THIN LAYER ADSORBENT FOR THE REMOVAL OF METHYLENE BLUE VIA BRUSHING, AIRBRUSHING AND ELECTROSPINNING

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by

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LIST OF SYMBOLS

q_e	Adsorption capacity (mg/g)
Qm	Maximum adsorption capacity of adsorbent (mg/g)
K_L	Constant of Langmuir isotherm (L/mg)
C_i	Initial concentration (ppm)
C_f	Final concentration (ppm)
K_F	Freundlich isotherm constant (mg/g) $(L/mg)^{1/n}$
1/n	Adsorption intensity or factor of heterogeneity
ppm	Parts per million
β	Dubinin-Kadushkevich constant
∈	Polanyi potential
R	Universal gas constant (8.314 J/mol.K)
E	Mean adsorption energy
T	Absolute temperature
b	Temkin constant that is related to the heat of sorption (J/mol)
A_T	Temkin isotherm constant (L/g)
C_e	Equilibrium constant of adsorbate (mg/L)
°	Degree of angle
V	Volume
m	Mass
%	Percentage
rpm	Revolution per minute
k_1	Pseudo-first-order

LIST OF ABBREVIATIONS

AC	Activated carbon
EDX	Energy dispersive X-ray
FTIR	Fourier transform infrared
MB	Methylene blue
SEM	Scanning electron microscopy
PVA	Polyvinyl alcohol
PVB	Polyvinyl butyral
UV-VIS	Ultra-violet spectrophotometer

PENJERAP NIPIS UNTUK PENYINGKIRAN METILINA BIRU MENGGUNAKAN CARA BERUSAN, BERUSAN ANGIN DAN PEMUTARAN ELEKTRIK

ABSTRAK

Paintosorp^{TM} adalah satu penjerap inovatif yang dicipta untuk penyingkiran pewarna daripada air kumbahan industri. Fokus kajian ini adalah untuk mencari cara untuk menerapkan Paintosorp dengan menggunakan cara berusan, berusan angin dan pemutaran elektrik. Berusan angin menggunakan tekanan udara untuk mengecat Paintosorp^{TM} dalam bentuk titisan kecil dan pemutar elektrik menggunakan sumber elektrik yang tinggi untuk menenun penjerap menjadi serat bersaiz nano. Kebolehan penjerap yang dibuat menggunakan berusan angin dan serat PVB/Bentonite yang dibuat menggunakan pemutar elektrik telah diuji dengan pertukaran kadar pusaran magnet, pH dan kepekatan awal pewarna. Salutan penjerap berusan angin Paintosorp^{TM} mencatatkan kadar penjerapan tinggi dan sedikit terjejas dengan perubahan pH dan kepekatan awal perwarna. Paintosorp^{TM} telah mencatat kadar penyingkiran MB 100% untuk kedua-dua kepekatan rendah (20 ppm) dan tinggi (200 ppm) dalam masa 4 jam pertama dan ianya memberi kesan dengan kadar penyingkiran MB yang rendah apabila diuji dengan pH dan kadar pusaran berlainan. Keupayaan penjerapan Paintosorp^{TM} adalah 45.0 mg/g apabila diuji dengan kepekatan 200 ppm. Serat PVB/Bentonite telah mencatat kadar penyingkiran MB yang rendah apabila dibandingkan dengan Paintosorp^{TM} di mana ia hanya mempunyai kadar penyingkiran MB sebanyak 88% di kepekatan 20 ppm dan 33% di kepekatan 200 ppm. Keupayaan penyingkiran MB untuk serat nano adalah 47.7 mg/g apabila diuji dengan kepekatan 200 ppm. Pertukaran pH dan kepekatan awal pewarna memberi kesan yang jelas dalam keupayaan penyingkiran MB. Serat PVB/Bentonite ini mempunyai kadar penyingkiran MB yang rendah apabila di dalam keadaan asidik dan kadar penjerapan jatuh apabila kepekatan meningkat. Apabila kepekatan meningkat dari 100 ppm ke 200 ppm, kadar penyingkiran MB jatuh daripada 47% kepada 33%. Kadar pusaran mencatatkan kesan yang rendah kepada keupayaan penyingkiran MB serat nano. Pencirian Paintosorp^{TM} berusan angin dan serat PVB/Bentonite dan serat nano telah dilaksanakan menggunakan SEM,EDX dan FTIR. Ia didapati bahawa serat PVB/Bentonite mempunyai lebih banyak liang apabila dibandingkan dengan Paintosorp^{TM} berusan angin tetapi Paintosorp^{TM} berusan angin mempunyai atom Al dan Si yang lebih banyak. Salutan penjerap mengikut isoterma Freundlich manakala serat nano mengikut isoterma Langmuir. Kajian kinetic menunjukkan bahawa kedua-dua salutan penjerap dan serat nano mengikut psuedo-tertib kedua.

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ABSTRACT

Paintosorp^{TM} is an innovative adsorbent coating that was designed for the removal of dyes from industrial wastewater. This research focuses on the methods of applying Paintosorp^{TM} and PVB/Bentonite via various methods such as brushing, airbrushing and electrospinning. Airbrushing uses air pressure to paint Paintosorp^{TM} in miniscule droplets meanwhile electrospinning utilizes high voltage to weave the adsorbent into nanofibers. The adsorption ability of airbrushed Paintosorp^{TM} and electrospun PVB/Bentonite nanofiber was tested with the change in stirring velocity, pH and initial adsorbate concentrations. Paintosorp^{TM} recorded high adsorption of 100% removal for both low (20 ppm) and high concentrations (200 ppm) in the first 4 hours of the experiment and is affected slightly with the change pH and stirring velocity. The adsorption capacity of airbrushed Paintosorp^{TM} were at 45.0 mg/g when tested with high concentration of MB of 200 ppm. The electrospun PVB/Bentonite nanofiber had lower removal compared to Paintosorp^{TM} where it had only 88% removal of MB at 20 ppm and 33% removal at 200 ppm. The adsorption capacity of the electrospun nanofiber were at 47.7 mg/g when tested with 200 ppm. The changes in pH and initial adsorbate concentrations had significant effect on its MB removal. The PVB/Bentonite nanofiber performs poorly in acidic conditions and the MB removal drops as the concentration increase from 100 ppm to 200 ppm, where the MB removal was at 47% removal to 33% removal respectively. The stirring rate only had slight effect on the nanofiber adsorption ability. The characterization of the airbrushed Paintosorp^{TM} coating and PVB/Bentonite nanofibers were done using SEM, EDX and

FTIR. It is found that the nanofiber were more porous than the coating but the coating had higher presence of Al and Si atoms. The airbrushed Paintosorp^{TM} coating fits the Freundlich isotherm model meanwhile the PVB/Bentonite nanofiber fits the Langmuir model. The adsorbent kinetics studies revealed that both the adsorbent coating and nanofiber fits the pseudo-second-order model.

CHAPTER 1

INTRODUCTION

1.1. Water and water pollution

Water are clear, tasteless, odourless substance that is essential for all forms of life and is an act as the universal solvent for many substances. Water is integral in the survival of a human being, apart from air and food. Of all the planets that exists in the solar system, the only planet that contains 73% of its surface covered in water is Earth, although 97% of the existing water is seawater and due to its high salinity, it is unsuitable for human consumption. The other 2.76% are fresh water out of which 2.4% is available and about 0.3% to 0.5% of it is available for drinking consumption. Water continuously change and constantly moving in a cycle called the hydrologic cycle (Dastrup, 2018). Water can be found in the ocean, atmosphere and on the surface. Water evaporates into the air as water vapour and condensed water vapour form precipitates into rain, or snow and goes back onto the Earth's surface. These precipitates fall into open bodies of water, absorbed by vegetation and become surface runoff and some are stored as groundwater. All the water then re-enter the ocean and continue the hydrologic cycle (Pagano & Sorooshian, 2014).

In the last century, the rapid growth of the world's population has severe effects on the resource use of Earth. The use of water was doubled in the 20th century when compared to the population growth. It is estimated in 2025, 1 800 million people will be living in absolute water scarcity, and two-thirds of the world population could be under stress conditions (Loucks & van Beek, 2005). Development of urban areas could worsen the estimated value as it would put pressure on the available water resources (Farha et al., 2012). Clean water supplies and sanitation persist to be a major problem in many parts of the world, with 20% of the global population lack access to safe drinking water. In developing countries, water-borne problems continue to plague the people and affects their health. Polluted water claimed many children lives annually (Loucks & van Beek, 2005).

Water pollution is mainly caused by wastewater, released by domestic, industrial agriculture, and transport use. The wastewater released by these sources affects the biotic and abiotic components of the ecosystem. Undesirable by-product released by industries undergo wastewater treatment before being released to a sanitary sewer or a surface water (Vunain *et al.,* 2016). Although treatment was done before release, some of undesirable by-product might slip away from the treatment and ended up released to the environment. Some of the pollutants that is released are such as organic compounds (benzene, chloroform, phenols and toluene), heavy metals (chromium, copper, lead and zinc), nitrogen compounds, natural and synthetic dyes and hydrocarbons.

1.2.Textile industry

The textile industry is a fast-growing industry in Malaysia. In the year of 2008, in the states of Kelantan and Terengganu, had produced close to 400,000 tonnes of man-made fibers, consisting of nylon, polyester filament, and staple (Pang & Abdullah, 2013). Considering the sheer amount of textile fibers produced, it is not surprising that it had significant effect on the environmental quality, with respect to the wastewater effluent.

Batik is one of the most recognized products from the Asian textile industry. Batik wastewater contains dyes originating from the dyeing process and in addition, the wastewater also contain synthetic ingredients that need to be degraded. In the colouring process, the compounds used in the dyeing process used about 5% of the primary compound and the other 95% was discarded as liquid waste (Sutisna et al., 2017).

The effect of textile industry operations have been studied numerously by various researchers. For example, textile effluent may contain suspended solids which can clog fish gills, risking the health and growth rate of the marine life. In addition, the dye released also reduce light penetration, and as a result, reduce the ability of algae to produce food and oxygen (Tüfekci et al., 2007).

1.3. Existing wastewater treatment methods

The industrial wastewater treatment plants have implemented numerous technologies to treat the effluents created before releasing the treated water to the environment. The said technologies can be generally classified into three categories, physical, chemical and biological. Physical method utilizes naturally occurring forces such as gravity and electrical attractions. It does not affect the chemical structure of the wastewater and some examples of physical methods used are sedimentation, filtration and adsorption. Chemical method uses chemical reactions to influence the wastewater. The examples for this method are chlorination, precipitation and chemisorption. Lastly, biological method uses bacteria and small organisms to break down the organic waste using cellular process (Pang & Abdullah, 2013). This method can be divided into aerobic and anaerobic processes.

1.4. Adsorption film/coating

The research on films or coatings is usually is for the application of medical treatments, scaffolding, and thermal barriers aesthetics. The use of film as adsorbents is still a niche application as the research on this is quite new. Up to recent years, the treatment of coloured wastewater had been dependent on the aerobic digestion (Buchanan, 2006), membrane separation (Gao, 2016), coagulation and flocculation (Prakash et al., 2008), trickling filtration (Daigger, 2012), ion exchange (Raghu & Ahmed Basha, 2007) and membrane bioreactor (Reif et al., 2011). These methods had been extensively used in industries, but each process faces technical and economical barriers.

An adsorbent coating is very versatile. Kadir et al., (2017) used surfactant modified bentonite adsorbent coating to soften hard water. The process of softening hard water is removing Ca^{2+} and Mg^{2+} ions. This coating was able to reach 66.67% removal efficiency of Ca^{2+} and Mg^{2+} ions from synthetic hard water.

An adsorbent coating that is able to remove methylene blue from water was developed by Azha et al., 2017 called Paintosorp™. This newly developed adsorbent coating utilizes water-based paint, bentonite clay and water to produce a slurry that is applied to a cotton fiber. It is a low cost and has high adsorption capability. This product has also been further research upon by Hamid, (2017) where the use of fin system and the mathematical formulae was researched upon. The fins function as the medium for the adsorbent coating and it is capable to remove up to 90% of methylene blue from the water. Paintosorp™ is created by mixing white water-based paint with bentonite into a slurry. The slurry is then applied onto a white cotton substrate via brushing or airbrushing. After the coating process, the coating is dried in an oven to ensure that it is fully dried.

1.5. Electrospinning

Nanofibers structures are desirable for the application of adsorption such wound dressings, scaffolding, membrane separation and drug delivery. There have been research on using electrospinning to produce an adsorbing-capable nanofibers. Deng et al.,(2011) implemented co-electrospinning in order to produce a nanofiber that is able to adsorp lead (II) ions. Co-electrospinning is a process where requires a polymer to be the shell and the other polymer, nonpolymeric Newtonian liquid or powder to fill the core. (Bazilevsky *et al.,* 2007). In addition, Haider & Park, (2009) studied electrospun chitosan nanofibers for the adsorption of Cu(II) and Pb(II) ions. The characteristics of electrospun nanofibers are desirable as they are highly porous, with high surface area to volume ratio, and has interconnected open pore structures which can offer reliable removal of pollutants from water (Aluigi et al., 2014). The nanosized fibers formed by electrospinning has better capability to collect particles because the flow slip between the fiber increases the diffusion and contact time.

Electrospinning is a versatile process that is capable of producing ultrafine fibers. The advantage of electrospinning is that the process is relatively quick and simple. Its ability to fabricate nanofiber from a variety of materials is also an advantage. The electrospinning process implement the self-assembly process which is induced by electromagnetic forces. The electrical charge enables the drawing of fibers from a polymer solution. A high-voltage power supply generates an electrical field between the needle tip to the collecting drum. A polymer drop forms on the tip of the needle, thus creating a Taylor's cone in the presence of the electrical field and from there, fluid jets is form from the apex of the cone. As the charged jet travels through the electrical field, the diameter of the jet decreases due to high extension rate and evaporation of the solvent (Svrcinova et al., 2010).

The study of electrospinning usually focused on four factor that affect the creation and quality of produced nanofiber. The polymers' molecular weight, topology and weight distribution are its factors. Next is the solvent for the polymer, where its surface tension, solubility parameter and relative permittivity play the major role in the mixing and spinning process. The produced polymer solution viscosity, concentration and specific conductivity is the other factor. The last factor is the process parameter of the electrospinner where the electric field strength, tip-to-collector distance, temperature and humidity (Huang *et al.*,2003).

Polyvinyl butyral is a well-established polymer that had been extensively used in the production of nanofibers. It has been used in the production of thermoelectric green tapes where the PVB acts as the binder (Salam *et al.*, 2000).

1.6. Problem statement

Paintosorp^{TM} is a thin coated adsorbent layer, a new type of adsorbent coating that was designed for the removal of dye from wastewater . It has been proven to have high adsorption capability and has potential to be used in industries. In spite of that, the process of applying the adsorbent via brushing could cause limitations in the adhesive strength and the thickness of the adsorbent. In addition, the management of waste fom the existing method could become costly.

A study on other possible methods of applying the adsorbent is important. Several other methods such as airbrushing and electrospinning can be implemented. The adsorption capabilities of these methods would be tested via vigorous stirring, acid and basic conditions and at different adsorbate conditions. Moreover, the result from the experiment will be used in equilibrium and kinetic studies to investigate the behaviour of the adsorbate with the adsorbent coating and nanofiber. Thus, this present work researches on the feasibility of other methods of applying Paintosorp^{TM} for the treatment of methylene blue.