaOH. The sodium silicate solution was neutralized using HNO_3 containing the metal to produce silica gel with the metal ion chemically incorporated into the silica matrix.

Sorbent characterization: A number of characterization techniques were used to characterize the physical properties of selected CFA/PFA/RHA sorbents before and after treated with heavy metals and dye.

Particle size distribution: Selected CFA/PFA/RHA sorbents was characterized for particle size distribution before and after treated with heavy metals and dye. In this analysis, eight samples of prepared and spent CFA/PFA/RHA sorbents were chosen to undergo the analysis. Four samples were taken from water hydration method (WH1 and WH2), two samples were taken from sol-gel method (SG1) and the remaining two were taken from activation by NaOH method (AN). The particle size distribution of the selected CFA/PFA/RHA sorbents was examined and the results are shown in Fig. 1-3.

It was shown that both prepared CFA/PFA/RHA sorbents (WH1 and WH2) (Fig. 1) has unimodal particle size distribution. While the spent CFA/PFA/RHA sorbents shows bimodal particle size distribution, which might be resulted from a process involving the agglomerating of smaller particles (which is most probably the iron and nickel ions that cover the surface of the sorbent) during the adsorption process. Although, the adsorption efficiency of the CFA/PFA/RHA sorbents prepared from water hydration method was almost the same (>90%), however, the analysis with the particle size distribution showed different results. This could be due to different affinity of metal ions towards the surface of CFA/PFA/RHA sorbent and as well as the present of impurities.

Table 1: Adsorption efficiency of CFA/PFA/RHA sorbents prepared from various methods

Preparation method	Sorbent efficiency (%)	Pollutant to be removed	Reference
Water hydration (WH)			
WH1	>90	Iron (Fe^{2+})	Mohd Zain (2011)
WH2	Nickel (Ni^{2+})	Mohd Razali (2011)	
Sol gel (SG1)	96-98	Zinc (Zn^{2+})	Naima (2011)
Activation by NaOH (AN)	68-91	Brilliant green dye	Mahdzir (2011)

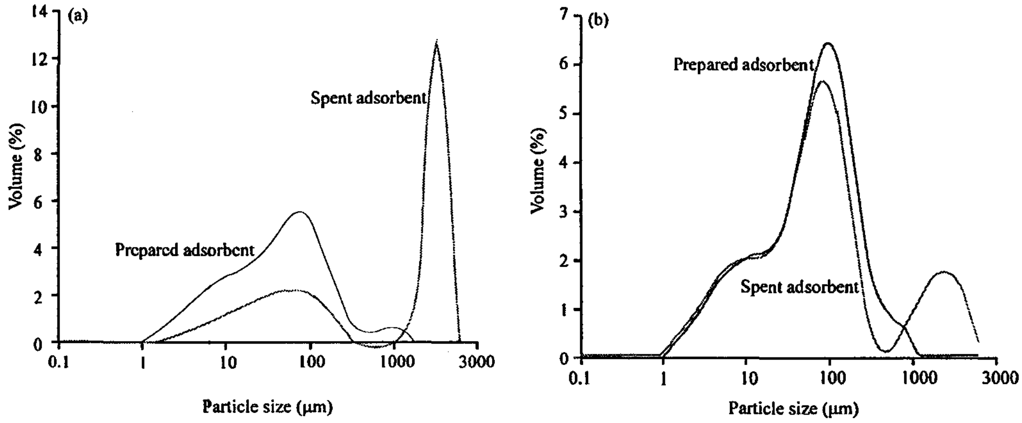

Fig. 1(a-b): Particle size distribution of prepared and spent CFA/PFA/RHA sorbent from water hydration method (high efficiency) in removing (a) Iron (Fe^{2+}) and (b) Nickel (Ni^{2+})

Whereas, the CFA/PFA/RHA sorbents prepared from sol gel method and activation by NaOH method, as well as their spent sorbents were shown to have bimodal particle size distribution (Fig. 2, 3). The bimodal particle size distribution of the prepared CFA/PFA/RHA sorbents might be resulted from a process involving breakup of multiple sources of particles or variable growth mechanisms during the preparation method which is more complex than water hydration method.

Specific surface area: The CFA/PFA/RHA sorbent prepared from water hydration method (WH2) and activation by NaOH method (AN) was selected for determination of specific surface area. The BET specific surface area obtained was tabulated in the Table 2.

Based on the observation in Table 2, the BET specific surface area for prepared WH2 sorbent and prepared AN sorbent was 16.11 and 7.71 $m^2\ g^{-1}$, respectively. Prepared WH2 sorbent showed the higher BET specific surface area. The BET specific surface area of the sorbent might be affected by the reaction between CFA/PFA/RHA and chemical used during the sorbent preparation and contact time.

Surface morphology: SEM was used to observe the surface morphology of the prepared and spent CFA/PFA/RHA sorbents. Using this analysis, the structure of the particles made up of the sorbent was clearly observed. In this analysis, three samples were chosen, i.e., two sample of sorbent prepared from activation by NaOH method (before and after treated with brilliant green dye) and one sample of spent sorbent (from sol-gel method) after treated with zinc (Zn^{2+}). Figure 4 and 5 show the surface morphology of the (selected) prepared and spent CFA/PFA/RHA sorbents.

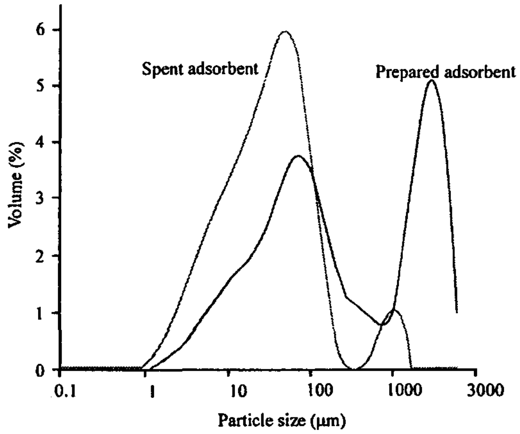

Fig. 2: Particle size distribution of prepared and spent CFA/PFA/RHA sorbent from sol gel method (high efficiency) in removing zinc (Zn^{2+})

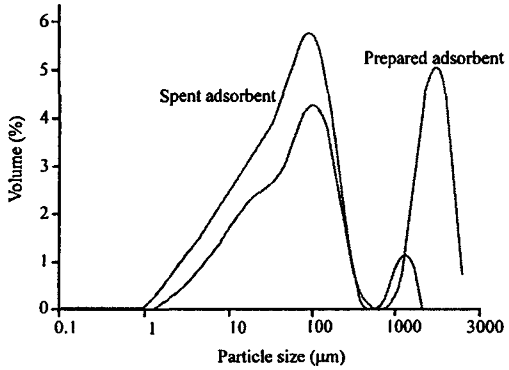

Fig. 3: Particle size distribution of prepared and spent CFA/PFA/RHA sorbent from activation by NaOH method (low efficiency) in removing brilliant green dye

Table 2: BET specific surface area of selected CFA/PFA/RHA sorbent

CFA/PFA/RHA sorbent	BET specific surface area ($m^2 g^{-1}$)
WH2	16.11
AN	7.71

Based on the observation of Fig. 4a, the surface of CFA/PFA/RHA sorbent (prepared from activation by NaOH method) has an irregular-shaped particle that unevenly scattered. After the adsorption of brilliant green dye, the sorbent was found to have more compact structures covered by rough irregular-shaped particles on the surface and inside the sorbent (Fig. 4b). On the other observation of spent CFA/PFA/RHA sorbent (which was initially prepared from sol-gel method), it was observed from Fig. 5 that the surface of coal fly ash particle was covered by needle-like structures which is most probably the zinc ions that covered the external surface of sorbent. Raw coal fly ash particle typically consists of smooth sphere particles/structures (Lee *et al.*, 2006). The presence of those structures showed that the adsorption was actually occurred and the sorbent was able to adsorb heavy metals and dye.

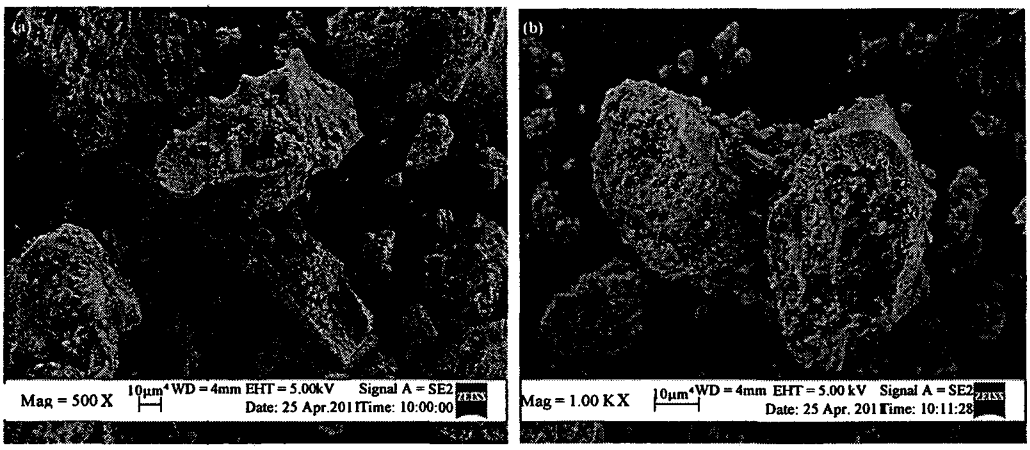

Fig. 4 (a-b): Scanning electron micrograph of (a) Prepared CFA/PFA/RHA sorbent and (b) Spent CFA/PFA/RHA after treated with brilliant green dye

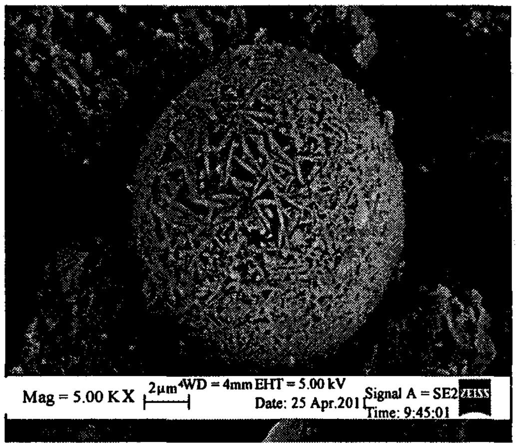

Fig. 5: Scanning electron micrograph of spent CFA/PFA/RHA after treated with zinc (Zn^{2+})

CONCLUSION

In this study, various physical characterizations has been carried out for prepared and spent CFA/PFA/RHA sorbents in order to obtain a better understanding of adsorption process in removing heavy metals and dye. The particle size distribution of the sorbents showed that the sorbents have a variation as a result of the reaction during the preparation of sorbent and as well as after treated with heavy metals and dye. The surface morphology of the sorbents revealed the structure of the prepared and spent CFA/PFA/RHA sorbents. Through this analysis, it showed that the adsorption process was affected by the physical characteristics of CFA/PFA/RHA sorbents.

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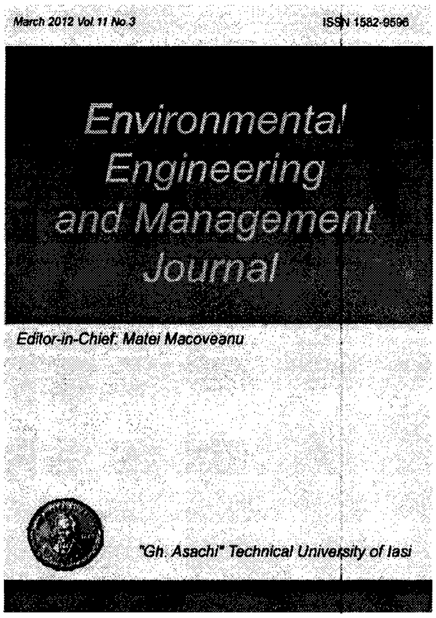
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A STUDY ON THE REMOVAL CHARACTERISTIC OF ACID VIOLET DYE FROM SYNTHETIC WASTEWATER USING A NOVEL RHA/PFA/CFA SORBENT

Irvan Dahlan*, Ahmad Shahril Mohamed Noor

School of Civil Engineering, Universiti Sains Malaysia,
Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia

Abstract

A novel RHA/PFA/CFA sorbent was developed by sol-gel method using three types of ashes, *i.e.* rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash. Batch studies were performed to evaluate the effect of various experimental parameters, *i.e.* initial concentration of acid violet dye, contact time and shaking rate. The results showed that the acid violet dye uptake at equilibrium time increases with contact time and initial concentration of acid violet dye. Shaking rate was found insignificant for high acid violet dye uptake at equilibrium time. From surface analysis of selected RHA/PFA/CFA sorbents, the spent sorbent had more compact structures covered by irregular rough particles and the specific structure of raw RHA, PFA, and CFA were no longer visible. In addition, lower specific surface area was obtained for spent RHA/PFA/CFA sorbent. The adsorption data was analyzed by the Langmuir, Freundlich, and Temkin isotherm models. The results indicate that the Freundlich model fits the data better as compared to the Langmuir and Temkin isotherm models in terms of correlation coefficient (R^2). This study demonstrated that RHA/PFA/CFA sorbent was successfully used for the removal acid violet dye by adsorption process.

Key words: Acid violet dye, adsorption, isotherm, sol-gel, waste material

1. Introduction

Environmental pollution, especially wastewater was a major issue in many countries. Over the last few decades, society had become sensitive towards wastewater pollution and the protection of

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* Author to whom all correspondence should be addressed: e-mail: ceirvan@eng.usm.my; Phone: +604-5996255; Fax: +604-5941009

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A review on zinc removal from wastewater using low cost adsorbents

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Complete List of Authors:	Zwain, Haider; Universiti Sains Malaysia, School of Civil Engineering Dahlan, Irvan; Universiti Sains Malaysia, School of Civil Engineering
Key Words:	Adsorption, Ash, Heavy Metals, Pollution Control, Waste-Water

A review on zinc removal from wastewater using low cost adsorbents

Haider M. Zwain and Irvan Dahlan*

School of Civil Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 NibongTebal, Pulau Pinang, Malaysia.

*Corresponding author's Tel.: +604-5996255; Fax: +604-5941009

E-mail: ceirvan@eng.usm.my / dahlan_irvan@yahoo.com

Abstract

This review investigates variety of various low price adsorbents in removal of zinc from wastewater. Today, heavy metal pollution has become one amongst the most serious environmental issues. The treatment of heavy metals is of special concern attributable to their persistence and recalcitrance within the surroundings. In recent, typical treatment technologies for the removal of these toxic heavy metals are not economical and any low potency of metal removals. Therefore, Adsorption process has been proven one amongst the most effective wastewater treatment technologies. Low-cost adsorbents utilization has been investigated to replace the current expensive methods for removing of heavy metals from answer attributable to their high capacity for heavy metals can be obtained, employed, and contribution within the reduction of prices for waste disposal, so contributing to environmental protection. Inexpensive adsorbents are developed by utilizing various agro-industrial and municipal waste materials. Modification of the adsorbents also can improve adsorption capacity. In this review, it's obvious from the literature survey that various low-cost adsorbents have shown sensible potential for the removal of zinc. Additionally, more research is needed to conduct the practical utility of low-cost adsorbents on commercial scale.

Keywords: Adsorption, Ash, Heavy Metals, Pollution Control, Waste-Water

1.0 Introduction

Water is a source of energy and life, although millions of people worldwide are suffering with the shortage of clean drinking and fresh water. Rapid pace of population expansion, industrialization and unplanned urbanization have largely contributed to the severe water pollution and surrounding soils. Discharge of toxic industrial wastes and untreated sanitary, dumping of industrial effluent, and runoff from agricultural fields can be the main sources of freshwater pollution. It is well known that 70-80% of all illnesses in developing countries are related to water contamination, particularly susceptible for children and women [1].

Contamination of aqueous environments by heavy metals is a worldwide environmental problem due to their toxic effects and accumulation through the food chain [2]. The major pollutants are heavy metals in ground, marine, industrial and even treated wastewaters [3]. The presence of heavy metals in drinking water will be hazardous to consumers. Zn, Cd, Hg, Pb, Cr, Cu, etc. can damage liver, nerves and block functional groups of vital enzymes and bones [4]. Metal ions in water can occur naturally from anthropogenic sources and from leaching of ore deposits, which mainly include solid waste disposal and industrial effluents. The levels of heavy metals in water system have substantially increased over time with rapid development of industrial activities [5].

Various regulatory bodies have set the maximum prescribed limits for the discharge of toxic heavy metals in the aquatic systems. However the metal ions are being added to the water stream at a much higher concentration than the prescribed limits by industrial activities, thus leading to the health hazards and environmental degradation (Table 1). In Malaysia, the selected parameter limits of effluent of heavy metals have shown with stipulated to the

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Utilization of Industrial Combustion Waste Materials as Potential Sorbent for the Removal of Zinc (Zn^{2+}) from Synthetic Wastewater

Irvan Dahlan*
School of Civil Engineering, Universiti Sains Malaysia,
Engineering Campus, Seri Ampangan, 14300 Nibong Tebal,
Pulau Pinang, MALAYSIA.
*Corresponding E-mail: ceirvan@eng.usm.my /
dahlan_irvan@yahoo.com

Haider Zwain
School of Civil Engineering, Universiti Sains Malaysia,
Engineering Campus, Seri Ampangan, 14300 Nibong Tebal,
Pulau Pinang, MALAYSIA.

Abstract – **In this work, the removal of zinc (Zn^{2+}) from aqueous solutions was investigated by adsorption method using three types of ashes resulted from burning industrial wastes *i.e.* rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA). In this study, sol-gel method was used in the preparation of RHA/PFA/CFA sorbent. Batch studies were performed to evaluate the effect of various experimental parameters, *i.e.* amount of sorbent, contact time, shaking rate, and pH. The optimum conditions for Zn^{2+} removal were obtained at sorbent amount of 1 g, contact time of 1 h, shaking rate of 100 rpm, and pH 8. From surface analysis of selected RHA/PFA/CFA sorbents, it was found that the surface of the sorbent after treated with Zn^{2+} had more compact structures covered by lumps of smaller particles with sharp needle-like structure. In addition, lower specific surface area was obtained for RHA/PFA/CFA sorbent after treated with Zn^{2+}.**

Key words – Synthetic wastewater; Zincs (Zn^{2+}); Sorbent; Waste material; Adsorption; Sol-gel.

1. INTRODUCTION

Nowadays, heavy metals are among the most important environmental pollutants, especially in Malaysia due to rapid industrialization. Heavy metal contaminations occur in aqueous waste streams from many industrial activities such as metallurgical processes, metal plating, mining, etc. Zinc (Zn^{2+}) has received special attention due to the fact that at low concentrations, zinc (Zn) is important for many biochemical processes, however when discharged into natural environment at high concentrations, it can have harmful impact due to acute toxicity and non-biodegradability characteristics, and zinc-containing solid and liquid wastes are considered as hazardous wastes [1,2]. Therefore in Malaysia, the threshold limit/standard of zinc-containing liquid from sewage and industrial effluents has been set to 1 mg/L [3].

The safe and effective disposal of Zn^{2+} containing wastewater is a challenging task for industries since cost effective treatment alternatives are not readily available. Over the year, various types of treatment technology have been developed to treat metal contaminated water/wastewater from industrial activities before discharging it into water stream. From various treatment technologies exist, adsorption technique using many type of sorbents is still the most favorable method in the removal of heavy metals from waste/wastewaters due to its efficiency, high adsorption capacity and low operational cost method [4-7]. From many type of sorbent, activated carbon (from many sources of raw materials) is currently of great interest, however carbon adsorption remains an expensive process and difficulties associated with regeneration [8]. Therefore, low-cost (sorbent) alternatives to activated carbons have attracted considerable research interest.

Apart from producing heavy metal-containing wastewater, industrial activities also leave behind a huge amount of solid waste in the form of ash. Therefore, attempts have been made to utilize waste materials as an alternative sorbents, especially waste-derived siliceous materials, *i.e.* rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA). These ashes are come from the burning of rice husk, palm oil fiber/shell, and coal to generate electricity, respectively. Although the utilization of RHA, PFA and CFA have been investigated/used as a sorbent to remove pollutants, nevertheless, all studies only use one type of ash (with or without modification) and most of these ashes were converted into activated carbon before utilizing as a sorbent. Furthermore, no work has been carried out to combine these waste-derived siliceous materials as a sorbent.

Therefore, the aim of this research is to synthesize a RHA/PFA/CFA sorbent with good adsorption properties to remove zinc (Zn^{2+}) from aqueous solutions (synthetic wastewater) using sol-gel method.

2. MATERIALS AND METHODS

2.1. Preparation of Sorbent.

The ashes from burning industrial fuels were collected and used in the process of synthesizing sorbent. The raw rice husk ash (RHA) was supplied by Kilang Beras & Minyak Sin Guan Hup Sdn. Bhd., Pulau Pinang. Palm oil fuel ash (PFA) was obtained directly from United Oil Palm Mill, Pulau Pinang. While coal fly ash (CFA) was collected from Stesen Janakuasa

Sultan Azlan Shah, Manjung, Perak. Prior to use, all three type of ashes were sieved to obtain less than 63 μm fine particle size and oven dried overnight at 110°C. Stock zinc solution (synthetic wastewater) for all experimental studies was prepared in deionized water using analytical reagent grade $ZnSO_4.7H_2O$.

Sorbent was prepared by sol-gel method [9-10]. About 15 g of each ash (RHA, PFA, CFA) was mixed and stirred in nitric acid (HNO_3 65%) for 24 h. Then, it was filtered and rinsed with deionized water until the pH of the rinse became constant. The mixture was subsequently dried in an oven at 110°C for one day. About 15 g of the acidified RHA/PFA/CFA sorbents were dissolved in 250 ml of 6 M NaOH, stirred for 12 h, and filtered to remove undissolved particles. The filtrant was titrated with 3 M nitric acid which contained 10% (w/w) Al^{3+} [$Al(NO_3)_3.9H_2O$ in HNO_3]. A black suspension was observed when the pH reached 11.5. Titration was carried out until the pH ~ 5. The RHA/PFA/CFA sorbents were then aged for 6 days. The soft gel formed was filtered and dried at 110°C for 24 h.

2.2. Batch Adsorption Studies

Batch adsorption studies were carried out at ambient temperature by varying amount of sorbent, contact time, shaking rate, and pH. All experiments were carried out in 250 ml conical flasks and the total volume of the synthetic wastewater was kept at 100 ml. The pH of solution was maintained at a desired value by adding 0.1 M NaOH or $HNCO_3$. The conical flasks were shaken at a certain speed in a SK-600 horizontal shaker. Samples were withdrawn at appropriate time intervals, filtered through fiber filter paper and filtrate was analyzed using DR 2500 Spectrophotometer. The percentage removal of Zn^{2+} was calculated using the following relationship:

$$\%\,\text{Removal} = \frac{C_o - C_e}{C_o}\ x\ 100 \qquad (1)$$

where C_o and C_e are the initial and equilibrium concentration of Zn^{2+} solution (mg/l), respectively. All experiments were duplicated to increase the precision of the results, and only the average value was reported throughout this study.

2.3. Characterization of Sorbent

The scanning electron microscopy (SEM) examinations were performed through Leo Supra 35 VP Scanning Electron Microscope to obtain the surface morphologies of the selected RHA/PFA/CFA sorbents. Surface analysis of the selected RHA/PFA/CFA sorbents was analyzed using Mastersizer 2000.

3. RESULTS AND DISCUSSION

3.1. Effect of Sorbent Amount

The amount of sorbent is one of the important parameter to obtain the quantitative adsorption of Zn^{2+} from syntheti wastewater. The dependence of Zn^{2+} adsorption on amoun was studied by varying the amount of RHA/PFA/CFA sorben from 0.25 to 4 g while keeping other parameters (contact time shaking rate, pH and initial Zn^{2+} concentration) constant Figure 1 shows the effect of sorbent amount on remova efficiency of Zn^{2+}. It can be observed that removal efficienc of Zn^{2+} increases with increase in sorbent amount. Zn^{2} removal efficiency significantly increased from 93.3% t 98.5% when the amount of RHA/PFA/CFA sorbent wa increased from 0.25 to 1 g. An increase in the adsorption wit the amount of sorbent might be attributed to greater surfac area and the availability of more exchangeable sites for meta ions. At the sorbent amount of greater than 1 g, the Zn^{2} removal efficiencies are almost similar, hence no additiona adsorption of Zn^{2+} to adsorption sites of the sorbent. There is slightly decrease in Zn^{2+} removal efficiency from 2 to 4 g, thi might be due to desorption effect, however, the effect is no significant.

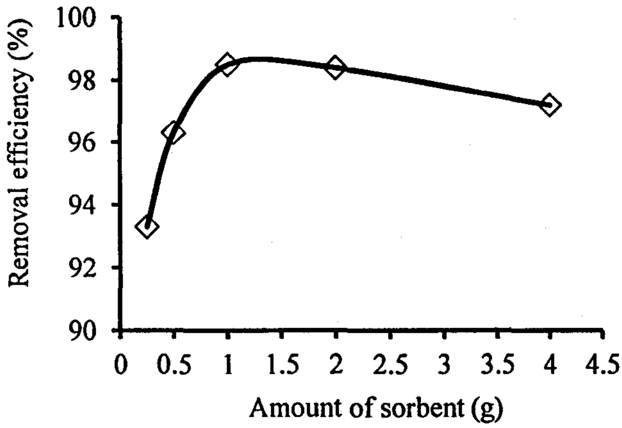


Figure 1: Effect of sorbent amount on the removal of Zn^{2+}.

3.2. Effect of Contact Time

Equilibrium time is another important parameters for a economical wastewater treatment process. To establish a suitable contact time between the RHA/PFA/CFA sorbent an Zn^{2+} solution, the removal efficiency of Zn^{2+} were studied as function of time over 0.5 to 2.5 h. Figure 2 shows the effect c contact time on removal efficiency of Zn^{2+}. The result showed that a half-hour (0.5 h) equilibrium time for th RHA/PFA/CFA sorbent is enough to remove more than 95 of Zn^{2+}. This shows that adsorption site are well exposed, thu quick reaction is occurred. As the contact time increase to 1 about 97.2% Zn^{2+} removal efficiency was achieved. Above 1 of contact time, there were no significant Zn^{2+} remov efficiency was observed, therefore equilibrium time wa reached in 1 h. Thus, to make sure that equilibrium was reached, it was decided to use the equilibrium time of 1 h in the rest of this study.

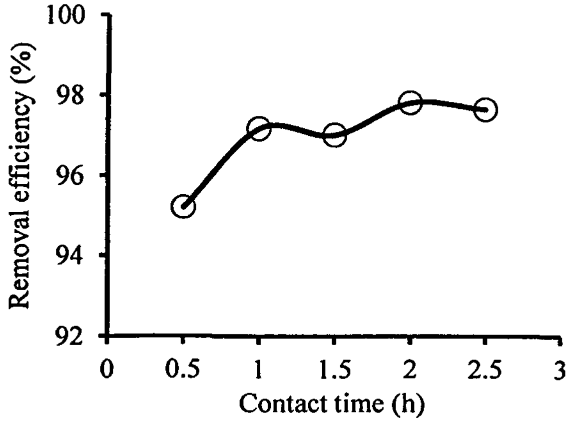


Figure 2: Effect of contact time on the removal of Zn^{2+}.

3.3. Effect of Shaking Rate

The effect of shaking rate was studied by varying the shaking rate from 50 to 250 rpm while keeping other parameters constant. Results shown in Figure 3 indicate that removal efficiency of RHA/PFA/CFA sorbent increased from 92.8% to 97.5% when shaking rate increased from 50 to 100 rpm. An enhanced adsorption rate at higher shaking rate is probably due to an increase in the mobility of sorbing species [11]. Apart from that, the increase of the shaking rate might improve the diffusion of the zinc ions towards the surface of the RHA/PFA/CFA sorbents. For shaking rate greater than 100 rpm, the removal efficiency of Zn^{2+} remained constant, thus a shaking rate of 100 rpm is sufficient to assure the surface binding for zinc uptake.

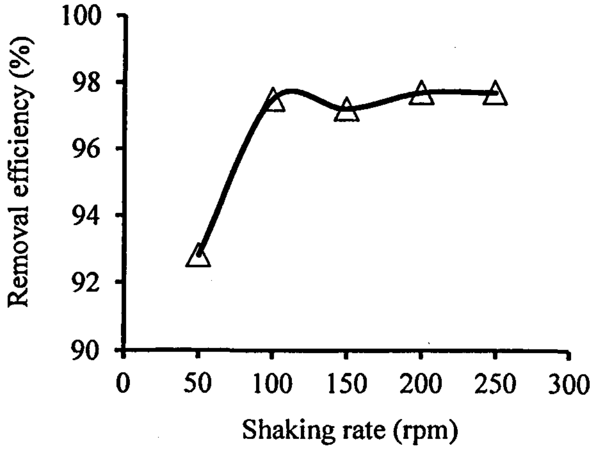


Figure 3: Effect of shaking rate on the removal of Zn^{2+}.

3.4. Effect of pH

The behavior of metal ions in aqueous solutions (synthetic wastewater) is influenced by pH of the solution. The pH does not only determine the speciation of metal ions in the solution but also determines the surface charge of the sorbent [12]. Thus, the role of pH was examined in the pH range 2 – 10 on the Zn^{2+} removal. The effect of pH on the Zn^{2+} removal is presented in Figure 4. It was shown that increasing pH of the solution from 2 to 8 caused the Zn^{2+} removal efficiency increased from 87% to 97%. The low adsorption removal of Zn^{2+} by RHA/PFA/CFA sorbents at low pH values can be attributed to the fact that at low pH values, the H^+ ion concentration is high, therefore protons can compete with the zinc cations for surface adsorption sites of the sorbent, since at low pH zinc are present in solution as Zn^{2+} free cations. Furthermore when pH increases, there is a decrease in positive surface charge, which results in a lower electrostatic repulsion between the positively charged metal ion and the surface of RHA/PFA/CFA sorbent's active site which favor adsorption process to occur.

From Figure 4, it was also found that there was a reduction in Zn^{2+} removal efficiency to 94%, when equilibrium pH was increased to 10. Therefore, in this study pH 8 was considered as an optimum condition for adsorption process. Different observations were reported by other researchers for Zn^{2+} adsorption. Study by Abdel Salam et.al. [13] reported that the optimum pH of 6 was obtained for Zn^{2+} adsorption using peanut husk charcoal and natural zeolite. Similar to that, Amuda et.al. [14] also found the optimum pH of 6 for the removal of Zn^{2+} using composite sorbents (chitosan-coated acid treated coconut shell carbon). The different results obtained in this study are probably caused by structural changes being effected in the Zn^{2+} molecules and the surface adsorption characteristics of RHA/PFA/CFA sorbent. Therefore, this study shows that the pH of the solutions plays an important role in the whole Zn^{2+} adsorption process and on the adsorption capacity of RHA/PFA/CFA sorbents.

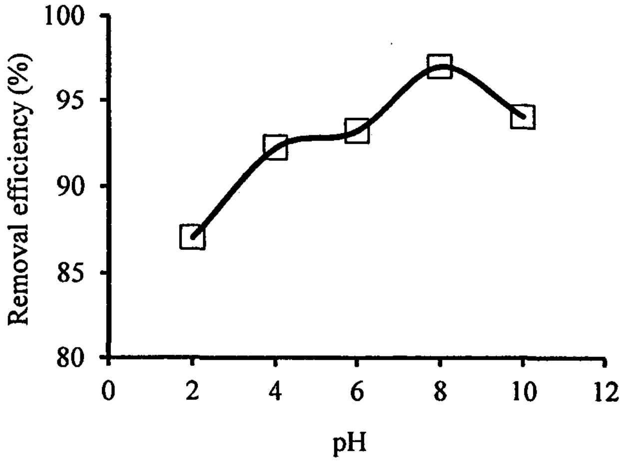
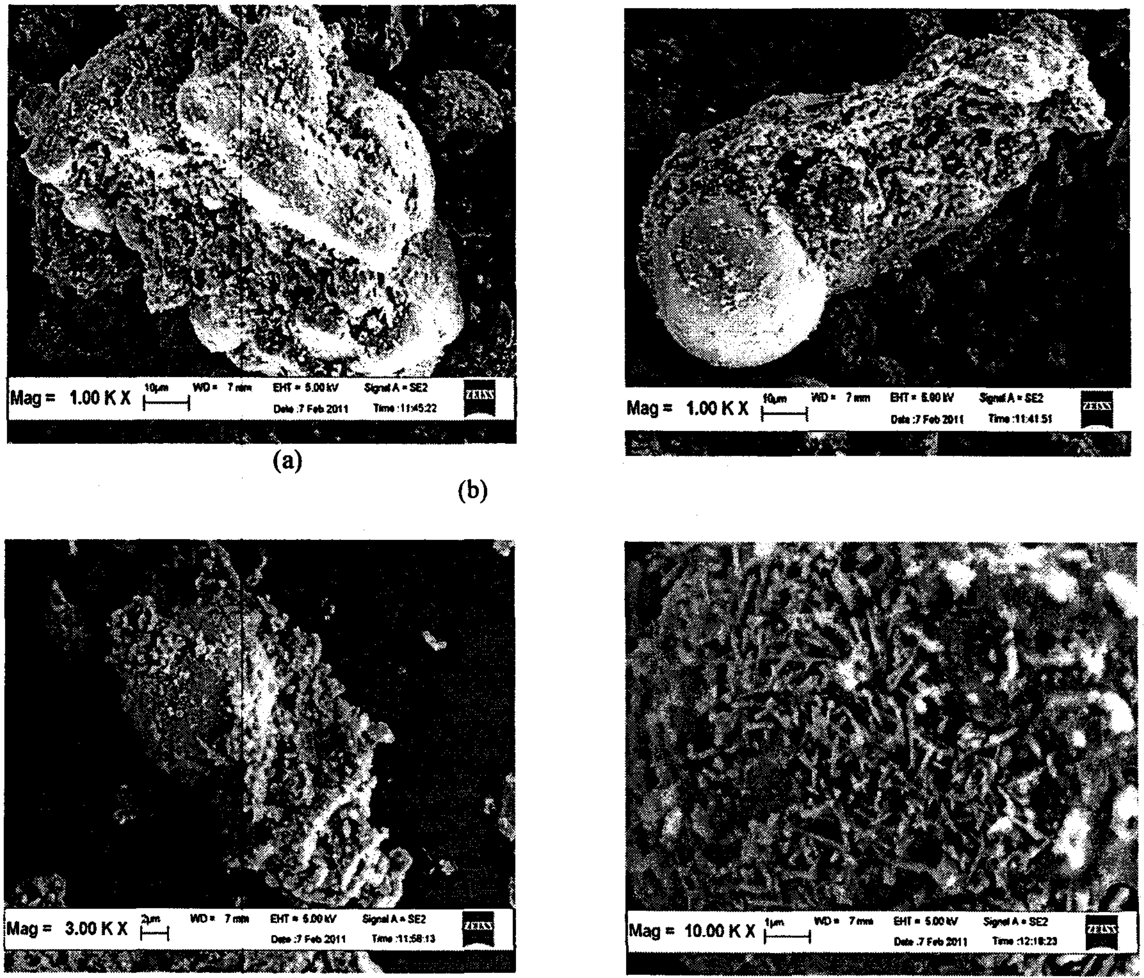


Figure 4: Effect of pH on the removal of Zn^{2+}.

3.5. Characterization of RHA/PFA/CFA Sorbents

The surface morphology of the selected RHA/PFA/CFA sorbents was examined using scanning electron microscopy (SEM). Figure 5 shows the image of the selected RHA/PFA/CFA sorbents before and after treatment with Zn^{2+}. It was observed from Figure 5 (a) & (b) that rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA) are combined to each other to form larger or complex particles with compact structures during the preparation of sorbent using sol-gel method. From previous studies, raw RHA was reported to have uniform structure with a dome-shaped and/or a skeletal structure [15]. While raw PFA usually has the shape of flat plate layers with small particles deposited on its surface [16] and raw CFA typically consists of smooth sphere particles/structures [17]. After the adsorption of Zn^{2+}, the surface of the RHA/PFA/CFA sorbents was found to have more compact structures covered by lumps of smaller particles (Figure 5 (c)), which is most probably the zinc ions. Clos view at higher magnification (10,000X) shows that the sorbe surface consists of a sharp needle-like structure with oth small granular particles (Figure 5 (d)), and again, this might b caused by zinc sorption which covered the external surface RHA/PFA/CFA sorbents.

To further strengthen this study, selected RHA/PFA/CF sorbents was also characterized for particle size distributio before and after Zn^{2+} removal. The particle size distributio (with specific surface area analysis) of selecte RHA/PFA/CFA sorbents is shown in Figure 6. It was show that RHA/PFA/CFA sorbent before and after treated with Zn has two (nearly) similar range of particle size distribution however the RHA/PFA/CFA sorbent after treated with Zn has more wider range of particle size distribution. Th volume of the first



(a)

(b)

(c)

(d)

Figure 5: Scanning electron micrograph of (a), (b) prepared RHA/PFA/CFA sorbents and RHA/PFA/CFA sorbents after removing Zn^{2+} at (c) 3000X and (d) 10,000X magnifications.

particle size distribution range (Figure 6 (b), *i.e.* RHA/PFA/CFA sorbent after treated with Zn^{2+}) is reduced as compared to RHA/PFA/CFA sorbent before treated with Zn^{2+} (Figure 6 (a)). Meanwhile, the volume of the second particle size distribution range of RHA/PFA/CFA sorbent after treated with Zn^{2+} is increased, which means that higher particle size distributions range are available after Zn^{2+} ion adsorption on the RHA/PFA/CFA sorbent surface.

It was also found that the specific surface area of RHA/PFA/CFA sorbent before treated with Zn^{2+} was much higher (0.774 m^2/g) than that of the RHA/PFA/CFA sorbent after treated with Zn^{2+} (0.375 m^2/g). The lower specific surface area of RHA/PFA/CFA sorbent after treated with Zn^{2+} could be due to the agglomerating of smaller particles (which is most probably the zinc ions that cover the surface of the sorbent) during the adsorption process. Apart from that, the average surface weighted mean and average volume weighted mean are dramatically increased (from 7.753 µm and 65.005 µm, respectively) to 15.984 µm and 353.178 µm, respectively, after the RHA/PFA/CFA sorbent was treated with Zn^{2+}.

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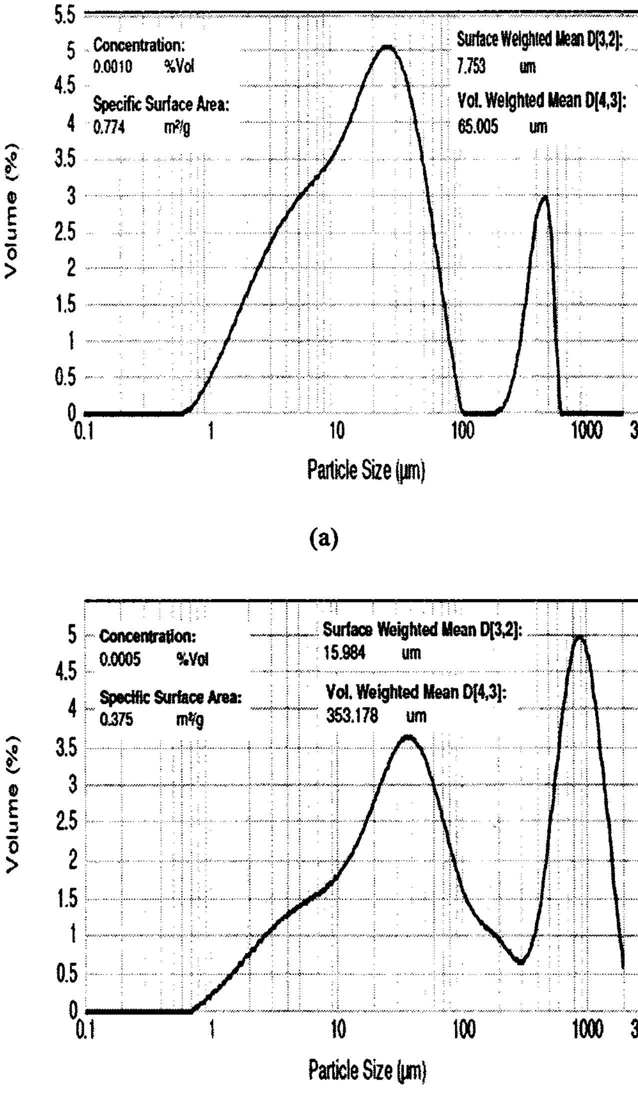

(a)

(b)

Figure 6: Particle size distribution of RHA/PFA/CFA sorbents (a) before and (b) after Zn^{2+} removal

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STUDY OF ADSORBENT PREPARED FROM RHA, PFA AND CFA USING RESPONSE SURFACE METHODOLOGY FOR BRILLIANT GREEN DYE REMOVAL

Sariyah Mahdzir and Irvan Dahlan

School of Civil Engineering, Universiti Sains Malaysia,
Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia.

Abstract

The usage of low-cost adsorbents has been widely investigated as an alternative to the current expensive methods for removal of various kinds of wastewater pollutants. Waste materials such as rice husk ash (RHA), palm fuel ash (PFA) and coal fly ash (CFA) were previously reported to have good adsorption properties for dyes removal. This study is concerning the preparation of adsorbent from RHA, PFA, and CFA using reflux method. The adsorbent was pre-treated with NaOH to increase its adsorption capacity. Response surface methodology (RSM) based on five-variable central composite rotatable design was used to determine the effect of (i) refluxing time, (ii) amount of RHA, (iii) amount of PFA, (iv) amount of CFA, and (v) concentration of additives (NaOH). The R^2 for quadratic model is 0.8812 for analysis of variance (ANOVA). Adsorption of the Brilliant Green dye on adsorbent surface was further confirmed by scanning electron micrographs (SEM). This study shows that the RHA/PFA/CFA adsorbent can be used for removal

Keywords: Adsorption, Waste material, Brilliant Green dye, Central composite design (CCD).

INTRODUCTION

Commercially, there are over 100,000 available dyes exist and more than $7x10^5$ tonnes are produced annually [1-2]. In water stream, the presence of very low concentrations of dyes is highly visible and undesirable [3]. The industries that using dyes include textile industries, paper and pulp mills industries, plastics industries and food companies. Dyes are widely used for coloring and adding into the products. The stable, recalcitrant, colorant, and even potentially carcinogenic and toxic characteristics of dyes might causes environmental, aesthetical and health problems [4-5]. Therefore, the removal of dyes from effluent becomes important.

The technologies of dyes removal or treatment can be divided into physical, chemical and biological methods. Physical methods include membrane-filtration and adsorption processes. Oxidative and photochemical processes [6] are the examples of chemical method, while biological method involves either aerobic or anaerobic degradation of the dyes by microorganisms. Adsorption technique is widely used due to its high efficiency, easy handling, availability of different adsorbents and cost effectives. However, the adsorption is dependent on dye or adsorbent interaction, adsorbent surface area, particle size, pH and contact time [7]. Activated carbon is the most popular material for adsorption of dyes because of its efficient capability in adsorbing a broad range of different types of adsorbates and simplicity of design of adsorber [8]. It is produced commercially by using natural materials such as wood or coal. However, the commercially activated carbon (CAC) cost is expensive and might not be economical for wastewater treatment [9]. For that reason, the researches on low-cost materials are widely performed as an alternative for CAC.

Rice husk ash (RHA), palm fuel ash (PFA) and coal fly ash (CFA) are abundantly produced in Malaysia. There are 408 000 tons of rice husk [10], 4.3 million tons of palm kernel shell [11] and 2 million tons of CFA [12] produced annually. The abundant production of these waste caused disposal problem, hence the utilization of these fly ashes are favourable as they have good sorption properties. Therefore, the analysis on adsorbent using combination of RHA/PFA/CFA is important to demonstrate its effectiveness in dye removal. The main purpose of this work is to study the removal of synthetic Brilliant Green dye by adsorption batch process using RHA/PFA/CFA adsorbent. Other objectives were to determine the optimum condition for adsorbent preparation from RHA, PFA, and CFA using response surface methodology.

MATERIALS AND METHODS

Brilliant Green

Brilliant Green dye was provided by the Sigma–Aldrich (M) Sdn. Bhd., Malaysia and used without further purification. The dye was chosen as the adsorbate because it is widely used as the textile dye and has toxic characteristic. Brilliant Green has a molecular formula $C_{27}H_{34}N_2O_4S$ and molecular weight of 482.64 g/mol. The structure of BG is shown below:

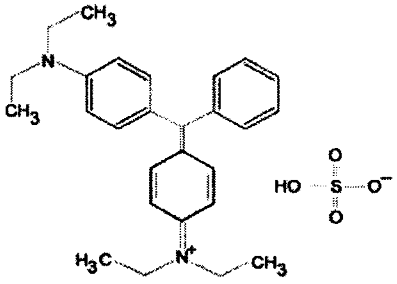

Figure 1: Structure of Brilliant Green

Preparation of Adsorbent

The raw rice husk ash was collected from Kilang Beras & Minyak Sin Guan Hup Sdn. Bhd., Nibong Tebal while the coal fly ash was collected from Kapar Coal-Fired Power Plant, TNB, Selangor. The oil palm waste was collected from United Oil Palm Mill, Penang. The raw waste materials were washed with deionized water and oven dried at 110°C overnight. The adsorbent was prepared through reflux method. The RHA, PFA and CFA were grind separately before preparation of adsorbent. Then the ashes were sieved through a stack of U.S. standard sieves into fine particle size of 75 μm. Certain amount of RHA/PFA/CFA was refluxed with 250 ml of additives for 4 hours at 80 °C in round bottom flask. The slurry was air-cooled and filtered with a glass fiber. The filter cake was repeatedly washed with deionized water until the filtrate was neutral. It was then dried in an oven at 110°C before use.

Design, Statistical Analysis, Model Fitting and Optimization

Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used in developing mathematical model that correlates the adsorbent preparation variables with its adsorption capacity. Preparation of the adsorbent was designed by using a standard response surface methodology (RSM) which is called a central composite design (CCD). Five variables were studied which include reflux time (x_1), amount of RHA (x_2), amount of PFA (x_3), amount of CFA (x_4), and concentration of chemical (x_5). The alpha value entered in the designed was fixed at 2.0 (rotatable). The complete design matrix for the experiments based on CCD is shown in Table 1.

The data were utilized to develop a correlation between the adsorbent preparation variables with its adsorption capacity by fitting it to the second-degree polynomial equation as given by Eq. 1 below [13].

(1)

where Y is the predicted adsorption capacity (%), b_0 is the offset term (constant), b_i is the linear coefficients, b_{ii} is the interaction coefficients, x_i, x_j are the coded values of the various adsorbent preparation variables and *n* is the number of adsorbent preparation variables. The significant of data was determinate using the analysis of variance (ANOVA). The model generated then used to optimize the adsorption capacity for the parameter studied.

Adsorption Test

Adsorption experiments were carried out by adding a fixed amount of adsorbent (1.0g) to a 250mL conical flask filled with 200mL of Brilliant Green diluted solutions (200mg/L). The conical flasks were sealed and placed in a shaker Sartorius, Ceriomat® SII, then shaken at 150 rpm at 30°C for 1.5 hours and natural pH (pH 7). pH adjustment was done using solutions of 0.1M NaOH and 0.1M HCl. The flasks were then removed from the shaker and the final concentration of dye in the solution was measured at wavelengths of 455 nm) using DR 2500 spectrophotometer (Shimadzu, Japan).

Characterization of Adsorbent

The concentration of Brilliant Green in the supernatant solution before and after adsorption was determined using a DR 2500 spectrophotometer (Shimadzu, Japan). Scanning electron microscopy (SEM) analysis was carried out on selected adsorbent to study the surface morphology and to verify the presence of porosity.

RESULTS AND DISCUSSION

Response Surface Model

The experimental and predicted result for adsorption capacity of Brilliant Green dye at different preparation variables was presented in Table 1. From the data presented, adsorbent R26 exhibited the highest adsorption capacity with the 90.96% dyes adsorption while adsorbent R5 shows the lowest adsorption capacity with 67.51%. The fitness of the model was checked with analysis of variance (ANOVA) as shown in Table 2. The significance of the empirical model can be evaluated from the Prob. > F values. Prob.> F values less than 0.500 for 95% confident interval shows that the model is significant. In this experiment, the overall quadratic model generated is significant with the Prob. > F value of 0.0102. The percentage of dye removal was fit the equation 2 below and obtained in terms of coded factor. Positive sign indicates synergistic effect, whereas negative sign indicates antagonistic effect [14].

$$\text{Dye adsorbed (\%)} = 84.30 + 2.11x_1 + 4.23x_2 - 2.17x_3 - 0.12x_4 + 1.26x_5 - 0.78x_1^2 - 1.42x_2^2 - 0.94x_3^2 - 0.98\,x_4^2 + 0.40\,x_5^2 - 0.19x_1x_2 - 1.26x_1x_3 - 1.96x_1x_4 - 0.43x_1x_5 + 1.34x_2x_3 - 1.38x_2x_4 - 0.33x_2x_5 - 1.17x_3x_4 + 0.16x_3x_5 - 0.83x_4x_5 \qquad (2)$$

Table 1: Experimental design matrix and results for RHA/PFA/CFA adsorbents.

Run	x_1	x_2	x_3	x_4	x_5	**Adsorption Efficiency (%)**	
						Experimental	**Predicted**
R1	120.00	10.00	10.00	10.00	2.00	73.01	74.58
R2	240.00	10.00	10.00	10.00	1.00	79.38	81.11
R3	120.00	20.00	10.00	10.00	1.00	76.62	78.80
R4	240.00	20.00	10.00	10.00	2.00	88.53	92.29
R5	120.00	10.00	20.00	10.00	1.00	67.51	66.73
R6	240.00	10.00	20.00	10.00	2.00	77.11	77.91
R7	120.00	20.00	20.00	10.00	2.00	85.14	86.39
R8	240.00	20.00	20.00	10.00	1.00	86.35	87.76
R9	120.00	10.00	10.00	20.00	1.00	80.66	79.67
R10	240.00	10.00	10.00	20.00	2.00	83.47	84.05
R11	120.00	20.00	10.00	20.00	2.00	83.42	84.46
R12	240.00	20.00	10.00	20.00	1.00	85.80	86.99
R13	120.00	10.00	20.00	20.00	2.00	77.13	75.21
R14	240.00	10.00	20.00	20.00	1.00	73.30	71.53
R15	120.00	20.00	20.00	20.00	1.00	83.25	81.94
R16	240.00	20.00	20.00	20.00	2.00	79.58	79.84
R17	60.00	15.00	15.00	15.00	1.50	76.37	76.97
R18	300.00	15.00	15.00	15.00	1.50	88.25	85.40
R19	180.00	5.00	15.00	15.00	1.50	68.65	70.17
R20	180.00	25.00	15.00	15.00	1.50	90.85	87.09
R21	180.00	15.00	5.00	15.00	1.50	89.29	84.88
R22	180.00	15.00	25.00	15.00	1.50	74.06	76.22
R23	180.00	15.00	15.00	5.00	1.50	85.43	80.60
R24	180.00	15.00	15.00	25.00	1.50	77.54	80.13
R25	180.00	15.00	15.00	15.00	0.50	83.07	83.37
R26	180.00	15.00	15.00	15.00	2.50	90.96	88.42
R27	180.00	15.00	15.00	15.00	1.50	82.46	84.30
R28	180.00	15.00	15.00	15.00	1.50	83.95	84.30
R29	180.00	15.00	15.00	15.00	1.50	83.16	84.30
R30	180.00	15.00	15.00	15.00	1.50	85.53	84.30
R31	180.00	15.00	15.00	15.00	1.50	84.47	84.30
R32	180.00	15.00	15.00	15.00	1.50	83.95	84.30

x_1 (reflux time), x_2 (amount of RHA), x_3 (amount of PFA), x_4 (amount of CFA), and x_5 (concentration of chemical).

Table 2: Analysis of variance (ANOVA) for percentage of dye removal

Source	Sum of Square	DF	Mean Squares	F Value	Prob > F	
Model	991.99	20	49.60	4.08	0.0102	significant
x_1	106.43	1	106.43	8.75	0.0130	
x_2	429.43	1	429.43	35.33	< 0.0001	
x_3	112.58	1	112.58	9.26	0.0112	
x_4	0.33	1	0.33	0.027	0.8719	
x_5	38.25	1	38.25	3.15	0.1037	
x_1^2	17.73	1	17.73	1.46	0.2525	
x_2^2	58.94	1	58.94	4.85	0.0499	
x_3^2	25.71	1	25.71	2.12	0.1738	
x_4^2	28.39	1	28.39	2.34	0.1547	
x_5^2	4.66	1	4.66	0.38	0.5483	
x_1x_2	0.61	1	0.61	0.050	0.8271	
x_1x_3	25.40	1	25.40	2.09	0.1762	
x_1x_4	61.62	1	61.62	5.07	0.0458	
x_1x_5	2.89	1	2.89	0.24	0.6354	
x_2x_3	28.68	1	28.68	2.36	0.1528	
x_2x_4	30.64	1	30.64	2.52	0.1407	
x_2x_5	1.70	1	1.70	0.14	0.7153	
x_3x_4	21.76	1	21.76	1.79	0.2079	
x_3x_5	0.42	1	0.42	0.034	0.8566	
x_4x_5	11.12	1	11.12	0.91	0.3594	
Residual	133.72	11	12.16			
Pure Error	5.61	5	1.12			
Cor Total	1125.71	31				

The R^2 value that fit this model is 0.8812. R^2 is a coefficient of determination which gives the proportion of the variance of one variable that is predictable from the other variable. High R^2 value represents the correlation between the predicted and experimental dye adsorption. Figure 2 shows the predicted value versus the experimental value for sorption capacity of prepared adsorbent.

Based on the Pred.>F values (Table 2), time of reflux (x_1), amount of RHA (x_2) and amount of PFA (x_3) were found to have significant effects on the adsorption capacity. Figure 3 shows the correlation between reflux time (x_1) and amount of CFA (x_4). From the figure, it can be seen that at constant time of refluxing process during adsorbent preparation, the adsorption capacity of adsorbent increased at lower amount of CFA but gradually decreasing after certain amount of CFA was used. This shows that the amount of CFA give the effect on dyes adsorption and least amount of CFA is needed for high optimum adsorption. However, by keeping the amount of CFA low and constant, while increasing time of reflux, the adsorption of prepared adsorbent on dyes material is increase.

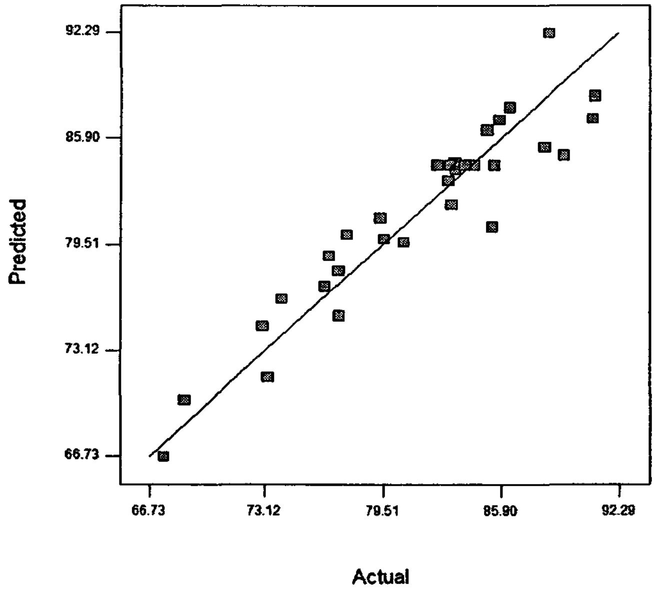

Figure 2: Predicted vs actual dye adsorption

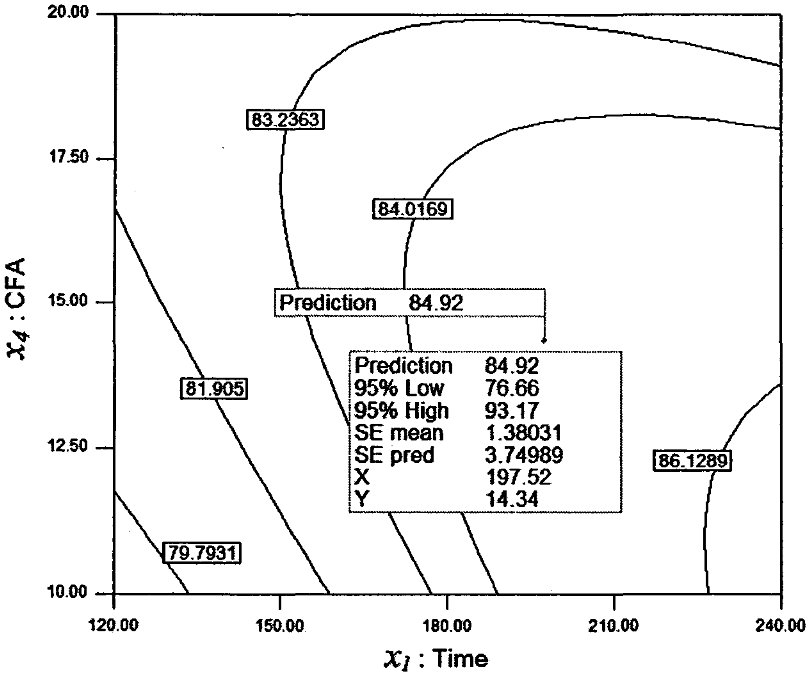

Figure 3: Contour plot of adsorption capacity

Optimization of Dye Adsorption

The optimization condition for dyes adsorption was determined by entering the desired values or condition of variables into the software to generate the prediction adsorption values. As the chemical reagents are usually costly and give difficulties in handling, lower concentration of the chemical is more desired. Thus, the optimum adsorption with low concentration of chemical should be found. The reflux time and amount of RHA, PFA and CFA are set to be in range because time should not be too long and no limitation of the usage of these three waste materials.

Ten possible desired optimum data was greeted by the software which the highest adsorption capacity is 90.1% with desirability of 0.981 as shown in Table 3. From this table, the optimum adsorption values was obtained by refluxing 20.0g, 12.3g and 10.0g of RHA, PFA and CFA respectively in 1 mol/L of NaOH for 240 minutes.

Table 3: Predicted optimization values for dyes adsorptions

No	Time	RHA	PFA	CFA	NaOH conc.	dye absorbed	Desirability
1	240.00	20.00	12.30	10.00	1.00	90.0863	0.981
2	240.00	20.00	11.63	10.77	1.00	90.0743	0.981
3	239.97	20.00	10.00	12.28	1.00	89.9440	0.978
4	240.00	20.00	10.51	11.04	1.01	90.0336	0.975
5	239.96	19.06	12.09	15.04	1.00	88.9135	0.955
6	240.00	17.02	10.04	14.33	1.00	88.8853	0.955
7	240.00	15.83	10.00	19.14	1.01	87.3458	0.914
8	239.71	13.26	10.00	18.39	1.00	86.4256	0.898
9	169.28	20.00	13.11	17.67	1.00	86.0684	0.890
10	240.00	10.00	10.60	18.93	1.00	83.3205	0.821

Characterization

SEM was carried out for morphological analysis of the adsorbent. It is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent [15]. Previous study shows that raw RHA usually has the shape of corn-like structure with the porous internal structure of honeycomb [16]. The raw PFA has angular and irregular form with crushed shape structure [17] while CFA consists of hollow smooth spherical particles [18-19].

Figure 4 the SEM images of the prepared adsorbent and spent adsorbents that reveal its surface texture and porosity. From the images, the presence of RHA, PFA and CFA in the adsorbent can be seen. RHA, PFA and CFA might combine to each other to form larger or complex particles during preparation of adsorbent (reflux) process. However, for the prepared adsorbent, combined compounds might lower the total surface area hence decrease the adsorption capacity of the adsorbent.

Figure 4 (a) shows the present of micro-size particles attached on the spherical CFA compound and on the internal surface of porous RHA. The particles might be forming during refluxing process. From Figure 4 (b), the agglomeration of particles was seen on the RHA, PFA and CFA surfaces. The agglomerate seen is the dyes compound that attached on the adsorbent surfaces.

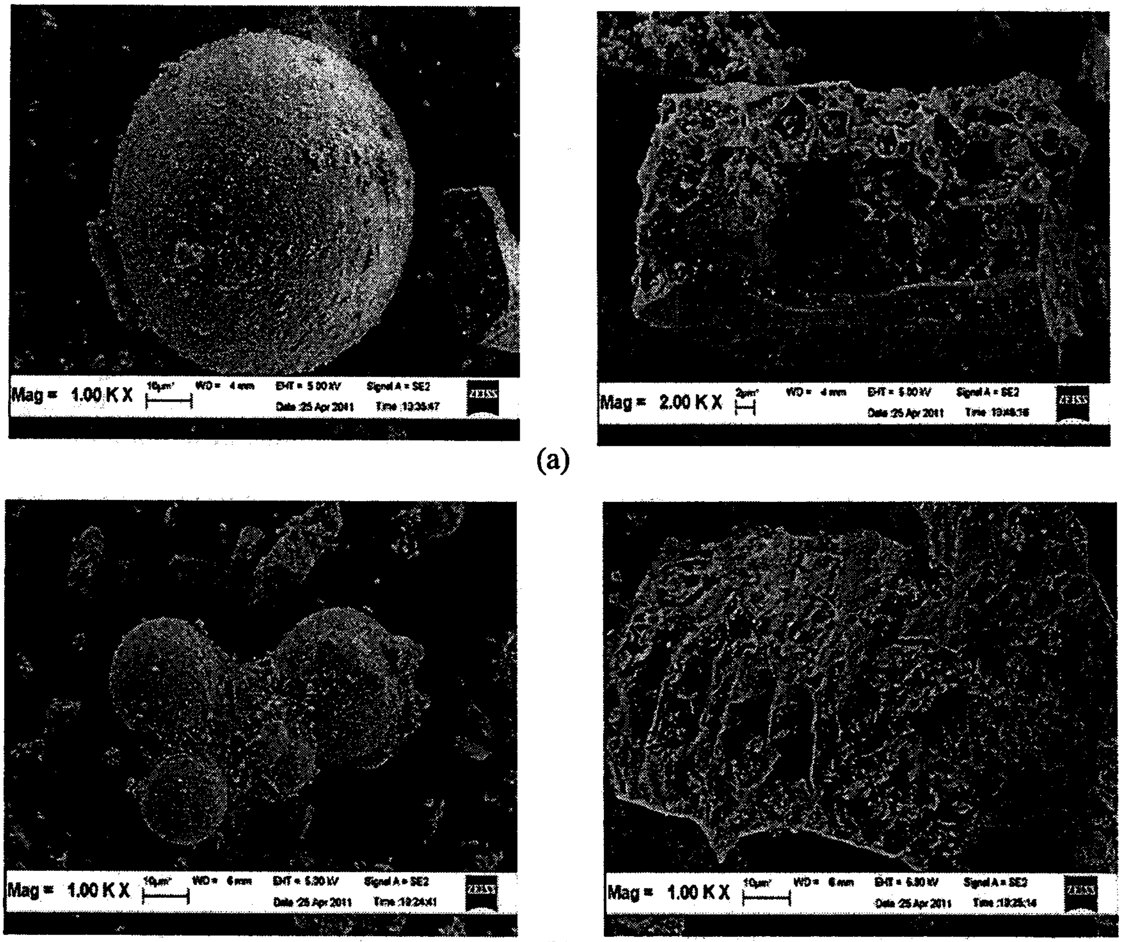

Figure 4: Scanning electron micrograph of (a) prepared and (b) spent RHA/PFA/CFA sorbents.

CONCLUSIONS

The experimental works shows that the adsorption capacity of prepared adsorbent was ranging from 67.51 to 90.96% for adsorption of 200 ppm Brilliant Green dye. This result shows that the mixture of RHA/PFA/CFA gave high adsorption capacity and suitable for dye removal. The statistical regression analysis (ANOVA) resulting in generation of quadratic model with Prob. > F value of 0.0102. The result from ANOVA test shows the correlation between reflux time and amount of CFA and no distinct relation happen between other variables. The R^2 value that fit this model is 0.8812 which also represents the correlation between the predicted and experimental dye adsorption. The optimum condition for preparation of RHA/PFA/CFA adsorbent was carried out using CCD. At minimum concentration of NaOH while other variables are kept in range, the highest predicted adsorption capacity is 90.086%. This value was obtained at optimum refluxing time, RHA/PFA/CFA ratio and NaOH concentration of 240 minutes, 2:1.2:1 and 1mol/L respectively. The observation on SEM data reveals the present of RHA, PFA and CFA materials in the adsorbent. Some of the materials were seen to be combined to each other which it caused during preparation of RHA/PFA/CFA adsorbent and adsorption of Brilliant Green dye.

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bank. In this study, Kemaman River Estuary of Terengganu was selected to investigate the energy of waves wake induced by boats. The water level logger measurements weredeployed to measure the wave parameter in one tidal cycle. The result shows that the maximum energy level generated by boats during the study time is an approximately about 1260 Joules. From the data obtained, the relationship between the total energy level and maximum energy level is found. The findings of these results could provide the useful information to the authority and policy maker for making a guideline to create the policies and regulation for the users of the Kemaman River Estuary of Terengganu.

EO11

Modeling Of Climatological Wind-Driven Circulation and Thermohaline Structures Of Peninsular Malaysia's Eastern Continental Shelf Using Princeton Ocean Model

Halimatun Muhamad, Fredolin T. Tangang & Liew Juneng
Research Centre for Tropical Climate Change System (IKLIM),
Faculty of Science and Technology,National University of Malaysia
43600 Bangi, Selangor.
Email: halimatunmuhamad@gmail.com

This research was conducted to simulate the seasonal hydrodynamic and thermohaline structures of the Peninsular Malaysia's eastern continental shelf sea using the Princeton Ocean Model (POM). The POM was configured with rectilinear grids of ~11 km and 15 sigma levels for a domain of 96°E to 116°E in longitude and 5°S to 15°N in latitude. The bathymetry was taken from ETOPO5 dataset. The climatological surface air pressure and surface wind used to force the model were from the National Center of Environmental Prediction (NCEP) Reanalysis Project. The temperature and salinity fields were initialized with data from World Ocean Atlas. The results showed that wind stress play an important role in the simulated current pattern. During the northeast monsoon, the simulation results shows an anti-clockwise (cyclonic) surface circulation and clockwise (anti-cyclonic) during southwest monsoon. The wind-driven circulation in the region together with associated eddies for both during northeast and southwest monsoon seasons also captured. At 30 m depth, a relatively different current from the surface simulated suggesting the role of bathymetry in current pattern. An extended experiment was conducted by flatten the bathymetry at the eddy area (east coast of Peninsular Malaysia) for both monsoon. The result showed the current circulation was more uniform and the eddy was disappeared. The model also reasonably simulated the climatological temperature and salinity structure. The upward tilted thermohaline structure as shown by a cross-section at 5°N during southwest monsoon indicates a possibility of the occurrence an upwelling due to off-shore Ekman transport. During the northeast monsoon, the opposite was simulated.

EO12

Manganese (Mn^{2+}) Removal From Aqueous Solutions Using Sorbent Prepared From Waste-Derived Siliceous Materials

Irvan Dahlan, and Mohd Nor Ismilhadi Che Soh
School of Civil Engineering, Universiti Sains Malaysia,
Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia.
E-mail: ceirvan@eng.usm.my

The rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA) are highly abundant waste materials in Malaysia. Therefore, it was selected to develop waste-derived siliceous materials as a sorbent for manganese removal. Different preparation methods were used to synthesize RHA/PFA/CFA sorbent and selected RHA/PFA/CFA sorbents were characterized based on its physical and chemical properties. Batch experiments were conducted to estimate removal efficiency of manganese from synthetic wastewater. The removal efficiency was found to correlate with the initial manganese (Mn^{2+}) concentration, pH, shaking rate, and as well as contact/shaking time between Mn^{2+} and the sorbent concentration. From the result of surface analysis showed that the surface of the prepared sorbent after treated with manganese was covered by manganese ion, due of this the surface area was decreased as compared to prepared sorbent before treatment. Isotherm studies shows that adsorption equilibrium of manganese can be better described by Langmuir model. It was concluded that the sorbent prepared from these siliceous waste materials can be used as an effective sorbent for manganese removal from synthetic wastewater.

EO13

Design and Development of a Real Time Monitoring and Control System for Water Quality for Recirculating Aquaculture System

[1]Azizi A, [2]Muhammad Suzuri H, [1]Khalid S, and [3]Ahmad J
[1] *Institute of Oceanography, University Malaysia Terengganu*
21030 Kuala Terengganu, Terengganu Malaysia
[2] Department of Computer Science, University Malaysia Terengganu
21030 Kuala Terengganu, Terengganu Malaysia
[3] Department of Engineering Science, University Malaysia Terengganu
21030 Kuala Terengganu, Terengganu Malaysia
E-mail: *azizi@umt.edu.my, ahmadj@umt.edu.my, suzuri@umt.edu.my*

This paper presents the design and development of a real time monitoring and control system for water quality for Recirculating Aquaculture System (RAS). In this project, three main water quality parameters were identified, i.e. temperature, pH and dissolved oxygen. The main objective of this project is to regulate the water quality parameters in the RAS so that it i able to be controlled within specific measurement range set by the operator. The developed system is also allows the user to monitor water quality parameters remotely using user's mobile phone as well as online visualization at remote location using wired RS-485 communication protocols. The prototype system was developed in four stages. The first stage is the requirement analysis of the pilot scale RAS. The second stage is the development of the data acquisition module. The third stage is the development of the software for monitoring and control of the water quality in a RAS environment and finally the development of a database management and visualization system for the RAS. The Matlab programming language is employed to develop the software for monitoring and control of the RAS and the MySQL database is used for data management system. The prototype RAS system used proprietary water quality sensors and this system was tested to simulate the actual environment to rear catfish. Extensive experimental investigations were carried out to test the performance the developed prototype including the simulated dry run and in actual environment for rearing the fish at variable stocking rate. In all of the trail runs, it is found that the developed prototyped is able to be controlled in dynamically changing setting environment.

EO14

Bioethanol Production from Liquid Pineapple Waste using Immobilized Baker's Yeast in Modified PVA-alginate beads

Ng Sew Shen and Nor Azimah Mohd Zain
Department of Industrial Biotechnology,
Faculty of Biosciences and Bioengineering,Universiti Teknologi Malaysia
81310 Skudai, Johor, Malaysia.
Corresponding author, Phone: +607 5532714, Fax: +607 5531112, Email: azimah@fbb.utm.my

This study focuses on the production of bioethanol from liquid pineapple waste using Baker's yeast immobilized in modified PVA-alginate matrix. Bioethanol is one of the well-known sustainable alternatives to replace fossil fuels and it could be produced through biological process. Pineapple waste could be an excellent source of bioethanol production since it is high in fermentable sugar eliminating the need for saccharification. Annually, Malaysia contributes to almost 1% of total world pineapple production and concurrently generates abundant amount of wastes. In this study, Baker's yeast was immobilized in modified PVA-alginate beads that

EO12

Manganese (Mn^{2+}) Removal From Aqueous Solutions Using Sorbent Prepared From Waste-Derived Siliceous Materials

Irvan Dahlan*, and Mohd Nor Ismilhadi Che Soh

School of Civil Engineering, Universiti Sains Malaysia,
Engineering Campus, Seri Ampangan, 14300 Nibong Tebal, Pulau Pinang, Malaysia.

*Corresponding author's e-mail: ceirvan@eng.usm.my / dahlan_irvan@yahoo.com

Key words: Manganese (Mn^{2+}); Synthetic wastewater; Sorbent; Siliceous wastes; Adsorption.

Introduction.

One of the major problems concerning environmental pollutants is removing heavy metals from water and wastewater generated from industrial activities. Rapid industrialization has led to increased disposal of heavy metals into the environment [1] and this has created undesirable impact to the environment. Heavy metals are not easy to biodegrade and tend to accumulate in soil and water reservoirs. Manganese (Mn^{2+}) is one of the transition metallic elements, can be found in natural waters both in its most reduced and soluble form. If it is not oxidized, manganese (II) ions can easily escape through water treatment processes and, once in the distribution system, can gradually be oxidized to insoluble manganic dioxide causing several problems such as water discoloration, metallic taste, odor, turbidity, and corrosion, staining of laundry and plumbing fixture [2].

Various methods have been employed to treat metal contaminated water/wastewater before discharging it into water stream. From various treatment technologies exist, adsorption technique using many type of sorbents is still the most favorable method in the removal of heavy metals from waste/wastewaters due to its efficiency; high adsorption capacity and low operational cost method [3-6]. From many type of sorbent, activated carbon (from many sources of raw materials) is currently of great interest, however carbon adsorption remains an expensive process and difficulties associated with regeneration [7]. Therefore, low-cost (sorbent) alternatives to activated carbons have attracted considerable research interest in recent years.

Attempts have therefore been made to utilize waste materials as alternative sorbents, especially waste-derived siliceous materials, *i.e.* rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA). These ashes are come from the burning of rice husk, palm oil fiber/shell, and coal to generate electricity. The utilization of RHA [8,9], oil palm by-product [10-12] and CFA [13] as an adsorbent has been investigated/reviewed in literature. Nevertheless, most of these ashes were converted to activated carbon before utilizing as a sorbent. Furthermore, no work has been carried out to combine these waste-derived siliceous materials as a sorbent. Therefore, the objective of this study is to synthesize a RHA/PFA/CFA sorbent with good adsorption properties to remove manganese (Mn^{2+}).

Materials and Methods

Raw Materials. Three type of ashes resulted from burning industrial fuels were collected and used in the process of synthesizing sorbent. The raw rice husk ash (RHA) was collected directly from Kilang Beras & Minyak Sin Guan Hup Sdn. Bhd., Pulau Pinang. Palm oil fuel ash (PFA) was obtained from United Oil Palm Mill, Pulau Pinang. While coal fly ash (CFA) was supplied by Stesen Janakuasa Sultan Azlan Shah, Manjung, Perak. Prior to use, all three type of ashes were sieved to obtain less than 63 μm fine particle size and oven dried overnight at 110°C. Whereas synthetic wastewater (which contain Mn^{2+}) was used and it was prepared from $MnSO_4$. H_2O (Acros Organics, 99+%).

Sorbent Preparation. In the preliminary study, water hydration and reflux methods were used to prepare RHA/PFA/CFA sorbent in order to select the best method for sorbent preparation. Different prepared RHA/PFA/CFA sorbents were resulted from this preparation, i.e. hydrated RHA/PFA/CFA sorbent, hydrated RHA/PFA/CFA sorbent with $Ca(OH)_2$ addition, NaOH-treated RHA/PFA/CFA sorbent, HCl-treated RHA/PFA/CFA sorbent, and HCl-NaOH treated RHA/PFA/CFA sorbent and these sorbents were labeled as sorbent S1-A, S1-B, S2, S3 and S4, respectively [14].

Batch Adsorption Studies. The experiments were carried out by shaking a series of bottles containing certain amount of sorbent and Mn^{2+} ion. In choosing the best preparation method, the following parameter values were used for adsorption studies, i.e. Mn^{2+} concentration of 25 mg/l, shaking rate of 130 rpm, 2 h contact time and pH values of about 4 to 5. After the selection of the sorbent based on method, then further study was conducted to obtain the best ratio (RHA/PFA/CFA) during the sorbent preparation. After that, the effect of pH, contact time, and initial concentration of Mn^{2+} were investigated to know the sorption capacity of RHA/PFA/CFA sorbent. All experiments were duplicated to increase the precision of the results, and only the average value was reported throughout this study.

Analysis and Characterization. Spectrophotometer DR2800 was used to measure the concentration of synthetic (Mn^{2+}) wastewater. The scanning electron microscopy (SEM) examinations were performed through Leo Supra 35 VP Scanning Electron Microscope to obtain the surface morphologies of RHA/PFA/CFA sorbents.

Results and Discussion

Table 1 shows the result of manganese removal using different prepared RHA/PFA/CFA sorbents. It was shown that S- 1(B) sorbent (hydrated RHA/PFA/CFA sorbent with $Ca(OH)_2$ addition) was found to have highest manganese removal. Therefore, S- 1(B) sorbent prepared using water hydration method with $Ca(OH)_2$ addition was used for the next study.

Table 1: Manganese removal based on different preparation methods

Method	Sorbent label	Removal efficiency (%)
Water hydration	S- 1(A)	96
	S- 1(B)	99
Reflux	S- 2	92
	S-3	79
	S-4	98

After selecting the sorbent based on preparation method, the water hydration method with $Ca(OH)_2$ addition was used to prepare the sorbents with various RHA/PFA/CFA ratio. It was found out from Table 2 that sorbent prepared with RHA/PFA/CFA ratio of 0:6:3 gave the highest manganese removal. Thus, it was decided to prepare hydrated PFA/CFA sorbent with $Ca(OH)_2$ addition (with PFA/CFA ratio of 6:3) in the rest of this study.

Table 2: Manganese removal based on ratio

RHA/PFA/CFA ratio			Manganese removal (%)
RHA	PFA	CFA	
3	3	3	97
0	3	3	97
3	0	3	97
3	3	0	98
0	3	6	97
6	3	0	96
3	0	6	97
6	0	3	98
3	6	0	96
0	6	3	99

Effect of pH. Knowledge of the optimum pH is very important since pH affects not only the surface charge of sorbent, but also the degree of ionization and speciation of sorbent during adsorption. The pH was varied from 2 to 10 (by adding 0.I M NaOH or 0.I M HCl), other operational parameters (sorbent dosage, contact time, initial Mn^{2+}concentration, shaking rate) were kept constant. From Fig. 1, it is shown that increasing pH of the solution from 2 to 8 caused linear increase in manganese removal efficiency. The removal efficiency remained almost constant above pH 6. This might be due to the formation of soluble hydroxyl complexes. Under acidic conditions, the sorbent surface will be completely covered with H+ ions and the manganese ions cannot compete with them for adsorption sites. However, with increasing pH, the competition from the hydrogen ions decreases and the positively charged manganese ions can be adsorbed at the negatively charged sites on the sorbent [15]. It was also found that there was a reduction in manganese removal from 99.87% to 99.5% when equilibrium pH was increased from 8 to 10. This might be due to the fact that the covalent coordination bonds between manganese ions and the surface functional group of the sorbent, such as carboxylic and hydroxyl, are very weak in basic condition.

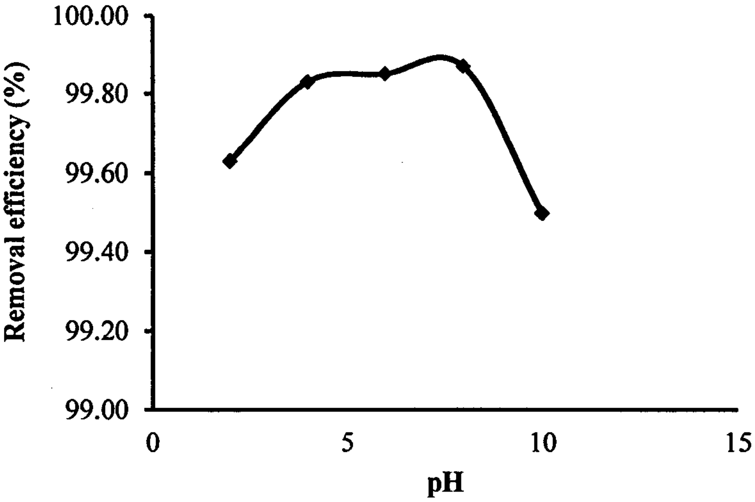


Fig. 1: Effect of pH on the adsorption of Mn^{2+} using PFA/CFA sorbent.

Effect of Contact Time. Equilibrium time is another important operational parameter for an economical wastewater treatment processes. Fig. 2 shows manganese removal efficiency as function of contact time. It is shown that increase in shaking time increased removal efficiency until equilibrium adsorption was established. It is obvious that increase in contact time from 5 to 60 minutes enhanced the percent removal of manganese significantly. The initial rapid adsorption gives away a very slow approach to equilibrium .The nature of sorbent and its available sorption sites affected the time needed to reach the equilibrium [16]. In the beginning fast adsorption, may be explained due to the availability of more number of adsorption sites. After initial adsorption of adsorbate, the available sites in the adsorbent reduced and thus rate of adsorption further decreased, which attained a limiting value at equilibrium

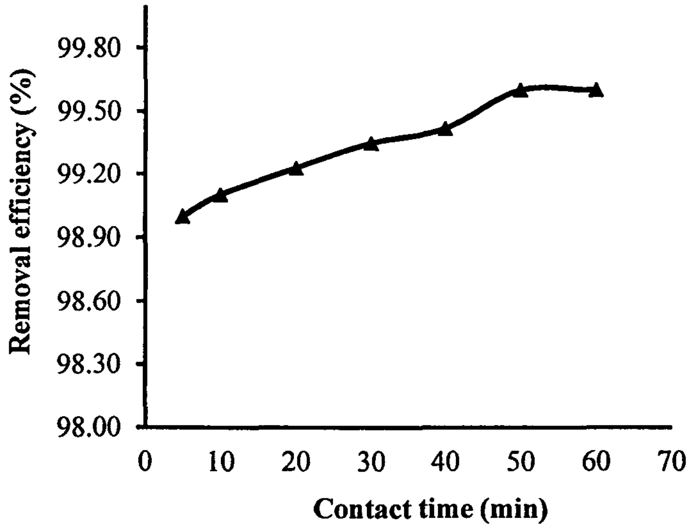


Fig. 2: Effect of contact time on the adsorption of Mn^{2+} using PFA/CFA sorbent.

Effect of initial Mn^{2+} concentration. The effect of initial concentrations on metal ion uptake was investigated by varying the initial concentrations of the manganese from 5mg/L to 500 mg/L. It can be seen from Fig. 3, the adsorption capacities were increased with increasing the initial Mn^{2+} concentrations. At initial Mn^{2+} concentrations of 5 - 10 mg/l, there was rapid increased of manganese removal from 86% to 98% this is because at low initial concentration, the surface area and the availability of adsorption sites of PFA/CFA sorbent were relatively high, and the manganese ions were easily adsorbed. At higher initial concentration the removal efficiency of manganese is remains constant this is because the total available adsorption sites become limited.

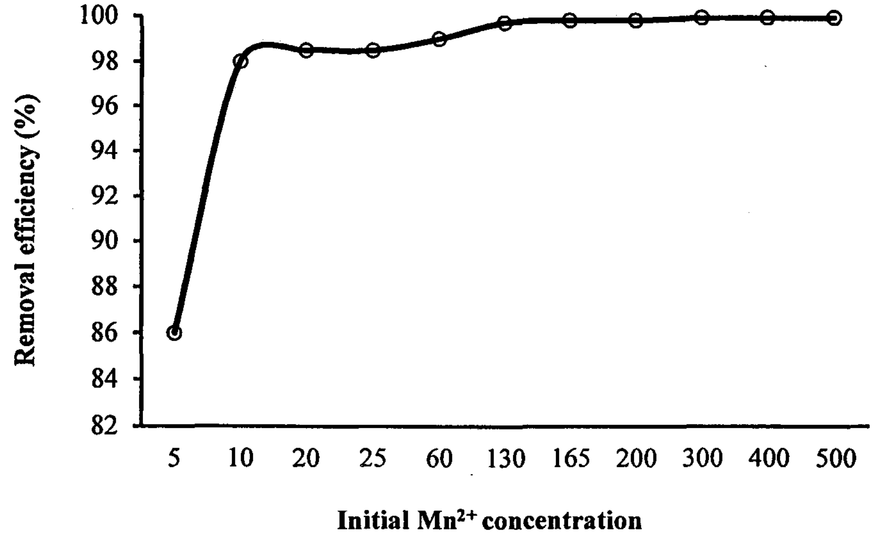
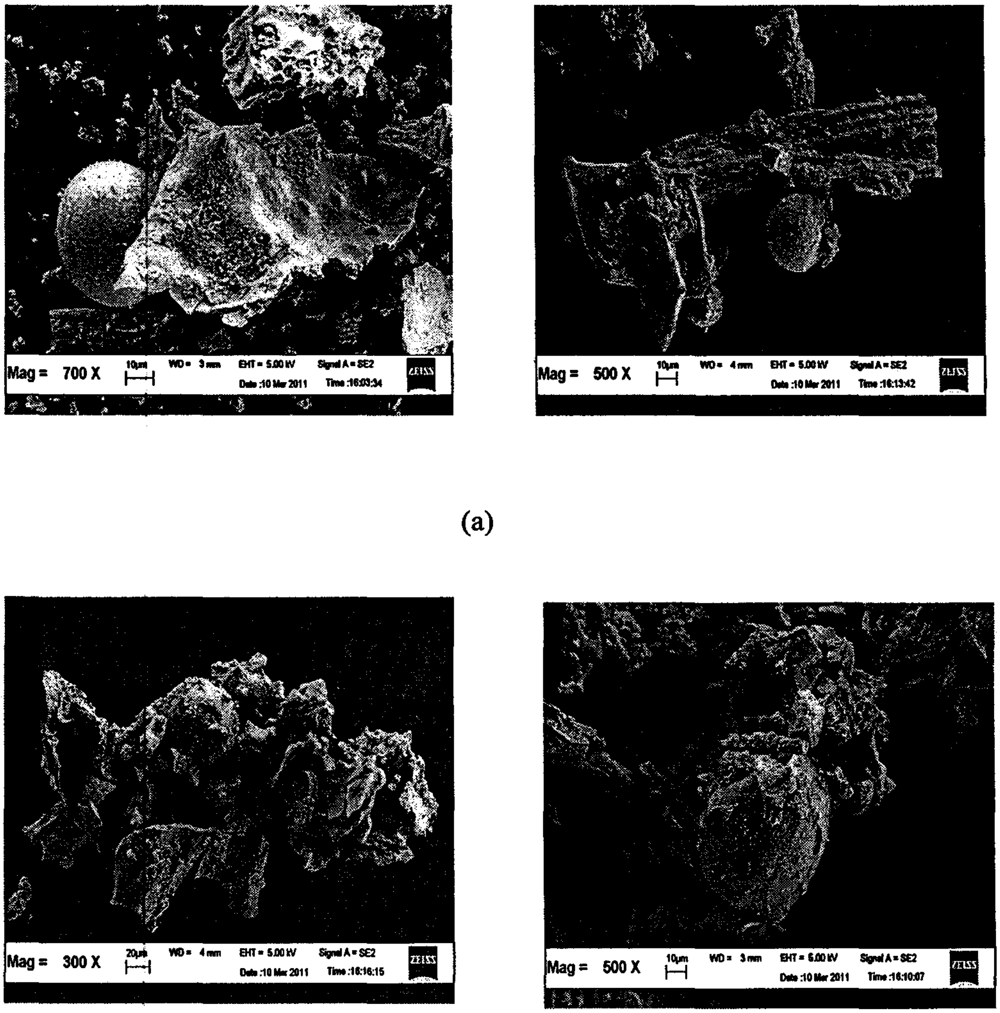


Fig. 3: Effect of initial Mn^{2+} concentration on the adsorption of Mn^{2+} using PFA/CFA sorbent.

Scanning Electron Microscopy (SEM) Analysis. The Fig. 4 shows the image of the PFA/CFA sorbent before and after treatment with manganese. SEM photographs shown in Fig. 4 (a) revealed that PFA and CFA are combined to each other to form larger or complex particles during the preparation. From previous studies, raw PFA usually has the shape of flat plate layers with small particles deposited on its surface [17] and raw CFA typically consists of smooth sphere particles/ structures [18]. After the adsorption of manganese, the surface of the PFA/CFA sorbent was found to have more compact structures. The rough irregular-shaped particles are attached on the surface and inside of the PFA/CFA sorbent and this might be caused by manganese sorption which covered the external surface of PFA/CFA sorbent as shown in Fig. 4 (b).



(a)

(b)

Fig. 4: Scanning electron micrograph of (a) prepared PFA/CFA sorbent and (b) PFA/CFA sorbent after treated with manganese.

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ZINC REMOVAL FROM SYNTHETIC WASTEWATER BY ADSORPTION USING RICE HUSK ASH, PALM OIL FUEL ASH AND COAL FLY ASH

BY

HAIDER MOHAMMED NAIMA

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PENYINGKIRAN ZINK DARI AIR SISA SINTETIK MENGGUNAKAN PENJERAPAN DENGAN ABU SEKAM PADI, ABU BAHAN API KELAPA SAWIT DAN ABU TERBANG ARANG BATU

ABSTRAK

Para saintis masa kini lebih berminat untuk mengkaji proses penjerapan dengan sisa pertanian, ini kerana keberkesanan proses tersebut menyurih logam berat yang banyak. Ini dilakukan dengan cecair (air) tiruan yang menggandungi logam berat (Zn^{2+}) bagi menggantikan sisa industri. Dalam penyelidikan ini proses penjerapan dikaji dengan campuran tiga jenis abu dari sistem pembakaran bahan bakar industri seperti sekam padi, hampas kelapa sawit dan arang batu yang diubahsuai secara "sol-gel". Skop tesis ini adalah jumlah hasil penjerapan, masa hasil penjerapan, hasil gegaran penjerapan dan nilai hasil pH. Jumlah penjerapan sekam padi, hampas kelapa sawit dan arang batu yang digunakan adalah 2.5 g/l, 5 g/1, 10 g/1,20 g/l dan 40 g/1. Pada permulaan, terdapat peningkatan terhadap jumlah penjerapan, namun kemudian menjadi hampir tetap sehingga ianya mencapai keseimbangan. Sementara itu perubahan dalam keberkesanan penyingkiran ion Zn^{2+} diperhatikan dalam sela masa 0.5, 1, 1.5, 2 dan 2.5 jam. Namun didapati bahawa penyingkiran Zn^{2+} meningkat mengikut masa. Penyingkiran Zn^{2+} pada kelajuan gegeran berbeza diperhatikan antara 50 hingga 250 rpm, dan secara umumnya penyingkiran ini meningkat mengikut kelajuan gegaran. Manakala hasil pH pula dikaji antara nilai pH 2 hingga pH 10. Kesimpulannya, diapati 10 g/L jumlah penjerapan menggambil masa 2 jam, 200 rpm kelajuan gegaran dan nilai pH 10 untuk pencapaian 97% penyingkiran. Disamping itu kinetik dan isoterna juga digunakan dalam penyelidikan ini. SEM, XRD, FTIR dan kajian taburan saiz zarah dilakukan untuk mendapatkan penjerapan bahan. Keseimbangan data adalah penjelasan terbaik untuk model isoterma langmuir dengan memaksimumkan penjerapan ekalapisan dengan kapasiti 1.4mg/g.

ZINC REMOVAL FROM SYNTHETIC WASTEWATER BY ADSORPTION USING RICE HUSK ASH, PALM OIL FUEL ASH AND COAL FLY ASH

ABSTRACT

Adsorption process with agricultural waste is attracted by many scientists because of the effectiveness for removal of heavy metals ions at trace quantities. Synthetic water containing (Zn^{2+}) metal ions was used as a representative of industrial wastewater. In this study, a three types of ash resulted from burring industrial fuels (rice husk ash (RHA), palm oil fuel ash (PFA) and coal fly ash (CFA)), mixed together and modified with sol-gel method, were used in the study as adsorbents. In thesis scope, adsorption characteristics were investigated by means of batch studies of adsorbent amount effect, contact time effect, shaking rate effect and pH effect. The amount of RHA/PFA/CFA adsorbent used were 2.5 g/l. 5 g/l, 10 g/l, 20 g/l and 40 g/l. It was seen that increasing adsorbent amount results increase in adsorption efficiency, then becomes almost constant when its reach the equilibrium. Meanwhile, the change in the removal of Zn^{2+} ion was observed during 0.5, 1, 1.5, 2 and 2.5 hr time intervals. It was found that Zn^{2+} removal is increasing slightly with increase in time. Removal of Zn^{2+} ion was observed for shaking speed varied from 50 to 250 rpm. Zn^{2+} removal generally increased with increasing shaking speed. The effect of pH on Zn^{2+} removal was investigated in the pH ranges of 2–10. It was found that 10 g/L adsorbent amount, 2 hours contact time, 200 rpm shaking rate and 10 pH are able to achieve 97% removal. Additional to these studies, adsorbent characterization and kinetic and isotherm studies were also investigated. SEM, XRD, FTIR and Particle size distribution tests have been investigated in order to show adsorbent material characteristics. Equilibrium data were adapted to Langmuir, Freundlich and Temkin isotherms and the equilibrium data were best described by Langmuir isotherm model, with maximum monolayer adsorption capacity of 1.4 mg/g.

STUDY OF ADSORBENT PREPARED FROM COMBINATION OF RHA, PFA AND CFA BY REFLUX METHOD FOR REMOVAL OF BRILLIANT GREEN DYE

By

Sariyah binti Mahdzir

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KAJIAN KEATAS BAHAN PENJERAP YANG DISEDIAKAN DARI CAMPURAN RHA, PFA DAN CFA MENGGUNAKAN KAEDAH REFLAK UNTUK MENYINGKIRKAN BAHAN PENCELUP BRILLIANT HIJAU

ABSTRAK

Penggunaan bahan-bahan penjerap murah telah dikaji secara meluas sebagai alternatif kepada kaedah semasa yang mahal untuk menyingkirkan pelbagai jenis bahan pencemar dari air sisa. Bahan buangan seperti abu sekam padi (RHA), abu bahan api kelapa sawit (PFA) dan abu terbang arang batu (CFA) dilaporkan memiliki sifat penjerapan yang baik untuk penyingkiran bahan pencelup. Kajian ini berkaitan dengan penyediaan bahan penjerap diperbuat dari RHA/PFA/CFA menggunakan kaedah reflak. Pra-rawatan keatas bahan penjerap dilakukan menggunakan NaOH untuk meningkatkan kapasiti penjerapannya. Rekaan rencam pusat (CCD) digunakan untuk merancang kajian keatas hubungan lima pembolehubah iaitu (i) jangka masa reflak, (ii) jumlah RHA, (iii) jumlah PFA, (iv) jumlah CFA, dan (v) kepekatam bahan tambah (NaOH). CCD digunakan untuk membangun persamaan model matematik. Analisa varian (ANOVA) menunjukkan nilai penentuan pekali, R^2 untuk model kuadrat ialah 0.8812. Penjerapan pencelup Brilliant Hijau pada permukaan bahan penjerap disahkan dengan menggunakan pengimbas mikrograf elektron (SEM). Kajian spektroskopi inframerah transformasi Fourier (FTIR) mendedahkan kehadiran kumpulan berfungsi hidroksil, Si-R, karbonil dan metil pada permukaan bahan penjerap. Data belauan sinar-X (XRD) menunjukkan kehadiran komponen berasaskan natrium (Na-) pada bahan penjerap yang disediakan dan komponen berasaskan sulfur (S-) pada bahan penjerap yang telah digunakan untuk menjerap pencelup Brilliant Hijau. Ini menunjukkan bahan penjerap boleh digunakan untuk menyngkirkan pencelup Brilliant Hijau.

STUDY OF ADSORBENT PREPARED FROM COMBINATION OF RHA, PFA AND CFA BY REFLUX METHOD FOR REMOVAL OF BRILLIANT GREEN DYE

ABSTRACT

The usage of low-cost adsorbents has been widely investigated as an alternative to the current expensive methods for removal of various kinds of wastewater pollutants. Waste materials such as rice husk ash (RHA), palm fuel ash (PFA) and coal fly ash (CFA) were previously reported in another study to have good adsorbent properties for removal of dyes. This study is concerning the preparation of adsorbent from RHA/PFA/CFA using reflux method. The adsorbent was pre-treated with NaOH to increase its adsorption capacity. Central composite design (CCD) was used to design experiments for the evaluation of the correlation between five variables which are (i) refluxing time, (ii) amount of RHA, (iii) amount of PFA, (iv) amount of CFA, and (v) concentration of additives used (NaOH). The CCD was used for developing mathematical model equation. Analysis of variance (ANOVA) showed that the coefficient of determination value, R^2 for quadratic model is 0.8812. Adsorption of the Brilliant Green dye on adsorbent surface was further confirmed by scanning electron micrographs (SEM). Fourier transform infrared spectroscopy (FTIR) studies revealed the presence of hydroxyl, Si-R, carbonyl and methyl groups on the adsorbent surface. X-ray diffraction (XRD) data showsthe presence of sodium-based (Na-) compounds for prepared adsorbent and sulfur-based (S-) compound for spent adsorbent that had been used for Brilliant Green dyes adsorption. This shows that the adsorbent can be used for removal of Brilliant Green dye.

CHARACTERIZATION OF PREPARED AND SPENT CFA/POFA/RHA ADSORBENTS IN REMOVING HEAVY METALS AND DYES

By

SHAJARATULDUR BINTI ISMAIL

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PENCIRIAN BAHAN PENJERAP YANG DISEDIAKAN DARI CFA/POFA/RHA DAN BAHAN PENJERAP YANG TELAH DIGUNAKAN DALAM MENYINGKIRKAN LOGAM BERAT DAN BAHAN PENCELUP

ABSTRAK

Kewujudan kilang menyumbang kepada pertambahan kepekatan bahan pencemar dalam air sisa. Kepekatan tinggi logam berat dan bahan pencelup mengakibatkan masalah kesihatan dan persekitaran. Pelbagai kaedah rawatan telah diaplikasikan. Dalam kajian ini, pencirian bahan penjerap dari abu terbang arang batu (CFA)/ abu bahan api kelapa sawit (POFA)/ abu sekam padi (RHA) dikaji untuk lebih memahami proses penjerapan dalam menyingkirkan logam berat dan bahan pencelup. Bahan penjerap disediakan menggunakan kaedah penghidratan air, sol-gel dan pengaktifan oleh natrium hidroksida (NaOH). Bahan penjerap digunakan untuk menyingkirkan ferum (II), nikel, mangan, zink, pencelup acid violet 7 dan Brilliant hijau. Bahan penjerap yang disediakan dari kaedah sol-gel menunjukkan keberkesanan penjerapan yang tinggi. Bahan penjerap terpilih digunakan untuk pencirian melalui analisa fizikal dan kimia. Taburan saiz zarah menunjukkan pelbagai saiz zarah hasil dari tindak balas semasa penyediaan bahan penjerap. Permukaan morfologi menunjukkan struktur CFA/POFA/RHA dan selepas penjerapan. Pengkhususan kumpulan berfungsi menunjukkan kewujudan kumpulan hidrokarbon, hidrosil dan silikon.Komposisi kimia menunjukkan kehadiran kompleks komponen hasil dari percantuman tindak balas pelbagai komponen asas dalam CFA/POFA/RHA. Kajian ini membuktikan CFA/POFA/RHA boleh digunakan sebagai bahan penjerap.

CHARACTERIZATION OF PREPARED AND SPENT CFA/POFA/RHA ADSORBENTS IN REMOVING HEAVY METALS AND DYES

ABSTRACT

Existence of various factories had contributed to increasing of contaminants concentration in wastewater. High concentration of heavy metals and dyes creates health and environmental problem. Different types of treatment have been applied. In this study, characterization of coal fly ash (CFA) /palm oil fuel ash (POFA)/ rice husk ash (RHA) adsorbent has been investigated to obtain a better understanding of adsorption process in removing heavy metals and dyes. The adsorbents were prepared using water hydration method, sol-gel method and activation by NaOH method. The prepared adsorbents were used to remove single components of ferum (Fe^{2+}), nickel (Ni^{2+}), manganese (Mn^{2+}), zinc (Zn^{2+}), acid violet 7 and brilliant green dye. The adsorbent prepared from sol-gel method showed high adsorption efficiency. The selections of adsorbents were characterized through physical and chemical analysis. The particle size distribution of the adsorbents showed that the adsorbents have a variation of particle size as a result of the reaction during the adsorbents preparation. The surface morphology of the adsorbents revealed the structure of CFA/POFA/RHA and after the adsorption. The specific functional group of the adsorbent showed the present of hydrocarbon, hydroxyl and silicon groups. The chemical compositions of the adsorbent showed that it consists of some complex compound as the results of combination reaction of different basic compounds existed in CFA/POFA/RHA. This study proves that CFA/POFA/RHA can be used as adsorbent.

UTILIZATION OF INDUSTRIAL COMBUSTION WASTE MATERIALS AS POTENTIAL SORBENT FOR HEAVY METAL ION NICKEL (II) REMOVAL

By

MOHD HAFIZ BIN MOHD RAZALI

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NAME : MOHD HAFIZ BIN MOHD RAZALI
(CAPITAL LETTER)

I hereby declare that all corrections as suggested by supervisor/s and examiner have been taken into consideration to the best of my ability.

(Signature of Student)

04/05/2011
(Date)

We hereby declare that we have read this dissertation and in our opinion it is sufficient in terms of scope and quality as partial fulfillment of requirements for the degree of Bachelor of Engineering (Civil Engineering).

(Signature of Supervisor)	(Signature of Examiner)
DR IRVAN DAHLAN	DR MOHD SUFFIAN BIN YUSSOF
(Name of Supervisor)	(Name of Examiner)
Dr. Irvan Dahlan Pensyarah Pusat Pengajian Kejuruteraan Awam Kampus Kejuruteraan Universiti Sains Malaysia 4.5.2011	4.5.2011
(Date)	(Date)

ABSTRACT

Nickel is one of the heavy metals which often present in our environment. It exists as contaminant, causing adverse effects to the human body and environments. Nickel also has many useful applications in our life and is harmful if discharged into natural water resources. Human use nickel for many different applications. Commonly used treatment technologies were mostly effective except for their high capital and operational cost. Therefore, the low cost sorbent such rice husk ash (RHA), coal fly ash (CFA), and palm fuel ash (PFA) derived from industrial combustion waste material was investigated as replacement of current expensive methods for treating wastewater contaminated by Nickel(II) ion. RHA/PFA was selected as best sorbent to further batch experiments. Mastersizer was used to examine surface analysis of sorbent, scanning electron microscope (SEM) was used to examine the sorbent surface morphologies and X-ray diffraction (XRD) spectrum was recorded using X-ray diffractometer to investigate the various phases present in the sorbent. Adsorption studies were carried out to delineate the effect of initial concentration, pH, agitation time and agitation speed. The optimum pH for Ni(II) adsorption were pH 4, agitation speed of 130 rpm and agitation time of 40 minutes. The two most common isotherm models, Langmuir and Frendlich, were used to described the adsorption equilibrium data.

PENGGUNAAN BAHAN BUANGAN PEMBAKARAN PERINDUSTRIAN SEBAGAI BAHAN SERAP BERPOTENSI UNTUK PENYINGKIRAN ION LOGAM BERAT NIKEL (II)

ABSTRAK

Nikel adalah satu logam berat yang wujud di dalam persekitaran kita. Ia wujud sebagai pencemar, menyebabkan kesan-kesan buruk terhadap sistem badan manusia malah ekosistem semulajadi. Nikel juga mempunyai banyak kegunaan yang berguna dalam hidup kita dan berbahaya jika dilepaskan ke dalam sumber-sumber air semulajadi. Nikel digunakan oleh manusia untuk banyak aplikasi yang berbeza. Kebanyakan kaedah rawatan yang biasa digunakan adalah berkesan jika tidak berdasarkan kepada kos modal dan operasi yang tinggi. Oleh sebab itu, bahan serap kos rendah seperti abu sekam padi (RHA), abu terbang batu arang (CFA), dan abu kelapa sawit (PFA) berasal daripada bahan buangan pembakaran perindustrian telah dikenalpasti sebagai penggantian kaedah-kaedah rawatan yang mahal untuk merawat air buangan yang dicemari oleh Nikel(II) ion. RHA/PFA telah dipilih sebagai bahan serap terbaik untuk eksperimen-eksperimen kelompok selanjutnya. Mastersizer digunakan untuk memeriksa analisa permukaan bahan serap, mikroskop elekton pengimbas (SEM) digunakan untuk memeriksa permukaan bahan serap morphologies dan belauan sinar-X (XRD) spektrum telah dicatatkan menggunakan difraktometer sinar X menyiasat hadiah pelbagai fasa dalam bahan serap. Kajian penjerapan telah dilakukan untuk menggambarkan kesan konsentrasi awal, pH, masa pengocakan dan kelajuan pengocakan. pH optimum untuk penjerapan Nikel(II) ialah pH 4, kelajuan pengocakan 130 rpm dan masa pengocakan 40 minit. Dua model isoterma yang sering digunakan, Langmuir dan Freundlich, digunakan untuk menggambarkan data keseimbangan penjerapan.

RICE HUSK ASH (RHA), COAL FLY ASH (CFA) AND PALM OIL FUEL ASH (PFA) AS A POTENTIAL SORBENT FOR MANGANESE REMOVAL

By

MOHD NOR ISMILHADI BIN CHE SOH

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NAME : MOHD NOR ISMILHADI CHE SOH
(CAPITAL LETTER)

I hereby declare that all corrections as suggested by supervisor/s and examiner have been taken into consideration to the best of my ability.

(Signature of Student)

3/5/11
(Date)

We hereby declare that we have read this dissertation and in our opinion it is sufficient in terms of scope and quality as partial fulfillment of requirements for the degree of Bachelor of Engineering (Civil Engineering).

(Signature of Supervisor)

(Signature of Examiner)

DR IRVAN DAHLAN
(Name of Supervisor)

Dr. Irvan Dahlan
Pensyarah
Pusat Pengajian Kejuruteraan Awam
Kampus Kejuruteraan
Universiti Sains Malaysia

04 05 2011
(Date)

Dr Ir. MOHD. NORDIN ADLAN
(Name of Examiner)

27/4/11
(Date)

ABSTRACT

The removal of manganese from water is an important problem due to various sensitive issues and becoming more important with the increase of industrial activities. In order to solve heavy metal pollution in the ecosystem, it is important to bring applicable solution to the subject. There are several methods to treat the manganese contaminated effluent such as, oxidation, chlorination, ozonation, chemical precipitation and also membrane filtration, but the selection of wastewater treatment methods is based on the concentration of manganese and the cost of treatment. This study is focused on the removal of manganese from synthetic wastewater by using adsorption method with the sorbent being the combination of rice husk ash (RHA) palm fuel ash (PFA) and coal fly ash (CFA). These materials were obtained from the waste industrial. This study tried to determine how effective the sorbent in removing manganese from wastewater. This study reveals that the optimum shaking time for the adsorption is 50minutes, the optimum pH is 8, the optimum shaking rate is 190rpm and the adsorption was able to remove up the manganese with nearly 90% with concentration 300 mg/L. This study also was determined the characteristic of the sorbent by chemical and physical analysis.

ABU SEKAM PADI (*RHA*), ABU ARANG BATU TERBANG (*CFA*) DAN ABU KELAPA SAWIT (*PFA*) SEBAGAI BAHAN SERAP YANG BERPOTENSI UNTUK PENYINGKIRAN MANGAN.

ABSTRAK

Penyingkiran mangan dalam air merupakan satu perkara yang penting kerana pelbagai isu sensitif dan menjadi semakin penting dengan peningkatan aktiviti perindustrian. Dalam menangani pencemaran logam berat dalam ekosistem, pendekatan yang sesuai perlu dijalankan untuk mengatasinya. Terdapat banyak kaedah yang dapat dilakukan untuk merawat air buangan seperti pengoksidaan, pengklorinan, Ozonisasi, presipitasi kimia dan juga filtrasi membran, namun pemilihan kaedah pemprosesan air kumbahan berdasarkan kepada kepekatan mangan dan kos rawatan. Tujuan utama kajian ini adalah untuk menerokai proses penyingkiran mangan daripada air buangan sintetik menggunakan kaedah resapan dengan menggunakan gabungan bahan serap dari abu sekam padi (*RHA*), abu arang batu terbang (*CFA*) dan juga abu kelapa sawit (*PFA*). Bahan-bahan mentah ini didapati daripada sisa industri. Kajian ini akan melihat setakat mana kebolehan *RHA/CFA/PFA* bagi menyingkirkan mangan dari air buangan sintetik. Keputusan daripada kajian menunjukan masa pengoncangan optimum adalah 50 minit, tahap optimum pH adalah pH 8, kadar pengoncangan 190rpm dan penyerapan berupaya menyerap mangan sehingga lebih 90% pada konsentrasi 300mg/L. Kajian ini juga akan melakukan analisis mengenalpasti sifat-sifat fizikal dan kimia penyerap.

REMOVAL OF IRON (II) FROM AQUEOUS SOLUTIONS USING PREPARED FROM WASTE-DERIVED SILICEOUS MATERIALS

By

MOHD LUQMAN HAKIM BIN MOHD ZAIN

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as partial fulfillment of requirements for the degree of

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Universiti Sains Malaysia

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TITLE: REMOVAL OF IRON (II) FROM AQUEOUS SOLUTIONS USING SORBENT PREPARED FROM WASTE-DERIVED SILICEOUS MATERIALS

NAME : MOHD LUQMAN HAKIM BIN MOHD ZAIN
(CAPITAL LETTER)

I hereby declare that all corrections as suggested by supervisor/s and examiner have been taken into consideration to the best of my ability.

(Signature of Student)

03·05·2011
(Date)

We hereby declare that we have read this dissertation and in our opinion it is sufficient in terms of scope and quality as partial fulfillment of requirements for the degree of Bachelor of Engineering (Civil Engineering).

(Signature of Supervisor)	(Signature of Examiner)
DR IRVAN DAHLAN	Dr Ir. MOHD. NORDIN ADLAN
(Name of Supervisor)	(Name of Examiner)
Dr. Irvan Dahlan Pensyarah Pusat Pengajian Kejuruteraan Awam Kampus Kejuruteraan Universiti Sains Malaysia	
03.05.2011	29·04·2011
(Date)	(Date)

ABSTRACT

Iron is one of the heavy metals that abundance in present environment. It differs from other metals through its chemical behavior, bioavailability and toxicity. It can be toxic pollutant which causing adverse affects severe environmental problem as well as to human body and natural ecosystem. Thus, the treatment on Iron in waste water must be properly conducted before discharge into water bodies. Commonly the technologies used for the treatment are effective but high cost. Therefore, this study was carrying out using sorption as a treatment method. The combination of rice husk ash (RHA), Palm fuel ash (PFA) and coal fly ash (CFA) are used as sorbent in this study. The effect of initial Iron concentration, pH, agitation time, agitation rate, sorbent dosage on removal efficiency of Iron was investigated. pH 2 was found to be optimum conditions to remove Fe2+ from solutions. The agitation time was found to be 40 minutes. At 60 mg/l, the removal efficiency was the highest while 0.9 g of sorbent affected the highest removal efficiency. Besides that, physical and chemical analyses have been done to study the physical and chemical characteristic respectively. X-ray diffraction (XRD) was used to determine the crystal structure that present in the selective sorbent while Scanning electron microscope was done to identify sorbent surface morphologies. Thus, from the study, this treatment method is able to remove Iron from aqueous solutions using waste-derived materials.

PENYINGKIRAN BESI (II) DARI LARUTAN BERAKUA MENGGUNAKAN BAHAN PENYERAP DARI BAHAN-BAHAN BUANGAN YANG BERSILIKA

ABSTRAK

Besi adalah salah satu logam berat yang banyak dipersekitaran ini.Besi berbeza dari logam lain melalui tindak balas kimia,kewujudan secara biologi, dan kadar ketoksidan. Besi boleh menyebabkan kesan sampingan terhadap persekitaran serta tubuh manusia dan ekosistem alam. Dengan demikian, rawatan terhadap besi dalam air sisaperlu dilakukan dengan sebaik mungkin sebelum dibuang ke sistem saliran air. Umumnya teknologi yang digunakan untukrawatanadalah berkesan tetapimelibatkan kos yang tinggi. Olehkeranaitu, kajianini dilakukanmenggunakanserapansebagaikaedahrawatan. Kombinasiabusekampadi, abu kelapasawit danabu arang batu digunakansebagai agen penyerapdalamkajianini. Pengaruhkepekatanbesi, pH, masa tindakbalas, kadar tindakbalas, kuantiti bahan penyerap pada keberkesanan penyingkiran besi diselidiki. pH_2 merupakan pH optimum untuk menyingkirkan Fe daripada larutan. Masa tindakbalas dikenalpasti pada masa 40 minit. Pada 60 mg/l, kecekapan penyingkiran adalah yang tertinggi sementara 0.9g agen penyerap mempengaruhi kecekapan penyingkiran tertinggi. Selain itu, analisis kimia dan fizik dilakukan untuk kenalpasti sifat masing-masing. X-ray difraksi untuk menetukan struktur kristal penyerap semntara SEM berfungsi kenalpasti morfologi permukaan penyerap. Dengandemikian, kaedah rawatan ini berjaya menyingkirkan besi daripada larutan berakua menggunakan sisa bahan buangan.

PREPARATION AND CHARACTERIZATION OF RHA/CFA/PFA SORBENT FOR THE REMOVAL OF ACID VIOLET DYE

By

Ahmad Shahril bin Mohamed Noor

This dissertation is submitted to

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USM
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TITLE: PREPARATION AND CHARACTERIZATION OF RHA/CFA/PFA SORBENT FOR THE REMOVAL OF ACID VIOLET DYE

NAME : AHMAD SHAHRIL BIN MOHAMED NOOR
(CAPITAL LETTER)

I hereby declare that all corrections as suggested by supervisor/s and examiner have been taken into consideration to the best of my ability.

(Signature of Student)

(Date)

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(Signature of Supervisor)

A . A . Mokammel Haque
(Signature of Examiner)

DR. IRVAN DAHLAN
(Name of Supervisor)

Dr. Irvan Dahlan
Pensyarah
Pusat Pengajian Kejuruteraan Awam
Kampus Kejuruteraan
Universiti Sains Malaysia

3.05.2011
(Date)

DR. ABU AHMED MOKAMMEL HAQUE
(Name of Examiner)

Dr. Abu Ahmed Mokammel Haque
Senior Lecturer
School of Civil Engineering, Engineering Campus.
University of Science Malaysia (USM)
14300, Nibong Tebal, P. Pinang, Malaysia

05/05/2011
(Date)

PENYEDIAAN DAN PENCIRIAN BAHAN SERAP RHA/CFA/PFA UNTUK PENYINGKIRAN PENCELUP UNGU ASID

ABSTRAK

Air sisa yang mengandungi pencelup daripada pelbagai industri seperti industri tekstil selalu menyebabkan masalah alam sekitar dan ia berkait rapat dengan isu estetika. Dengan menggunakan sisa industri di Malaysia yang mudah didapati dan sumber yang banyak, kajian ini telah dilakukan untuk mengkaji kemungkinan penggunaan abu sekam padi, abu arang dan abu kelapa sawit dalam menyingkirkan pencelup daripada larutan akues. Kajian ini memfokuskan terhadap penyingkiran pencelup ungu asid daripada larutan akues menggunakan kaedah penjerapan dengan penggunaan bahan serap yang dihasilkan daripada kombinasi abu sekam padi, abu arang dan abu kelapa sawit. Kajian kelompok telah dijalankan untuk memeriksa kesan pelbagai parameter seperti kepekatan awal pencelup, masa goncangan, kadar goncangan dan pH. Ia juga akan menentukan keberkesanan bahan serap dalam menyingkirkan warna dan sebagai rujukan untuk kajian masa hadapan. Daripada kajian kelompok yang telah dilaksanakan, didapati masa goncangan optimum adalah 80 minit sementara pH optimum adalah 2. Penjerapan pencelup telah diterangkan oleh garis sesuhu Langmuir, Freundlich dan Temkin. Garis sesuhu Freundlich menunjukkan analisa yang lebih sesuai berbanding dua garis sesuhu yang lain. Analisa fizikal dan kimia juga telah dilakukan untuk megkaji sifat fizikal dan kimia. Mikroskop pengimbas elektron digunakan untuk memeriksa struktur permukaan bahan serap dan pemancaran sinar-X digunakan untuk mengenalpasti struktur kristal yang hadir dalam bahan serap. Analisa permukaan telah memeriksa luas permukaan dan isipadu di dalam bahan serap.

PREPARATION AND CHARACTERIZATION OF RHA/CFA/PFA SORBENT FOR THE REMOVAL OF ACID VIOLET DYE

ABSTRACT

Wastewater containing dye from various industries such as textile industries often caused environment problems and which were closely related with aesthetic issues. By using locally available and abundant resources of industrial waste in Malaysia, this research was conducted to explore the possibility of using rice husk ash, coal fly ash and palm oil fuel ash for the removal of dye from aqueous solution. This research focused on the removal of acid violet dye from aqueous solution using adsorption method where combination of rice husk ash, coal fly ash and palm oil fuel ash were used as sorbent. Batch studies were carried out to investigate the effect of various parameters such as initial dye concentration, shaking time, shaking rate and pH. It also determined the effectiveness of sorbent for removing color which would be referred for future research. From the studies those have done, the optimum shaking time was 80 minutes while the optimum pH is 2. Adsorption of dye was described by Langmuir, Freundlich and Temkin isotherm. Freundlich isotherm showed a better fit compared to the other two isotherms. Chemical and physical analyses were done to study its physical and chemical properties. Scanning electron microscope was used to examine the sorbent surface morphologies and X-Ray diffraction was used to identify crystal structure presents in the sorbent. Surface analysis was investigated the specific surface area and the volume in the sorbent.