REMOVAL OF CONGO RED AND REACTIVE BLACK 5 DYES FROM AQUEOUS SOLUTION USING POLYETHYLENIMINE-MODIFIED COFFEE WASTE ADSORBENT

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"My dearest mak, ayah, family, and friends"

This is for all of you

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ABSTRACT

The industrial wastewater especially from textiles industry contain high concentration of dyes that could bring adverse health effect to the human and aquatic life. In past researches, it has been shown that coffee waste is a potential adsorbent for cationic dye in comparison to anionic dye. Thus, in this study, polyethylenimine-modified coffee waste (PEI-CW) was synthesized through crosslinking reaction to evaluate its use as a potential adsorbent in removal of hazardous anionic Congo Red (CR) and Reactive Black 5 (RB5) dyes from aqueous solution. The type of characterizations that were conducted on the adsorbent are FTIR, BET, BJH and XRD analysis. The presence of substantial amine group on PEI-CW was confirmed through FTIR analysis. The BET and BJH analysis showed a decrement in surface area and total pore volume of CW along with an increase in pore diameter after modification with PEI. The XRD analysis showed there is no obvious difference in crystalline structure of CW after being modified with PEI. Through batch adsorption experiment, PEI-CW has been proven to be a potential adsorbent due to 99% removal of 50 mg/L CR and RB5 dye from aqueous solution. The optimum parameter for CR dye aqueous solution is 60°C, pH 3, 0.1 g PEI-CW and 120 minutes. Whereas, for RB5 dye adsorption, the optimum parameter is 25 °C, pH 7, 0.1 g PEI-CW and 60 minutes. Model-fitting study showed Langmuir adsorption isotherm and pseudo-second order kinetic model as a better fit for both CR and RB5 dyes adsorption process. From Langmuir model, the maximum adsorption capacity was found to be higher for RB5 dye adsorption, which is at 77.5194 mg/g compared to 34.3543 mg/g for CR dye. The thermodynamic analysis suggested that both CR and RB5 dyes adsorption process is physisorption, spontaneous and endothermic in nature. From this study, it is inferred that PEI-CW could be potential low-cost adsorbent in removal of anionic CR and RB5 dyes from the aqueous solution, although higher adsorption is observed towards RB5 than CR dyes.

ABSTRAK

Air kumbahan perindustrian terutamanya dari industri tekstil mengandungi pewarna berkepekatan tinggi yang mendatangkan kesan kesihatan yang buruk kepada kehidupan manusia dan akuatik. Dalam penyelidikan masa lalu, ia telah menunjukkan bahawa sisa kopi adalah penyerap berpotensi untuk pewarna kationik berbanding dengan pewarna anionik. Dalam kajian ini, sisa kopi *polyethylenimine*-terubahsuai (PEI-CW) telah disediakan melalui reaksi paut silang bagi menilai kegunaannya sebagai penyerap berpotensi dalam penyingkiran pewarna anionik *Congo Red* (CR) dan *Reactive Black 5* (RB5) yang berbahaya daripada larutan akueus. Kewujudan kumpulan *amine* pada PEI-CW dapat disahkan melalui analisis FTIR. Analisis BET dan BJH menunjukkan pengurangan dalam luas permukaan dan jumlah isipadu liang CW serta peningkatan dalam garis pusat liang selepas pengubahsuaian dengan PEI. Analisis XRD menunjukkan tiada perbezaan jelas dalam struktur kristal CW selepas diubahsuai dengan PEI. Melalui eksperimen penyerapan berkumpulan, PEI-CW telah dibuktikan sebagai penyerap berpotensi kerana 99% penyingkiran 50mg/L pewarna CR dan RB5. Parameter optimum bagi penyerapan pewarna CR adalah 60°C, pH 3, 0.1 g PEI-CW dan 120 minit. Bagi penyerapan pewarna RB5 pula, parameter optimum adalah 25 °C, pH 7, 0.1g PEI-CW dan 60 minit. Kajian *model-fitting* menunjukkan model penyerapan isoterma *Langmuir* dan model kinetik *pseudo-second-order* sesuai unuk proses penyerapan kedua-dua pewarna CR dan RB5. Daripada model Langmuir, kapasiti penyerapan maksimum didapati lebih tinggi untuk penyerapan pewarna RB5, iaitu pada 77.5194 mg/g berbanding dengan pewarna CR, iaitu pada 34.3543 mg/g. Analisis termodinamik mencadangkan bahawa kedua-dua proses penyerapan pewarna CR dan RB5 adalah *physisorption*, *spontaneous*, dan *endothermic*. Daripada kajian ini, disimpulkan bahawa PEI-CW adalan penyerap berpotensi berkos rendah dalam penyingkiran pewarna anionik CR dan RB5 daripada larutan akueus, walaupun ia lebih cenderung kepada pewarna RB5 daripada pewarna CR.

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LIST OF ABBREVIATIONS

CW	-	Coffee waste
PEI	-	Polyethylenimine
PEI-CW	-	Polyethylenimine-modified coffee waste
CR	-	Congo Red
RB5	-	Reactive Black 5
FTIR	-	Fourier Transform Infrared Spectroscopy
BET	-	Brunauer, Emmett and Teller
BJH	-	Brunauer, Joyner and Halenda
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

q_e	-	Adsorption capacity at equilibrium time
q_t	-	Adsorption capacity at instant time
q_m	-	Maximum adsorption capacity
t	-	Time
C_e	-	Equilibrium dye concentration in solution
C_o	-	Initial dye concentration
C_i	-	Dye concentration at instant time
K_a	-	Isotherm constant for Langmuir
K_f	-	Capacity of adsorbent constant for Freundlich
n	-	Intensity of adsorption constant for Freundlich
k_1	-	Kinetic rate constant for pseudo-first-order model
k_2	-	Kinetic rate constant for pseudo-second-order model
R^2	-	Linear relation regression coefficient
ε %	-	Percentage error
ΔG^o	-	Change in gibbs free energy
ΔS^o	-	Change in entropy
ΔH^o	-	Change in enthalphy

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CHAPTER 1

INTRODUCTION

1.1 Background Study

Water pollution is a major environmental concern that is caused by pollutants that are discharged to water stream from sources with inadequate water treatments. Industrial wastewater is apparently one of the main sources that released these harmful compounds, also known as pollutants. There are many types of pollutants that originate from industrial wastewater effluents and one of them is dye. Dyes are extensively utilised in different type of industries which includes textile, leather, plastics and rubbers, food processing, wood, photography and pigments industry. As a result of its wide usage, approximately 5,000 to 10,000 tonnes of dyes are released into water streams annually (Pirkarami and Olya, 2014; Yagub *et al.*, 2014). The high concentration of dyes existing in industrial water is a troubling issue as dye can cause several health effects to human and aquatic life.

Anionic dye is one of the types of dye that can cause severe environmental concern. This group of dyes is water-soluble and carries negative-charge in their molecule. Congo red (CR) and Reactive Black 5 (RB5) belong to this anionic dye group that are widely used in industries such as textile, food, pharmaceutical, printing and paper manufacturing industries. These dyes are considered toxic and harmful as it can cause several health effects to human and aquatic life due to it being carcinogenic, teratogenic and mutagenic. In addition to that, it can also lead to a decrease in sunlight penetration for photosynthesis process in aquatic life because of its recalcitrance property (Shen and Gondal, 2013).

Various low-cost materials especially natural or wasted materials have been extensively explored for adsorption removal of dyes from aqueous solution. Coffee waste is one of the available adsorbent that can be used to remove dyes by adsorption. Coffee is known as one of the beverage that is heavily consumed with annual worldwide consumption of 8.8million metric tonnes (Jang *et al.*, 2015). The large consumption of coffee leads to a significant amounts of coffee waste being generated. Therefore, an efficient utilization of coffee wastes has been gaining considerable attention. In the effort of using coffee waste as removal of dye, impressive sorption ability is shown for cationic dye (which is a positively-charged dye) compared to anionic dye groups (Lafi and Hafiane, 2016)

For improving the affinity of a material to anionic dye, various cationic surface modifications have been explored and studied. Polyethylenimine (PEI) is a relatively cheap cationic polymer that can be used for surface modification of an adsorbent. It has been proven in previous researches that it has the capability to enhance the removal anionic pollutant such as anionic metals and dyes (Deng and Ting, 2005; Won *et al.*, 2011). This polymer can readily bind with anionic substrate. Therefore, with the surface modification of coffee waste, adsorption of dyes using coffee waste can be widely implemented in industries in the future to remove various classes of dyes from wastewater.

1.2 Problem Statements

The industrial wastewater especially from textiles industry contains high concentration of dyes. Substantial amount of dyes presented in wastewater are required to be removed before being discharged to the environment due to it being carcinogenic, mutagenic and teratogenic in nature. It is vital that an alternative material which is cost-effective as well as abundant is used as the adsorbent for dye removal from wastewater to replace the expensive commercial activated carbon that is used in industry nowadays (Yagub *et al.*, 2014). Coffee waste which is regarded as an inexpensive and abundant material left from the extraction process of instant coffee manufacturing and the final residues originated from cafeteria could act as a promising adsorbent for dye removal (Lafi *et al.*, 2014). The surface of coffee waste consist of functional groups such as carboxyl and hydroxyl group which could aid in the adsorption of dyes. However though, the anionic dyes uptake of coffee waste is still considered quite low (Namane *et al.*, 2005; Safarik *et al.*, 2012; Lafi and Hafiane, 2016). Hence, to enhance the removal efficiency of anionic dyes for coffee waste adsorbent, there must be a surface modification on the coffee waste. Polyethylenimine (PEI) is a cationic polymer that is proved to be exemplary in its surface modification role for the removal of anionic pollutant such as anionic metals and dyes (Deng and Ting, 2005; Low *et al.*, 2008; Won *et al.*, 2011; Sadaf *et el.*, 2014). This is due to the significant amount of positively charged amine groups from PEI introduced to the surface of adsorbent in which it can readily bind to anionic substrate. Therefore, coffee waste modified with PEI could be used as a potential adsorbent for anionic dye removal from aqueous solution.

1.3 Objectives

The objectives of this research are:

i) To synthesize and characterize polyethylenimine-modified coffee waste (PEI-CW) as the adsorbent for Congo Red (CR) and Reactive Black 5 (RB5) dye removal.

ii) To investigate the effect of the physicochemical parameters such as contact time, initial dye concentration, temperature, solution pH, and adsorbent dosage on the dye adsorption performance of polyethylenimine-modified coffee waste (PEI-CW).

iii) To study the adsorption behaviour of polyethylenimine-modified coffee waste (PEI-CW) using isotherm, kinetic, and thermodynamic analysis.

1.4 Scope of study

In this study, the preparation of polyethylenimine-modified coffee-waste (PEI-CW) adsorbent was carried out through crosslinking reactions of coffee waste with polyethylenimine (PEI). Moreover, the type of characterizations that was conducted on the adsorbent were Fourier Transform Infrared Spectroscopy (FTIR) analysis, Brunauer, Emmett and Teller (BET) and Barrett-Joyner-Halenda (BJH) analysis, and X-Ray Diffraction (XRD) analysis.

Furthermore, the Congo Red (CR) and Reactive Black 5 (RB5) dyes adsorption study was done under various parameters which are contact time, initial dye concentration, temperature, solution pH and adsorbent dosage. For initial dye concentration, the adsorption process was conducted with initial dye concentration between 50 mg/L to 100 mg/L. As for operational temperature, the adsorption study was conducted in the range of 25°C to 60°C. Moreover, the range of the solution pH that the adsorption study was carried out is in the range of pH 3 to pH 9. Also, the adsorbent dosage that was used in this study is in the range of 0.1 to 1.0 g. Lastly, the adsorption behavior of adsorbents for this research was studied using adsorption isotherm and kinetic models, as well as thermodynamic analysis.

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