Chemical Regeneration of Modified Magnetic-PEI-Cellulose Adsorbent for Removal of Anionic Reactive Black 5 Dyes

Abu Hassan Nordin, Norzita Ngadi Zurina Mohamad, Mazura Jusoh, Agus Arsad

Abstract: Adsorption process has been heavily used to remove pollutants from waters and wastewaters. However, the economical competitiveness of the adsorption process depends upon the reusability of exhausted adsorbent. This study investigated the chemical regeneration of magnetic-PEI-cellulose adsorbent presaturated with dyestuffs by using two different regenerants which are hydrochloric acids (HCl) and sodium hydroxide bases (NaOH) using batch experiments. The magnetic-PEI-cellulose adsorbent was synthesized by using crosslinking method. Adsorption experiment was conducted to remove a constant 0.1 g/L of anionic reactive black 5 (RB5) dyes and desorption experiment was conducted by regenerating dye loaded adsorbent using HCl and NaOH regenerants at 0.1, 1.0 and 5.0 mol L-1. From the batch desorption test results, 5 mol L-1 of HCl was found to be the optimal regenerant for the RB5 dyes. A higher concentration of acidic regenerant could improve the dye adsorption efficiencies up to 4 times of cycles with adsorption efficiency (74.9%). Meanwhile, basic regenerant has low capability to desorb RB5 dyes and the lower concentration of NaOH (0.1 mol L-1) showed better adsorption performance after 4 times of cycles with adsorption efficiency (1.9%). Therefore, acidic regenerant indicates better results to be used as to desorb RB5 dyes from magnetic-PEI-cellulose adsorbent.

***Index Terms*: Keywords: Low-Cost, Adsorption, Adsorption Efficiency, Desorption, Dye Wastewater, Regenerants.**

I. INTRODUCTION

Textile industry discharges effluent with high content of suspended solids, dissolved organic substances, and color that pollute natural water sources. In response to this, more stringent regulations to preserve the environments have been adopted, thus, requiring textile industry players to improve existing dye effluent treatment processes that adhere to regulations. Among the dye effluent treatment processes, adsorption process promises great economic benefits to textile industry, attributed to high efficiency and inexpensive treatment cost. Adsorption relies on the source and adsorbent properties. In dye effluent color removal, adsorbents constituted of conventional activated carbon have been heavily utilised in the adsorption of dye molecules. Despite this, these conventional adsorbents are highly costly and require complex processes in regenerating depleted activated carbon. In industries, the adsorbent is typically packed in columns which allows adsorption of contaminants to take place as fluids flows through the columns. Adsorption by these columns loses effectiveness once the columns are fully filled with contaminant-saturated adsorbent. Once full adsorption capacity of the adsorbent is reached, the adsorbent must be regenerated or replaced in order to reinstate the capability to adsorb contaminants. Replacement is unfavorable as it involves incinerating exhausted adsorbent, which is seen as detrimental to the environment as well as prohibitive in operating cost for the industry players. Therefore, the process of regenerating adsorbents is favorable as it involves less cost in comparison to adsorbent replacement.

In literature, various techniques have been proposed to regenerate contaminant-saturated adsorbents (1-4). However, these techniques were widely used for desorption of heavy metal ions. Motivated by this, conventional chemical treatment is appealing and merits a reconsideration to regenerate anionic dye loaded adsorbents as it can be done without degrading the structure of the adsorbent when compared with other methods (5). This study aims to investigate the regeneration of magnetic-PEI-cellulose adsorbent that is pre-saturated with dyestuff. The study conducts the regeneration using two regenerants consisting of acid (HCl) and base (NaOH) via batch experiments. The adsorbent is evaluated in terms of pollutant removal and regeneration. This study sheds insights into the effectiveness of regenerating adsorbents in terms of economic reasons and impact on the environment.

II. LITERATURE REVIEW

A. Classification of dyes

Two essential components of dye molecules include colour-producing chromophores and auxochromes which promotes dye affinity onto textiles. The textile industry utilises numerous dyes, including direct dyes, acid dyes,

Revised Manuscript Received on December 22, 2018.

Abu Hassan Nordin, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Johor, Malaysia, norzita@cheme.utm.my
Norzita Ngadi, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Johor, Malaysia
Zurina Mohamad, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Johor, Malaysia
Mazura Jusoh, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Johor, Malaysia
Agus Arsad, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, Johor, Malaysia

reactive dyes, and basic dyes, whereby, most of these dyes are derived from azo derivatives.

Table I : Typical dyes used in textile industry (6).

Dye Class	Description
Reactive	Water-soluble, anionic compounds; largest dye class
Direct	Water-soluble, anionic compounds; can be applied directly to cellulosics without mordants
Basic	Water-soluble, applied in weakly acidic dye baths; very bright dyes
Acid	Water-soluble anionic compounds

B. Low-cost adsorbents for dye removal

Several factors are considered prior to selecting the source materials to be used in developing low-cost adsorbents. The factors include free availability, low-cost, and non-toxic to the environments. In dye removal treatments, numerous cost-effective adsorbents which offer great economic benefits have been utilised, including agricultural and industrial waste products, organic products, and biosorbents. Certain precursors have undergone rigorous laboratory tests and entered the market as commercialised products in dye effluent treatment.

Table II : Different type of low-cost adsorbents (7).

Low-Cost Adsorbent	Source	Characteristics
Chitosan	Crustaceans and fungi	Biocompatible, chemical reactivity, biodegradable, polyelectrolyte nature, non-toxic, chelating property, activity and dyeing improve ability.
Cellulose	Green plants, algae and oomycetes	Biodegradable, hydrophilic, insoluble in water and most organic solvents.
Lignin	Vascular green plants	Biodegradable, and have many functional group such as phenolic, hydroxyl, carboxyl, benzyl alcohol, methoxyl, and aldehyde groups.

C. Regeneration

Regeneration promotes the concept of treating saturated adsorbent through recycling, whereby, desorption of dyes from exhausted adsorbent is carried out to eliminate adsorbed dye content. Various techniques have been proposed in adsorbent regeneration, including oxidative regeneration, super-critical regeneration, bio-regeneration, thermal treatment, microwave irradiation, ultrasonic regeneration, and chemical extraction. Among these regeneration treatments, exhausted adsorbents have been primarily regenerated utilizing chemical and thermal treatments.

Table III : Chemical treatment for regeneration

Adsorbent	Dye	Regenerant	Desorption/ readsorption efficiency (%)	Reference
CA-EFB	Methylene blue	HCl	69.8	(8)
PEI-EFB	Phenol red	HCl	64.2	(8)
MWCNTs	Reactive red M-2BE	NaOH	8.67	(9)
Chitin/graphene oxide	Remazol black	Alkaline solution	60	(10)

III. METHODOLOGY/MATERIALS

A. Materials

The desired regenerants concentrations were obtained from mixing distilled water with regenerants including acid and base solution. The acidic and basic solutions used to prepare the regeneration solutions were 37% HCl (QRec™, Malaysia) and 99% NaOH (QRec™, Malaysia), respectively. Reactive black 5 (Sigma-Aldrich, Malaysia) was used to prepare the synthetic dye wastewater for test.

B. Preparation of Magnetic-PEI-Cellulose Adsorbent

An amount of desired cellulose (5 g) was impregnated into the mixture solution that contain of PEI (2.5 ml) and magnetic nanoparticles (0.625 g) in the water bath for 6 hours at 65°C. Then, 1mL of glutaraldehyde was used as a crosslinker and was added into the mixture solution under vigorous stirring for 1 hour at 27°C. The yield was filtered and rinsed with ethanol and distilled water. The synthesized magnetic-polyethyleneimine-cellulose of Oil Palm Empty Fruit Bunch (OPEFB) was dried in oven at 65°C until the constant weight was obtained.

C. Adsorption-Desorption Experiment.

Briefly, adsorption experiment was carried out by adding 0.1 g of magnetic-PEI-cellulose adsorbent into a 50 ml of 0.1 g/L dye solution at pH7 while shaking at 200 rpm for 180 min at 27 °C. Then, the 0.1 g dye loaded adsorbent was separated and filtered from dye solutions before treated with 100 mL HCl and NaOH at different concentrations (0.1M, 1M, and 5M) for 30 min at 27°C and 200 rpm. The filtrated adsorbents were collected and washed with distilled water to reach neutral before it was dried in the oven until constant weight was obtained. Meanwhile, the filtrated dye solutions were measured to calculate the adsorption efficiency of adsorbent after undergoes desorption process by regenerants. The adsorption efficiency (AE) was then calculated by the following equation:

$$AE\% = \frac{A_0 - A_d}{A_0} \times 100$$

where A0 and Ad are the initial dye concentration and final dye concentration after adsorption, respectively. This adsorption-desorption experiments were repeated for four cycles.

IV. RESULTS AND FINDINGS

In order to investigate the regeneration and reusability cycles of magnetic-PEI-cellulose adsorbent, adsorption-desorption experiments were conducted for four cycles by treating dye loaded adsorbent using two regenerants; HCl and NaOH, at different concentrations (0.1, 1.0, and 5.0 mol L^{-1}). Referring to Fig. 1-3, the results showed that the higher the concentration of HCl solution (5 mol L^{-1}) used to desorb loaded dye, the better are the results in adsorption efficiency across four consecutive cycles. Specifically, in the first, second, third, and fourth adsorption-desorption cycle, the adsorption efficiency obtained was 100%, 85.1%, 76.2%, and 74.9%, respectively. However, the adsorption efficiency decreased as the HCl solution concentration was decreased to 1.0 mol L^{-1} (consequent adsorption efficiency: 100% (first cycle), 76.7% (second cycle), 58.8% (third cycle), and 41.9% (fourth cycle)) and 0.1 mol L^{-1} (consequent adsorption efficiency: 94.9% (first cycle), 53.7% (second cycle), 36.4% (third cycle), and 34.7% (fourth cycle)).

Meanwhile, for NaOH solution, the lower the concentration of the basic solution (0.1 mol L^{-1}) used for desorption, the better are the results in adsorption efficiency. The efficiency of adsorption obtained are as following: 49.4% (first cycle), 29.6% (second cycle), 22.1% (third cycle), and 1.9% (fourth cycle). On the other hand, further increase of NaOH solution concentrations to 1.0 mol L^{-1} and 5.0 mol L^{-1} resulted in poor re-adsorption performance, whereby, only two cycles of adsorption-desorption processes that yielded positive adsorption results.

A. Effect of regenerants

The results obtained (refer to Fig. 1-3) indicate that NaOH solution has a poor performance in desorbing dyes from adsorbents. The results suggest that NaOH is unsuitable to be utilised as a regenerant in reactive dyes of RB5. Since the RB5 dyes is anionic (negatively charged), the basic solution of NaOH did not exhibit effectiveness in desorbing loaded dye adsorbent due to electrostatic repulsion (11) that occurred between anionic dye (-SO3-) and base solutions (OH-). Consequently, this had reduced the potential of adsorbing loaded dye on adsorbent by NaOH solution via electrostatic attraction. Lesser amount of loaded dyes desorbed from the adsorbent had consequently led to a decrease in the number of available active sites that were re-used in subsequent adsorption process. In addition, the treatment using basic solution (NaOH) had triggered the deprotonation of adsorbent surface and certain functional groups. Particularly, hydroxyl group might have been formed on the surface of the adsorbent, which inevitably resulted in a weaker electrostatic interaction between adsorbents and dye molecules during adsorption process. The weak interaction had subsequently yielded poor adsorption of dye molecules.

In contrast, HCl solution showed superior desorbing ability of RB5 owing to a stronger attraction between H+ from acid solution and negative charge of dyes molecules, resulting in good desorption performance via electrostatic interaction. Desorbed dye molecules from adsorbent increases the quantity of available active sites on the adsorbent for reuse, thus, allowing more dye molecules to be adsorbed. In addition, owing to the rich presence of hydrogen atoms (H+) in the solution would protonate amine groups (–NH2) from the PEI of magnetic-PEI-cellulose adsorbent to form –NH3+. Therefore, the interaction via electrostatic force between adsorbent and anionic dyes was getting stronger which led to the higher percentage of dye removal from the wastewater solution. This was supported by Shukla and Pai (12), stated that the electrostatic interactions between RB5 anions and adsorbent with positively charged surface increase in acidic solution due to the protonation of active groups of adsorbent. Although the treated adsorbent was washed repeatedly to reach neutrality for reuse, the influence of acidic treatment was irrevocable (13), resulting in a higher removal efficiency during re-adsorption. Studies by Crini and Badot (14), also indicated that the protons of acid solution are effective in reducing the dissociation of anionic groups of dyes.

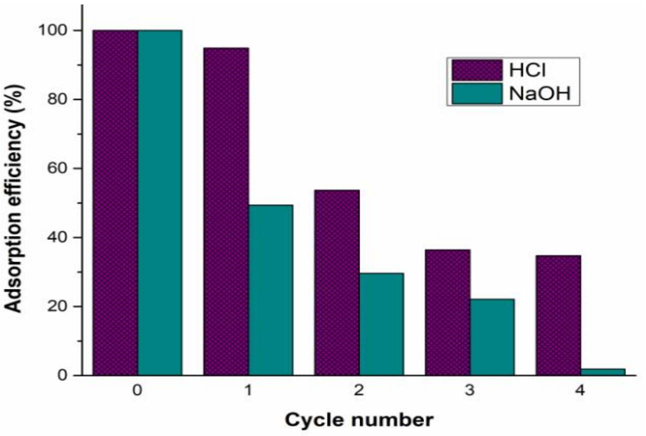

Fig. 1. Adsorption efficiencies of the reactive black 5 by acid and base at 0.1 mol L-1 (Conditions: initial dye concentration, 0.1 g/L; adsorbent dosage, 0.1 g; sample volume, 50 ml; solution pH, 7; contact time, 180 min; desorption time, 30 min; temperature, 27 °C).

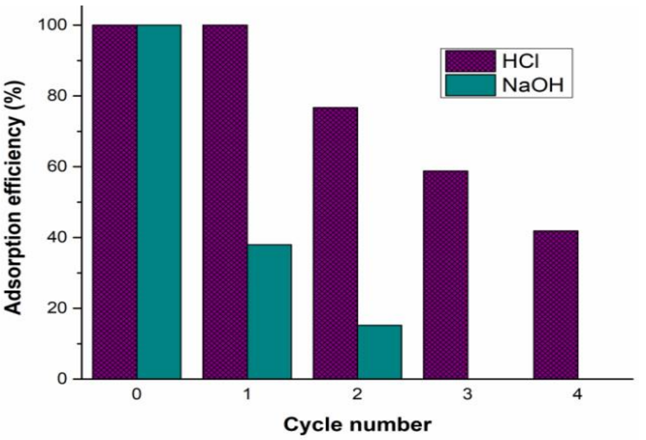

Fig. 2. Adsorption efficiencies of the reactive black 5 by acid and base at 1.0 mol L^{-1} (Conditions: initial dye concentration, 0.1 g/L; adsorbent dosage, 0.1 g; sample volume, 50 ml; solution pH, 7; contact time, 180 min; desorption time, 30 min; temperature, 27 °C).

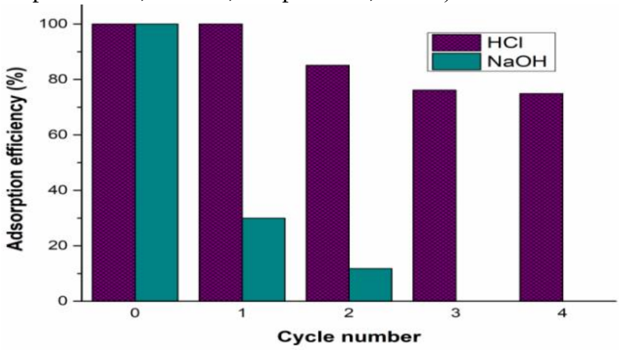

Fig. 3. Adsorption efficiencies of the reactive black 5 by acid and base at 5.0 mol L-1 (Conditions: initial dye concentration, 0.1 g/L; adsorbent dosage, 0.1 g; sample

volume, 50 ml; solution pH, 7; contact time, 180 min; desorption time, 30 min; temperature, 27 °C).

B. Effect of regenerants concentrations

The results in Fig. 1-3 indicate that the adsorption efficiency of adsorbent for several cycles is dependent on the concentration of the regenerants, since variation in concentrations leads to the variation in surface properties of adsorbent. From the experiments, it was observed that the HCl solution possesses excellent desorbing ability for RB5 dye at a higher concentration (i.e. 5 mol L-1), which recorded high adsorption efficiency (74.9%), after four cycles of adsorption-desorption process. On the contrary, a higher concentration of NaOH solution (i.e. 5 mol L-1) showed no ability in desorbing anionic RB5 dye, which was indicated by no removal of dye after four cycles of adsorption-desorption process.

Higher concentration of HCl solution contributes to a higher H+ concentration in the solution, thus, resulting in an increased electrostatic attraction towards dye loaded molecules. As more dye loaded molecules were adsorbed by adsorbent, more active sites were available to be reused in subsequent adsorption process. Besides that, a higher amount of H+ in the solution increased the protonation extent of adsorbent, which resulted in a higher quantity of H+ formed on the adsorbent surface. Therefore, a higher amount of dye molecules was adsorbed by magnetic-PEI-cellulose adsorbent via electrostatic interaction, as the electrostatic force was strengthened further, owing to the increase in the concentration of desorbing agent. According to (15), the effectiveness of desorption and adsorption of dye by strong acids, such as HCl, is heavily influenced by electrostatic attraction.

In contrast, a higher concentration of NaOH solution contributed to a higher presence of OH- in the solution, which was prohibitive for desorption of anionic loaded dyes. As both OH- and anionic loaded dyes possess negatively-charged ions, electrostatic repulsion occurred, resulting in low availability of active sites for further adsorption process. In contrast from HCl regenerant, the higher amount of OH- present in NaOH solution increased the protonation extent of adsorbent, which resulted in higher quantity of OH- formed on the adsorbent surface. Consequently, a smaller quantity of dye molecules was adsorbed by magnetic-PEI-cellulose adsorbent via electrostatic interaction, attributed to an insufficiency in terms electrostatic force that could be utilised to adsorb dyes.

V. CONCLUSION

In conclusion, the batch test was performed to desorb the RB5 dyes from magnetic-PEI-cellulose adsorbent. The electrostatic interaction has an important effect on the adsorbent-adsorbate interaction, which would be contributed by acidic (HCl) and basic (NaOH) solutions. The batch desorption test results show that the most effective regenerants to desorb the RB5 dyes is 5 mol L-1 of HCl. Increasing of acidic regenerants concentration can improve the dye desorption capability and deserves further study to optimize the dye desorption/readsorption efficiency. The adsorption capacities of adsorbent with repeated adsorption–desorption cycles decreased but seemed to be stabilized after 3 cycles. Therefore, it is proposed that the HCl solution can be a promising regenerant for desorbing and regenerating the magnetic-PEI-cellulose adsorbent from RB5 dyes.

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