SYNTHESIS AND INTERACTION MECHANISM OF ZWITTERIONIC ADSORBENT COATING FOR CATIONIC AND ANIONIC DYES REMOVAL

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by

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λ_{max}	maximum wavelength
V	volume
W	weight
C_0	highest initial adsorbate concentration
C_e	equilibrium concentration of adsorbate
C_t	liquid-phase concentrations
q_e	amount at equilibrium
Q_m	maximum adsorption amount
K_L	Langmuir constant
R^2	correlation coefficient
R	Universal gas constant

LIST OF ABBREVIATIONS

ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared
AAS	Atomic Absorption Spectrometry
APE	Acrylic Polymer Emulsion
AR 1	Acid Red 1
AB 75	Acid Brown 75
AO	Acid Orange
ASTM	American Society for Testing and Materials
BG	Brilliant Green
BY 28	Basic Yellow 28
CEC	Cationic Exchange Capacity
CMC	Carboxy Methyl Cellulose
CV	Crystal Violet
CS	Chitosan
DO	Dissolved Oxygen
EDX	Energy-dispersive X-ray spectroscopy
ENR	Epoxidized Natural Rubber
EPIDMA	Epichlorohydrin Dimethyl Amine
HDTMA-Br	Hexadecyltrimethylammonium bromide
ICP-OES	Inductively Couple Plasma Atomic Emission Spectroscopy
LDH	Layered Double Hydroxide
MB	Methylene Blue
MCM	Microfibriller Cellulose Mat
MG	Malachite Green

MMT	Montmorillonite
MR	Methyl Red
MIDA	Malaysian Investment Development Authority
PAA	Polyacrylate
PEG	Polyethylene glycol
pHpzc	pH potential zeta charge
PVA	Polyvinyl alcohol
PVC	Polyvinyl Chloride
PVDF	Vinylidene difluoride
RBBR	Remazol Brilliant Blue R
RO 16	Reactive Orange 16
SEM	Scanning Electron Microscope
SMX	Sulfamethoxazole
UV-Vis	Ultra- Violet Spectrophotometer
VOC	Volatile Organic Compound
XRF	X-ray Fluorescence
ZwitAd	Zwitterionic Adsorbent Coating

SINTESIS DAN MEKANISME INTERAKSI LAPISAN PENJERAP ZWITERION UNTUK PENYINGKIRAN BAHAN PEWARNA KATION DAN ANION

ABSTRAK

Penjerapan adalah satu teknik yang digunakan secara meluas dalam rawatan air sisa berwarna kerana proses ini pratikal, murah, cekap dalam pengoperasian dan fleksibel dalam reka bentuk bahan penjerapnya. Walaubagaimana pun, penjerap yang berbentuk serbuk halus dan berkepingan yang mempunyai nano-saiz, bentuk tidak sekata dan ketumpatan yang tidak stabil akan mengakibatkan kesukaran terutamanya dalam system aliran berterusan. Oleh yang demikian, kajian ini telah memberi tumpuan kepada penghasilan lapisan penjerap yang mempunyai fungsi zwitterion untuk penyingkiran bahan pewarna kation dan anion dari larutan akueus. Lapisan penjerap disediakan melalui kaedah yang mudah dengan menggunakan kombinasi bahan seperti aditif (tanah liat bentonit), surfaktan (polielektrolit kation, EPIDMA), pelarut (air suling) and pengikat (emulsi polimer akrilik, APE), yang kemudiannya di salut ke atas kain kapas sebagai substrak. Nisbah formula yang optimum telah disahkan sebagai 1: 2: 4, yang bersamaan dengan bentonit (g): APE (g): EPIDMA (wt.%). Lapisan penjerap zwiterion yang selepas ini dirujuk sebagai ZwitAd telah di cirikan dan di analisis untuk memastikan sifat kimia dan fizikalnya. ZwitAd mempamerkan prestasi yang baik dalam kecekapan penyingkiran dan keupayaan penjerapan untuk kedua-dua jenis pewarna sama ada secara penjerapan tunggal atau serentak, bersama-sama dengan kekuatan salutan yang baik, dan stabil dari sudut kimia dan haba. Mekanisma penjerapan pewarna boleh digambarkan melalui tarikan elektrostatik antara permukaan penjerap amphoterik (caj positif dan negatif) dengan anionik sulfonat

$-SO_3^-$ dari pewarna Acid Red 1 (AR1) dan $(=NH)^+$ dari pewarna Brilliant Green (BG). Tarikan lain juga melibatkan ikatan hidrofobik dan hidrogen. Kesan kepekatan awal pewarna (10 ppm-250 ppm), dos penjerap (0.1 g- 0.5 g), pH awal (2-12), kekuatan ionik (1 g / L - 5 g / L) dan kesan suhu (30-70 ° C), kesan pewarna binari dan tertiari, penjerapan pada jenis pencemar lain dan kajian kitaran juga dikaji secara mendalam. Di samping itu, keseimbangan isoterma, kinetik, termodinamik dan kajian mekanisme juga dinilai. Keputusan menunjukkan dengan bertambahnya masa dan kepekatan pewarna, membawa kepada pertambahan keupayaan penjerap ZwitAd terutama untuk penyingkiran pewarna AR 1. Variasi dalam kepekatan awal pewarna dari 50 mg/L hingga 250 mg/L memberikan peningkatan keupayaan penjerap dari 33.33 mg/g kepada 74.50 mg/g untuk pewarna AR 1 dan 34.83 mg/g kepada 183.01 mg/g untuk pewarna BG. Selain itu, ZwitAd sangat baik menjerap dalam jangkauan pH dari 2 hingga 12. Maksimum 10 kali kitaran penjerapan-penyahjerapan pewarna BG dicapai dengan menggunakan kebolehsanaan pemulihan secara terma. Data penjerapan yang diperolehi dinilai berdasarkan keseimbangan isoterma dan kedua-dua pewarna mengikut isotherm Freundlish. Model tersebut menunjukkan penjerapan terdiri daripada pelbagai lapisan heterogen. Kajian kinetik menunjukkan pewarna AR 1 mengikuti pseudo-tertib pertama dan pewarna BG mengikuti pseudo-tertib kedua. Kajian termodinamik juga mendedahkan bahawa penjerapan berlaku proses spontan dan endotermik. Kajian semasa mendapati ZwitAd berpotensi sebagai lapisan penjerap yang boleh dilaksanakan dan praktikal untuk teknologi rawatan air sisa di masa hadapan.

SYNTHESIS AND INTERACTION MECHANISM OF ZWITTERIONIC ADSORBENT COATING FOR CATIONIC AND ANIONIC DYES REMOVAL

ABSTRACT

Adsorption is an extensively used technique in color wastewater treatment since the process is practical in operation, economical, efficient and flexible in adsorbent design. However, the occurrence of fine powdery or flakes adsorbents with nano-sized, irregular shape and unstable density will cause complexity once applying in continuous flow system. Fast loss of adsorbent, leaching and obstruction phenomena in column among the problems created. Thus, this research focused on development of an adsorbent based coating with zwitterionic functionality for the removal of cationic and anionic dyes from aqueous solution. The adsorbent coating was prepared through a facile method based on the combined used of additive (bentonite clay), surfactant (cationic polyelectrolyte, EPIDMA), solvent (distilled water), and binder (acrylic polymer emulsion, APE), which then coated on cotton cloth as a substrate. The optimum formulation ratio was confirmed as 1:2:4, reciprocated to swelled bentonite (g): APE (g): EPIDMA (wt. %). The novel zwitterionic adsorbent coating which then referred as ZwitAd was characterized and analysed to ascertain its chemical and physical properties. The ZwitAd exhibited significant performance in removal efficiency and adsorption capacity for both working dyes (either in single or simultaneous adsorption) together with good coating strength, chemical and thermal stability. The mechanism of dyes adsorption can be ascribed via electrostatic attractions between amphoteric adsorbent surfaces (positive and negative charges) with the sulfonate anionic $-SO_3^-$ group of Acid Red 1 (AR1) dyes and $(=NH)^+$ groups of Brilliant Green (BG) dye. Another interaction may involved hydrophobic and hydrogen bonding. The effect of initial dyes concentration (10 ppm-250 ppm), adsorbent dosage (0.1 g- 0.5 g), initial pH (2 – 12), ionic strength (1 g/L - 5 g/L), temperature (30-70 °C), effect of binary and tertiary dyes, adsorption on other types of pollutants and reusability study were investigated in precise. In addition, the equilibrium isotherms, kinetics, thermodynamics and mechanism studies were also evaluated. The result showed increasing contact time and dye concentration led to a rapid increment in the adsorption capacities of ZwitAd especially for the elimination of AR 1 dye. Variation in initial dye concentration from 50 mg/L to 250 mg/L, gave a corresponding increase in adsorption capacities from 33.33 mg/g to 74.50 mg/g for AR 1 dye and 34.83 mg/g to 183.01 mg/g for BG dye. Besides, ZwitAd was excellent in relatively wide pH range from 2 to 12. Maximum 10 consecutive cycles of adsorption-desorption of BG dye was achieved by applying thermal regeneration study. The obtained adsorption data were assessed based on equilibrium adsorption isotherms and best described by Freundlish isotherm for both dyes. The model connotes that the multilayer adsorption on ZwitAd heterogeneous surfaces. The kinetic model revealed that pseudo- first-order was in better agreement with AR 1 and pseudo-second-order for BG dye. Thermodynamic studies also revealed that adsorption was spontaneous and endothermic process. The current study discovered the potential of ZwitAd as a feasible and practical coating adsorbent for future wastewater treatment technology.

CHAPTER 1

INTRODUCTION

1.1 Textile industry in Malaysia

Textiles industry in Malaysia featuring as a matured industry since country started an export-oriented industrial transformation since early of 1970s (MIDA, 2018). The textile industry has been a significant contributor to Malaysia's economy and was regarded as the backbone to be one of the active developing industry to the country. According to the latest report from Malaysian Investment Development Authority (MIDA) in 2017, Malaysia has become the eleventh largest export textile earner, contributing approximately RM 15.3 billion (1.6 %) to Malaysia's total exports of manufactured goods. In addition to that, Malaysia has approved 12 projects with the total investment of RM 428.8 million solely for textiles and textile product industry. Out of 12 projects, eight projects worth around RM 389.9 million of investment values were concerted in the production of primary textiles. The primary textiles include an upstream processing such as production of natural and synthetic fibre, yarn, woven, knitted as well as bleaching, dyeing, finishing and printing (MIDA, 2018). With the huge numbers of invested project, it has open up thousands of occupation vacancies remarkably for high-skilled Malaysian engineers and other workers.

1.2 Water pollution from textile industry and its adverse effect

Nevertheless, behind the positive progress, successful and growing industries, it also acts like a double-edged sword. The ruinous is, development of the textile industries has left a large footprint to the environment. The sources of pollution significantly due to the discharged of large volume of water containing synthetic waste dyes, colour residues, catalytic chemicals, excess nutrients (nitrogen, phosphorus), organic matters (sodium, potassium, magnesium, calcium, copper, lead, nickel and zinc), usually during dyeing and printing processes (Pang and Abdullah, 2013; Siddique et al., 2017). The arising problem may involve whole system include biota (flora and fauna), environment and the worst assuredly towards human health. Dyes can caused severe effect due to its toxicity, carcinogenicity or mutagenicity (Nandi and Patel, 2017; Rahman, 2015). Common problems include reducing sunlight penetration, obstructing photosynthesis, hindering growth of aquatic biota, and increasing biochemical and chemical oxygen demand (Aparecida et al., 2018).

Thus, since clean water is required nearly at every step of production even across a multitude industries, the contaminated wastewater must be carefully managed before discharged (Rahman, 2015). With the aim of alleviating the water pollution problems and safeguarding the aquatic life, the removal of the colour and chemical compounds from the wastewater is pertinent in order to meet the legislative requirements (Pang and Abdullah, 2013). Thus, an effective treatment for the removal of dyes and other contaminants are seriously required.

1.3 Textile effluent treatment

Wastewater treatment is a combination of unit processes (Pang and Abdullah, 2013). The developed treatment include physical, chemical and biological with the use of an integrated/hybrid method (more than two units) will produce an acceptable effluent before discharging into rivers. The output or effluent of one process become the input (influent) of the next process. Basically, several physical methods of decolouration include equalization and homogenization, floatation, membrane filtration (Nayak et al., 2018), ion exchange (Nabi et al., 2011) and adsorption (Azha et al., 2014; Fathi et al., 2018). The methods contain no gross chemical or biological changes except physical phenomena used to treat the wastewater. Whereby the chemical treatment methods consist of chemical reactions to improve the water quality. Different chemical methods are oxidative process, Fenton treatment (Vorontsov, 2018), Ozonation (Srinivasan et al., 2007), H_2O_2 UV radiation (Soon and Hameed, 2011), coagulation and sedimentation (Fosso-Kankeu et al., 2017), electrocoagulation (El-Ashtoukhy et al., 2017) etc. In biological treatment methods, most organism such as bacteria are used for the biochemical decomposition of wastewaters to stabilize end product. Biological treatment methods can be divided into aerobic and anaerobic methods (Crini and Lichtfouse, 2019).

In general, each of the techniques has its own merit and demerits/boundaries that need to be considered. This is due to the multi-components and different characteristics of dyes structure that can evade the individual treatment process in eliminating the organics pollutants (Hu et al., 2018; Jawad et al., 2017; Sellaoui et al., 2017). Thus, the combination method of treatments is a must for a systematic operation of a wastewater treatment plant. The treated wastewater then can be safely discharged into stream, applied to land or even reused in plant operations itself.

Therefore, the design of textile wastewater treatment plant should consider the difference in organic pollutants since the pollution profile of each industry may obviously varies. As been recommended by few researchers, the ideal wastewater treatment processes should include an initial step of the chemical treatment and then followed by the biological treatment to remove organic matters (Pang and Abdullah, 2013). Then, the physical treatment method as a finishing step for the treatment plant e.g. adsorption, membrane separation or with any other oxidation treatment processes that offer lowest cost for a complete treatment. The cost may be include both CAPEX (capital expenditure) and OPEX (operational expenditure) such as unit operation (machine), energy usage, intensive labours, maintenance or high sludge generation that require disposal cost and other expenses. However, the investment for wastewater treatment cannot be avoided in order to comply with the environmental regulatory discharged standard limit but there are rooms for cost minimization.

Process flow diagram of textile wastewater treatment exhibited in Figure 1.1 is commonly practice in the textile industries in Malaysia (Pang and Abdullah, 2013). It consist of the conventional treatment of chemical, biological and physical methods as an integrated wastewater treatment plant. Using chemical treatment often need high budget allocation due to too much chemical used, even they are very good in decolorizing the water. Besides, the accumulation of concentrated sludge after coagulation and flocculation process also creating disadvantages of the treatment. The route then followed by biological treatment.

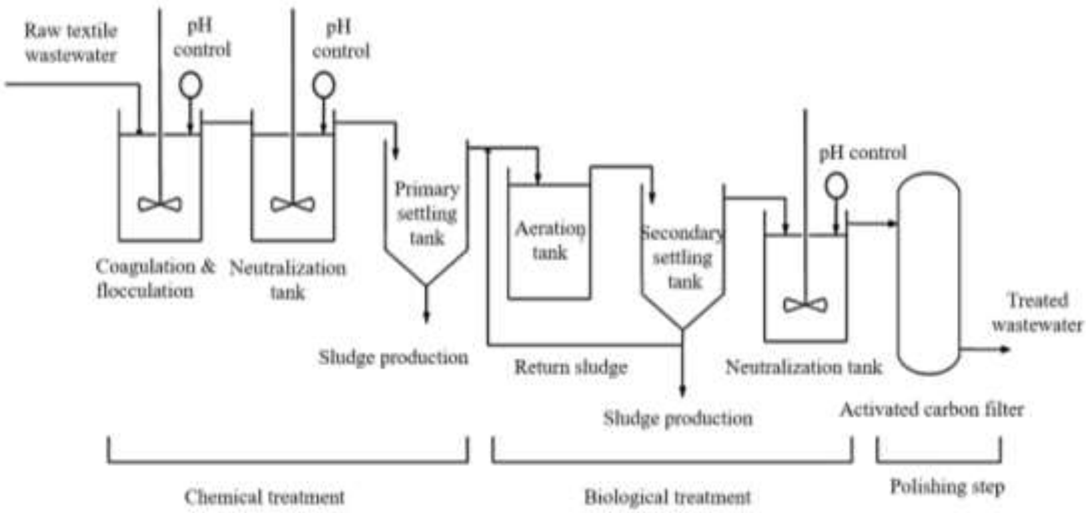

Figure 1.1 Process flow diagram of textile wastewater treatment plant in Kuala Lumpur (Pang and Abdullah, 2013)

The consideration need to be taken in this treatment is that, it's required a large aerobic tank/area due to the long hydraulic retention time since the bacteria has a slow growth rate. Besides, the sludge again produced and increased. These method indirectly cause secondary pollution and creating disposal problem to be solved. At its polishing step, the textile effluents were treated using activated carbon column/filter before discharge the treated wastewater into water bodies. Now, it is safe to the environment. Last but not least, it is suggested to prepare the treated effluent for recycle purpose to be reuse in the next production of textile.

Thus, among the treatment methods (physical, chemical and biological) available, the physical treatment will be the most effective process to be as a finishing step in wastewater treatment plant. The finishing step is important and recommended since the treatment offer high quality treated effluent with free/minimal contaminant and decolour the discharged water. Membrane filtration, ion exchange and adsorption are among the most extensive used techniques in physical treatment (Rahman, 2015). As for the membrane filtration, limitations include short lifetime of membrane before it starts to foul, need high working pressure and high cost for membrane system (Rahman, 2015). Besides that, ion exchange having constrain in terms of ineffective in removing several types of dyes e.g. reactive dye. Adsorption always comes with the adsorbent's problem due to sludge disposal and regeneration factor (Nidheesh et al., 2018). Therefore, comparing all the three techniques above, the most minimum restrains has been taken for consideration and adsorption process will be investigated for further deliberation. According to documented studies, adsorption has proven efficient in eliminating the pollutant, only if the suitable adsorbent is obtained in terms of high removal rate, high adsorption capacity and sustainable (Meili et al., 2018; Zbair et al., 2018).

1.4 Adsorption

Adsorption is known as one of the preferred and useful process to sequester away the organic dyestuffs from the water (Lima et al., 2018; Thue et al., 2018). It is a superior and efficacious technique in terms of high efficiency, simplicity and flexibility of design, ease of operation, and non-toxic of the utilized adsorbents

(Goswami and Moni, 2019; Vivek et al., 2016) as compared to other conventional wastewater treatment. However, the applicability and higher performance of adsorption process depend mainly on adsorbents; their physical as well as chemicals properties. Therefore, a supreme adsorbent should possess; high surface area, maximum adsorption capacity, appropriate pore size, easy accessibility, cost effective, mechanical stability, compatibility, ease of regeneration, sustainable practice, fast kinetic, environmental friendly, available with huge amount in local place as well as high selectivity to remove a wide range of dyes without requirement of various processing procedures (Crini and Badot, 2008; Meili et al., 2018; Tan et al., 2015).

In this regard, a number of adsorbents such as customary activated carbon (Wang et al., 2018; Zbair et al., 2018), natural and modified clays (Javad et al., 2017), resin (Syed et al., 2011), polymeric sorbent (Popescu and Suflet, 2016), bio-sorbents, modified agricultural by-product (Azzaz, 2016), industrial waste as well as chitosan (Lipatova et al., 2018; Vakili et al., 2014) were simulated and execute especially for colour removal from aqueous solution. Besides, it is noticeable from most of adsorbent's developed, it typically performed in nano-sized (Kyzas and Matis, 2015), powdered (Ab et al., 2017), beads and flakes (Vakili et al., 2015) as well as spherical pellet and fibre forms (Yesilada et al., 2003). However, very erratic in coating or film form adsorbent (Jawad et al., 2017; Rizzi et al., 2018).

1.5 Adsorbent coating

An adsorbent coating is a new approach in adsorption application where the ordinary form of adsorbent has been reformulating and transform into a liquid/slurry form which then been laminated onto an inert surfaces or substrate. Finally, once undergo drying procedure, a hardened layer of adsorbent was formed on the selected support. The adsorbent coating modify the classical adsorption concept, with simpler synthesis procedure and flexible working application afterwards. This new innovative solutions aimed at simultaneous increase of performances in terms of dyes removal and decrease of the energetic footprint by bringing to cost minimization in operation and time saving (Jawad et al., 2017; Junyi et al., 2016). Besides, the adsorbent with substrate/support will have a very good mechanical stability that can be very important if it faces different typologies of mechanical stresses including vibrations or collision during adsorption processes (Das and De, 2015; Nawi et al., 2010; Tahseen et al., 2016). The flexibility of the adsorbent coating to be used or applied in any condition become an extra advantages, since it can be layered or slotted in a narrow, small or bigger corners or spaces in a treatment plant. As long as the support used also flexible.

For few reasons, it is desirable to have the solid adsorbent deposited on a substrate as a coating instead of being contained in particulate form as pellets, beads, flakes, particles, powder etc. As reflected by one of the Patent publication from Dunne and Began group, there are an attractive and innovative reasons why solid adsorbent coating suggested to be used (Dunne and Began, 1994). First, to improve the adsorption properties of the solid adsorbents by improving the surface area to weight ratio. The coating can be layered as thin as desired, then directly will perform the adsorption over the entire coated surface. Larger the surface area, greater the adsorption capacity. Adsorbent coating also can reduce the amount of solid adsorbent required with exact formulation prepared. In addition to that, using substrate as support, the strength or form can be achieved. Means, it can prolong the lifetimes of used adsorbent. Other advantages of coating also indirectly can protect the underlying substrate materials from a harmful environment (Dunne and Began, 1994).

1.6 Zwitterionic adsorbent coating for cationic and anionic dyes removal

The content of industrial effluents comprises of anionic, cationic and non-ionic synthetic dyes molecule together with a variety of additives and surfactants (Kuppusamy et al., 2015). Cationic dye basically carry a positive charge in their molecule, while anionic depend on a negative ions (Salleh et al., 2011). One sort of adsorbent with both cationic and ionic groups is highly required to meet the current complexities related to industrial water treatment. Adsorption using only one type of ionic tail is usually incapable to eliminate different ionic dyes. Numbers of published research work just concentrated on single adsorbent which give affinity towards only specific types of dyes (Esan et al., 2014; Jiang et al., 2017; Sakthisharmila et al., 2018). Thus, the adsorption of cationic and anionic species on a single matrix has to give an attention to be explored more (Kai et al., 2016; Nasuha et al., 2011; Samaneh et al., 2017; Wenxuan et al., 2012). Since there are still very less information in the literature with regards to the amphoteric or zwitterionic adsorbents to target dye pollutants from wastewater.

In this study, the selection of two working dyes (cationic and anionic) are guided by their strong adsorption onto adsorbent as well as high solubility in water. In addition, the most important type of commercial dyes refers to azo dyes (Acid Red 1, AR 1), comprising over 50 % of the global production of dyes. The characteristic feature of these dyes is the presence of one or more azo bonds (-N=N-) in their chemical structure. Azo dyes are introduced into the industrial wastewaters at different stages of dyeing and textiles and discharging them into aquatic environments leads to serious problems to flora and fauna (Mehrizad et al., 2019). Brilliant Green (BG) dye is one of the important dyes in the paper, printing and textile industries. BG is an organic cationic dye that has been used for various purposes. The widespread use of this dye is controversial because it causes several effects on human beings including irritation to the gastrointestinal tract, nausea and vomiting, irritation to the respiratory tract and irritation to skin, and the toxic properties which can cause cancer and mutagenesis (Dominguez et al., 2019).

1.7 Problem statement

Direct application of adsorbents in fine powdery form may result in leaching or fast loss of adsorbent. Nano-sized, irregular shape or unstable density of adsorbent will enhance the hydrodynamic pressure drop and/or directly promote obstruction phenomena in the column (Jawad et al., 2017). The complexity will arise once applying in continuous flow systems. For example through the application of adsorption column using activated carbon. Even the treatment ultimately offers positive performances for certain targeted pollutant, nevertheless, from the other side, it also required high budget for the whole treatment and facilities including the installation of the column, the setting up of the piping systems, the positioning valve, etc. Thus, it require more process energy than expected to operate the system with the costs of operation rise up steeply e.g. due to the usage of pump and electric current for treatment operation. Another major cost item including maintenance operations.

Besides, after the treatment, an additional separation process is always needed especially to recover the nano-adsorbent from the treated water, and this has double up the work in a way to finish the treatment and clear the water (Markiewicz, 2016). Otherwise, the adsorbents itself will constitute contamination and defeat the primary purpose of treating toxic dye wastewater. In addition, the separation step between saturated adsorbent and water solution either by sedimentation or filtration could be difficult as well as time consuming and expensive. This segregation step during analysis is also laborious to execute. After all, one of the ways to overcome the above hindrances is by formulating an adsorbent in a form of coating. Also referred as adsorbent coating.

There are several issues that requires critical attention with appropriate assessment related to adsorbent coating in improving the adsorption performance as well as the behaviour of the coating. An adsorbent material consolidated in the form of coating could present lower adsorption capacity due to low accessibility of adsorbate to the surface or internal sites of adsorbent. There are also possibilities of the active sites blockage to the adsorbents by other additives of coating materials. Improving the whole formulation of the coating as the adsorbent will be an appropriate solution to ensure the whole adsorbent coating will play as an effective adsorbent. The role of surface area improvement and modification will also play an important role in improving its percentage removal. Hence, the selection of the major constituents for the formulation of adsorbent coating e.g. the best and functional additive, binder, solvent, surfactant and substrate will be the primary aims of this research study in order to improve the performance and behaviour of the coating.

Synthesizing bi-functionalised adsorbent coating for both cationic and anionic species on one single matrix is highly required to meet the current complexities in treating dyes-related effluent. The content of industrial effluents comprises of anionic, cationic and non-ionic synthetic dyes molecule together with a variety of additives and surfactant. The need for simultaneous active ionic adsorbing (cationic and anionic) sites at one time and accessible diffusion pathways (intraparticle and external diffusion) requires a strong electrostatic interaction and bonding, and high surface area. Therefore, studies on interaction, bonding and improving surface area for adsorbent coating are the crucial elements. The interactions can be different, either by charge interaction, physical adsorption, chemical bonding, van der Walls forces, etc.

Therefore modification of adsorbent with zwiterionic characteristics is highly important in order to show the versatality and good economy of adsorbent itself.

The sorbent with surface coating requires an optimized chemical and physical stability to be strongly adhere to the targetted support materials. This is to prevent peel off of the adsorbent from the substrate during the adsorption process. Otherwise, the consequences will be worst if the adsorbent itself creating pollution for the treated water. Furthermore, harsh condition of effluent and treatment plant should also be highlighted, especially in terms of thermal stuations (high temperature) and pH level. The chemical tolerance towards strong acid/alkali is desired to be deliberated throughout the synthesis and evaluation of the formulation of adsorbent coating so that it can stay attached at any condition or up to certain extend. Besides, the durability of adsorbent at various ranges of temperature, pH, in broad types of pollutants and reusability should also be encountered.

In addition, the effective definition of novel adsorbents require the identification of the most suitable adsorption equilibrium correlation that can predict the adsorption mechanism pathway, provide an accurate esteem of the adsorption capacity, help to understand surface adsorption properties and, last but not least, be an effective modelling tool for the design of the adsorption system. The equilibrium relationship, mostly known as adsorption isotherms, is a graphical representation of q_e vs C_e that indicates how the adsorption molecules distribute or spread between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state (Foo and Hameed, 2010; Largitte and Pasquier, 2016). Hereby, adsorption isotherm models are useful to provide valuable information for predicting adsorption capacities, process optimization and scalability as well in an overall evaluation of the convenience of the adsorption process as an unit operation (Foo and Hameed, 2010; Largitte and Pasquier, 2016; Shujun et al., 2018).

Herein, this study is aimed at synthesizing and preparing adsorbent coating with amphoteric functionality that can give adsorption sites to remove various kinds of ionic dyes especially that having electrostatic interaction based on ionization and bonding sites. The study will provide fundamental information or data at different angle of adsorption concept with different engineeration of adsorbent form. This is forecasted to be very economical and easily accepted by industries since it's able to face the typical complexity of industrial effluents. Hence, the proposed methodology will be beneficial for utilizing zwitterionic adsorbent coating as an adsorbent for dyes elimination. The adsorbent coating will further refer as ZwitAd in this research study.

1.8 Research objectives

The aim of the research is to develop an adsorbent coating with zwitterionic functionality for adsorption of cationic and anionic dyes from aqueous solution. Therefore, the aim of the research is achieve via the following objectives to:

1. Examine the characteristic of binder, surfactant, solvent and substrate, as well as screen and select the best additive for ZwitAd formulation.
2. Formulate a facile method for the development of ZwitAd to eliminate both cationic and anionic dyes based on preparation condition such as formulation ratio and removal efficiency, as well as determination of its chemical and physical properties.
3. Evaluate the operational performance of ZwitAd based on initial dye concentration, time and temperature, initial pH, ionic strength, adsorption on another types of adsorbates and effect on reusability studies for cationic and anionic dyes.
4. Determine the adsorbent coating-dyes interaction based on mechanism, kinetic, isotherm and thermodynamic of the adsorption process.

1.9 Research scope

The scope of this work covers the development and formulation of ZwitAd aiming to remove two types of dyes; cationic and anionic dyes from aqueous solution. The research work consisted of four major investigation sequences. There are consisted of (1) analysis the characteristics of substrate, binder, surfactant and select the best additive for the preparation of zwitterionic adsorbent coating. (2) The research then followed by deep exploration of obtaining the final formulation ratio and maximum performance of adsorption for both types of colour to be remove; (3) the characterization and stability testing of ZwitAd; (4) identification of ZwitAd performance through batch adsorption study; and the last section was (5) the adsorption interaction on equilibrium, kinetic and thermodynamic studies.

The characterization of the adsorbent coating include the adsorbent morphology, pore structure and bonding characteristic were performed with the aid of different analytical instrument such as Scanning Electron Microscope (SEM), elemental analysis (EDX), zeta potential, X-ray Fluorescence (XRF), viscometer and Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR). The physical performance of ZwitAd such as thermal, mechanical and chemical stability were also performed accordingly in this scope.

The adsorption experiment will focus on investigating various study effects by varying the parameters of adsorbate concentration (10 mg/L-250 mg/L), solution temperature (30 °C, 40 °C, 50 °C, 60 °C and 70 °C), solution pH (pH 3, pH 5, pH 7, pH 9 and pH 11) as well as the effect of adsorbent dosages, ionic strength, coating on various substrates, recycle studies, adsorption of others pollutants and tested on real wastewater from river.

Langmuir, Freundlich, and Temkin models, pseudo-first-order and pseudo-second-order, will be applied to analyse the equilibrium and kinetics of the adsorption process. Gibbs free energy, enthalpy and entropy parameters will be determined to evaluate thermodynamics influence on the adsorption process.

1.10 Organisation of the thesis

The thesis is alienated into five (5) chapters in addition to references, appendix and journal publications to provide sequential finding and overview of the entire research. Each chapter epitomises an important knowledge for complete structure of the thesis.

Chapter One (Introduction) presents a general background on water pollution caused by textile industry especially in Malaysia as well as their challenges faced to meet the DOE requirement. The conventional treatment of coloured wastewater also been emphasized in terms of its advantage and disadvantages. An adsorbent coating with zwitterionic functionalities as a new product and approach for wastewater treatment was introduced in this chapter to give a general view and understanding. The statement of the research problem, research objectives, scope of the study and organization of the thesis are précised in this chapter.

Chapter Two (Literature Review) gives the retrospective view of the necessary and important literatures from previous studies and various researchers. The related literature covers major wastewater treatment techniques for textile effluent with emphasis on conventional dyes removal as well as environmental health issues related to dye exposure. Beside, brief clarification on the theory of adsorption process including adsorption mechanism, adsorption types and adsorbent used. The backbone of the research highlighted on adsorbent coating combined amphoteric characteristics and its importance with detailed classification of it basic ingredients were also been sorting and investigated briefly from previous researchers. In addition, the added literature regarding cotton cloth and its diversified application also included. The final section in this chapter presents an overview regarding analysis of equilibrium and adsorption isotherms, kinetics and thermodynamics in brief.

Chapter Three (Research Methodology) covers the experimental and methodology applied throughout the research study. This section outlines the summary of research activities schematically presented in the process flow diagram. The chemicals and materials, description of adsorption study equipment and samples characterization techniques are presented in details. It also clearly structured the experimental procedure for the preparation of ZwitAd incorporated with the method for batch experimental study.

Chapter Four (Result and Discussions) as an innermost part of research finding represents the collated results obtained in the experimental sections, interprets and discussed the results in a systematic manner. The detailed synthesis of ZwitAd formulation, characterization and performance evaluation of the prepared adsorbents were further discussed comprehensively. In addition, the analysis of adsorption isotherms, kinetics, thermodynamics and mechanism of the adsorption process were briefly elaborated. All the presented results were then compared with the literatures for a strong justification and validation.

Chapter 5 (Conclusion and Recommendation) presents the conclusions derived from this research with few recommendations for consideration and improvement in future. Finally, the thesis contains list of references and appendices, together with list of published journals and book chapter, conferences, awards and recognition emanating from this research.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This section presents a general overview of related literature relevant to this study. The literature review covers dyes removal treatment with emphasis on adsorption using composite adsorbent coating and more specifically on clay based materials as adsorbent. Some discussion on a new approach of adsorbent coating as an adsorbent for dyes removal is presented. A review on the various parameters that affect and influence the adsorption process were also included. The basic principles and analysis of adsorption experimental data in-terms of isotherm, kinetics, mechanism and thermodynamic were also highlighted. Meanwhile, the theory behind the study is presented in this section.

2.2 Processing in textile industries

Clothes are the rudimentary and essential necessities for human being. Hence, indirectly it forced the textile industries to be amongst the major contributors to the nation's economy in order to fulfil the demands. This industry is water, energy, and chemical –intensive, where most of them utilized for wet processing method. The wet processing involved in various steps including washing, rinsing and drying the textiles. Subsequently, wastewater is generated with a highly variable mixture of contaminants that must be treated prior to disposal. The contaminants might saturated with dyes/colorants, detergents, bleaches, organic compounds, stabilizing agents, inorganic salts, heavy metals and etc. (Siddique et al., 2017). Surprisingly, approximately 93 % of the water intake at early stage of operation comes out as coloured wastewater with high concentration of dyes, organic compounds and heavy metal (Gupta et al., 2015).

2.3 Dyes: functions, structure and issues

Dyes are organic compounds used as a coloring agent to impart various colours to other substances (Adeyemo et al., 2017; Almasian et al., 2016). Presently, most dyes are artificially manufactured and known as synthetic dyes, which have replaced natural dyes due to their low cost and variation in colours. Dyes have a wide range of applications and extensively used in various fields; textiles industry, food technology industry, leather tanning industry, wools, fibres and fabric industry, pharmaceutical industry, rubber, plastic industry as well as in cosmetic and printing industry (Adeyemo et al., 2017; Nidheesh et al., 2018; Srinivasan et al., 2007). Dyes molecules contain highly complex aromatic structure (aromatic ring) which make them more stable, slightly slow to biodegrade as well as more resistant to light, heat and an oxidizing agent (Ngah et al., 2011; Ziane et al., 2018). These characteristic are highly looked-for in industries since they attribute high colour intensity and unease to fade away by time (Ngulube et al., 2017).

Dyes are classified into anionic (direct, acid and reactive dyes), cationic (all basic dyes), and non-ionic (disperse and vat dyes) (Zhihui et al., 2017). The compound of dyes can adsorb light with wavelengths in the visible range (400 to 700) nm (Jadhav and Phugare, 2012). The chemical structure of some important simulated synthetic dyes which have been frequently employed in adsorption study shown in Figure 2.1. They are Crystal Violet, Rhodamine B, Congo red, Methylene blue, Reactive Black 5, Brilliant Green, Amido Black 10B, Amaranth and etc.

In diverse classes of dyes, metal ions are used in the form of textile colorants. The metal contents in most of dyes consisted of copper, lead, zinc, chromium and cobalt. Releasing of these metals may cause negative influences or threats to human health and environment. Many hostile by the intake of dyes as some may mutagens and carcinogens, xenobiotic in nature and aerobically recalcitrant to biodegradation (Ngulube et al., 2017; Pang and Abdullah, 2013).

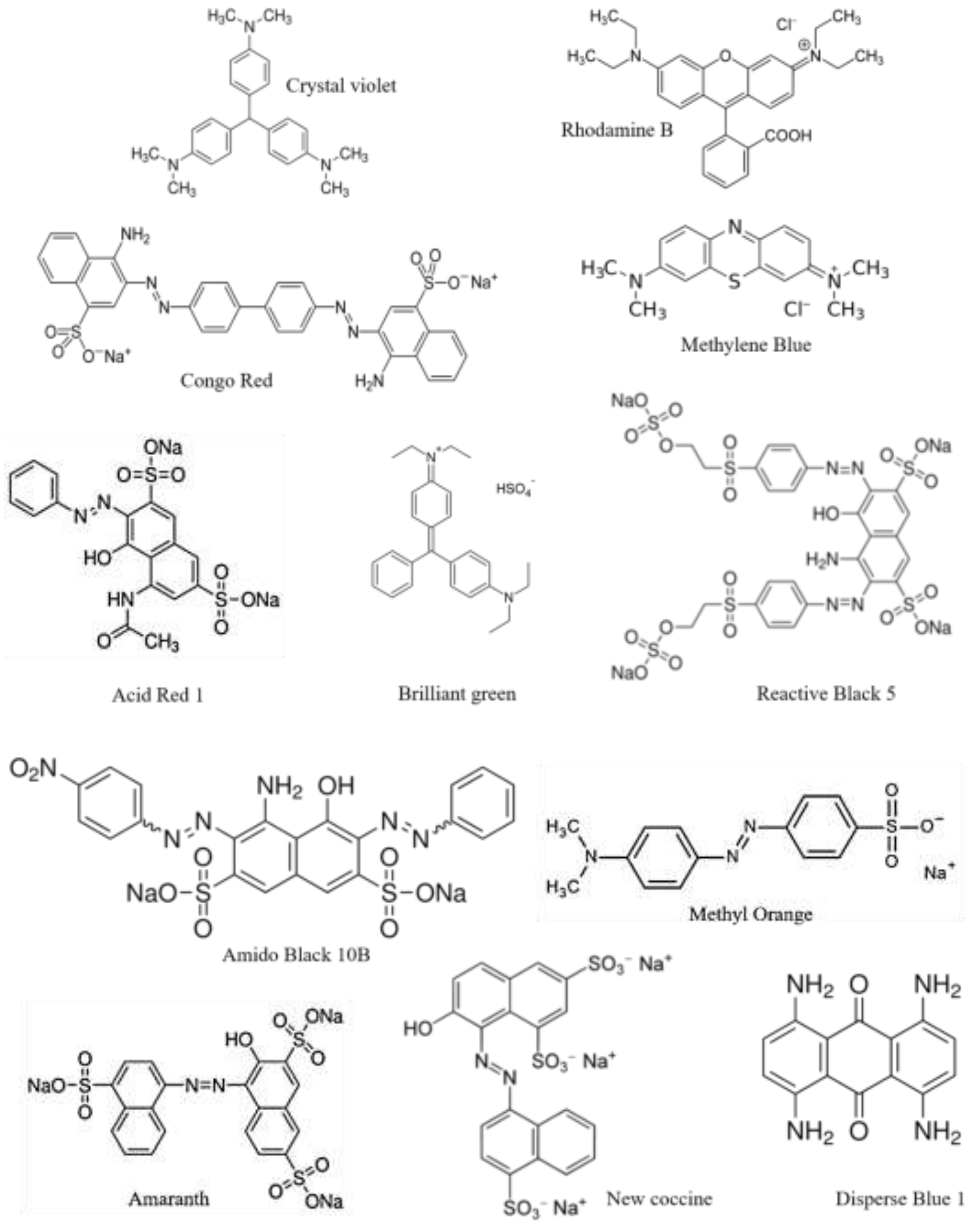

Figure 2.1 Chemical structure of synthetic dyes most frequently used in adsorption study

The environmental issues being a continuous problem for dyes industry, water treatment companies and environmental engineers. They being forced by the regulatory department to increase the quality of water by reducing the level of colour in wastewaters. Discharging of dye from various industries in water resources (sea, lake, river) enforces treat to the surroundings and ecosystem causing toxicity in aquatic organisms, chunk sunlight penetration, thereby obstructing photosynthesis activity and dissolved oxygen (DO) (Hajati et al., 2014; Solomon et al., 2013; Vakili et al., 2014). Therefore, it is important to remove environmental pollutants up to a permissible limit from dye-containing industrial effluent before releasing them into water bodies.

2.4 Current technology for the treatment of dye effluent

Research has been conducted since long to treat textile wastewater in an economical and efficient way (Crini and Lichtfouse, 2019). There are many processes for the removal of polluted compounds from water included combination of physical, chemical, physicochemical or/and biological treatment processes. At the present time, there are no single method capable of adequate treatment due to complex nature of industrial effluent. In practice, a combine method is often applied to achieve a desired water quality in the most economical way. The treatments techniques include adsorption, osmosis, membrane filtration, ion-exchange, coagulation/flocculation, electrochemical oxidation, biodegradation and advance oxidation. And, those mentioned techniques have been categorized into conventional methods, established removal method and emerging process which resulted in the recovery of various kind of dyes pollutant (Crini and Lichtfouse, 2019), as listed in Table 2.1.

However, each techniques has its own constrain and faced certain technical and economical limitations. Their advantages and disadvantages of each treatments have been extensively reviewed by (Crini and Lichtfouse, 2019; Forgacs et al., 2004;

Nidheesh et al., 2018; Yagub et al., 2014). Most of the constrain usually suffers from their high cost in terms of excessive chemical used and expensive reagents, low efficiency, long processing period, less flexible in operation and design, unable to remove wide ranges of dyes and creating secondary pollutants. Of all these methods, adsorption renowned as a potential technology for colour removal from wastewater. Justifications and recommendations regarding adsorption is detailing in next subsection.

Table 2.1 Existing technologies and treatment methods for dye treatment from wastewaters

Technologies	Treatment methods	References
Conventional treatment	Coagulation/flocculation	(Shankar et al., 2019)
	Adsorption/Precipitation	(Yong-Woon et al., 2019)
	Adsorption on activated carbon	(Gu et al., 2019)
	Electrocoagulation/ electroflotation	(Nippatla and Philip, 2019)
	Biodegradation	(Sreedharan et al., 2019)
Established recovery removal	Fenton Oxidation	(Bello et al., 2019)
	Membrane separation	(Wensong et al., 2019)
	Electrochemical treatment	(Santos et al., 2019)
	Ion-exchange	(Kaur and Jindal, 2019)
	Solvent extraction	(Abdul et al., 2019)
Emerging recovery method	Advanced oxidation	(Kadam et al., 2018)
	Selective bioadsorption	(Wei et al., 2019)
	Biosorption/biomass	(Grassi et al., 2019)

2.5 Adsorption of dyes

Adsorption is acknowledge as one of the chosen wastewater treatment methods for dye removal over other conservative approaches (Aljeboree et al., 2017; Ghaedi et al., 2012; Jing et al., 2019). Wide application of adsorption in terms of removal of textile pollutants from wastewater is due to its low initial capital, operating cost, and availability of low cost adsorbents which can be easily obtained from the surroundings.

A superlative adsorbents for dyes adsorption should be consisting of following properties; large surface area which contributes to higher adsorption capacity, suitable pore size, easy accessibility, economic, mechanically stable, compatibility, regeneration capacity, eco-friendly, high selectivity, and less of processing procedures (Crini, 2006; Tan et al., 2015; Vakili et al., 2014). Hence, a number of adsorbents including natural and modified clay (Adeyemo et al., 2017; Javad et al., 2017; Toor and Jin, 2012), activated carbon (Ab et al., 2017; Ndagijimana et al., 2019; Noorimotlagh et al., 2018), modified agricultural by-product, resin (Naushad et al., 2016), polymeric sorbent (Popescu and Suflet, 2016), industrial by-product/waste as well as chitosan (Qi et al., 2015; Umma et al., 2016a) based adsorbent were simulated and execute in order to remove the colouring agents.

Roughly, since 1996 to 2020, there are 79,727 of articles regarding dye adsorption have been figured out from Science Direct search engine using "dye adsorption" keyword (data access on 28th March 2019). According to bar graph in Figure 2.2, the quantity of publications keep increased year by year with the highest numbers of 9,385 in 2018. Extracting from that, there are innumerable types of adsorbents from natural, modified, and synthesizing materials which been extensively studied, developed and figured out by researchers. Besides, the dyes used as adsorbate coming majorly from synthetic dyes. Therefore, based on published data, studies on adsorption have generated global interest by scientists or researchers, which reflected in a significant increased on this topic. They have explored and developed myriad of a novel and effective adsorbents from various chemicals and materials in order to cater the wastewater treatment problems notably for dyes pollution.

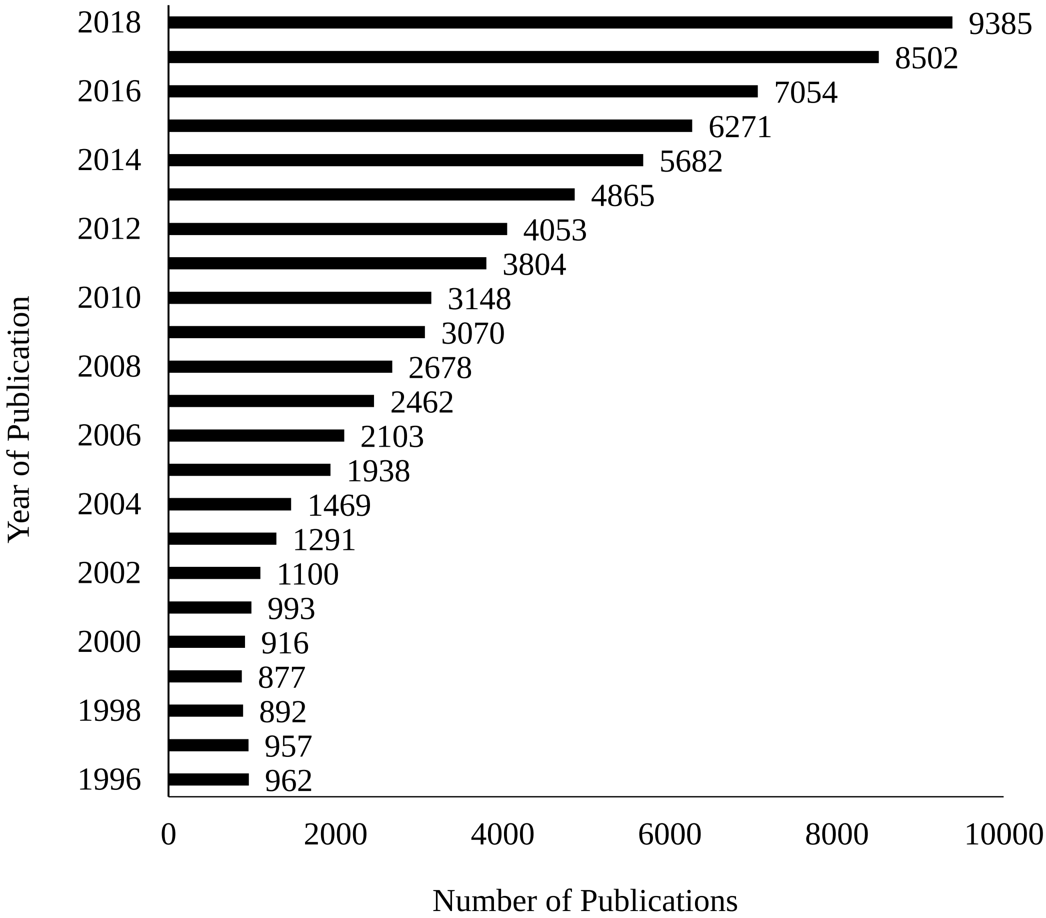

Figure 2.2 Number of publications listed by Science Direct on 28th March 2019 specifying "dye adsorption" as the keyword plotted against the publication year

A new and novel adsorbent which currently been investigated and start to raise an attention is on adsorbent coating studies. Applying similar concept of adsorption where basically to function as dyes removal, the form was improvised in terms of flexibility for the application process in wastewater treatment plant. The fundamental studies is crucial as it serves as a feeder for another stage of study in developing a pollution prevention system that does not require any new facilities or special equipment but only rely on a small modifications of the existing industrial facilities. This is an exploratory step in finding new approach of adsorption application by providing fundamental results from different angle of adsorption concept. Deeper understanding concerning adsorbent coating has been discussed further in Section 2.6.

Thereby, in recent years (2014-2019), there has been an increasing amount of work associated to adsorbent coating (Figure 2.3). This signifies that the research topic start gaining an attention and interest from researchers due to their promising characteristics, excellent performance and flexible in terms of application wise. Their researches were vast with various adsorbent synthesis methods for specific targeted pollutants, diversified substrate used, many types of binder applied, few method of coatings performed with excellent removal result. Nonetheless, the excellent removal can be achieved only if the adsorbent having potential to adsorb at its maximum type of dyes.

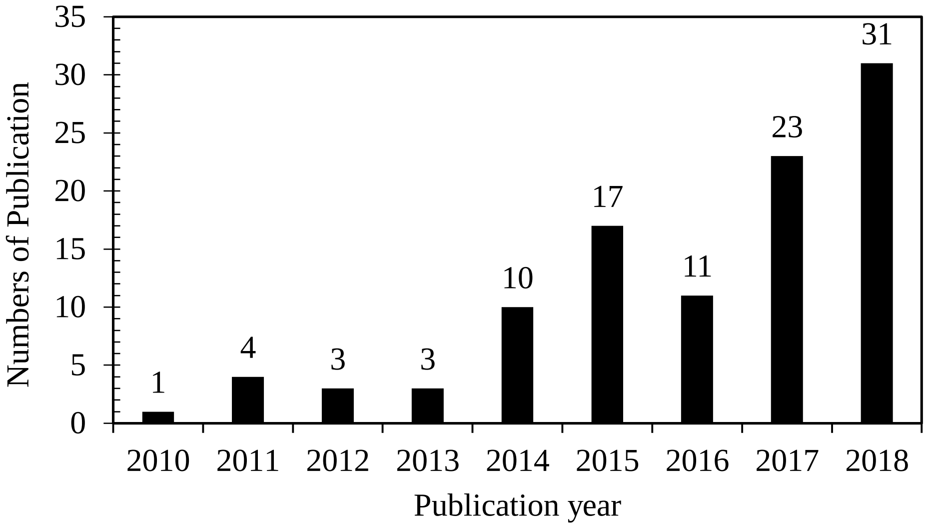

Figure 2.3 Publication numbers of adsorbent coating through 10 years studies

2.6 Introduction to adsorbent coating

Coating from English Cambridge Dictionary is defined as a layer of a particular substance that covers a surface. Another meaning is a thin layer or covering of something. According to Collins English Dictionary, a coating is a layer spread over a surface, for protection or decorative purposes. Coating can be varied in application such as for steel corrosion protection, resistance for garments and cloths, as thermal barriers insulation, aesthetics, self-cleaning coating, antifouling (synthesizing membrane, painting, undersides of boats), foundry etc. Nevertheless, the current study has open up a new approach of coating where it pay an attention on wastewater treatment, specifically in adsorption process. Adsorption that utilized adsorbent to adsorb particle of pollutants are modified, synthesized and developed in a layer format, entitled as adsorbent coating. Adsorbent coating, or in another term can be recognized as adsorbent laminating, adsorbent layer, immobilized adsorbent, or adsorbent film.

The fundamental definition of adsorbent coating that are highlighted in this study is an adsorbent (a material to adhere the adsorbate) in any form (liquid, solid, slurry, particles) been layered or contacted the surface of the inert substrate. The adsorbent optionally been modified with binder/adhesive to facilitate the adherence between adsorbent and substrate. The layered adsorbent-substrate then go through drying/heating procedure to form hardened surfaces, then producing adsorbent coating. It is aimed to have an excellent adsorption property over pelleted or beaded adsorbents as well as excellent physical and mechanical properties. Besides, in our definition of adsorbent coating, an adsorbent that perform as film form without underlying on substrates are also included. It stands on its own, as a film or sheet. The composite is targeted to have a variety of end user applications particularly in adsorption processes for separating molecular species from aqueous solution such as dyes, heavy metals, antibiotic etc.

For few reasons, adsorption study has been discovered at a different concept by applying adsorbent coating. It is desirable to have the solid adsorbent deposited on a substrate as a coating instead of being contained in particulate form as pellets, beads, flakes, particles, powder etc. As reflected by one of the Patent publications from Dunne and Begun (1994), there are attractive and innovative reasons why solid adsorbent coating suggested to be used. First, to improve the adsorption properties of the solid adsorbents by improving the surface area to weight ratio. The coating can be layered