Studies on the Adsorption of Phenol Red Dye Using Silica-filled ENR/PVC Beads

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Abstract

Adsorption of dyes on the solid surface of various materials represents a crucial and intensively studied phenomenon due to the growing concern on the environmental and public health. In this study, silica-filled ENR/PVC beads have been synthesized and the adsorption of organic dye (phenol red) from aqueous solutions by the beads was investigated. The beads are aimed to be used as adsorbent to treat Malaysian textile ‘batik’ dye effluents. Adsorption of phenol red (PR) onto the composite beads was studied by batch adsorption techniques at 25± 1°C using a rotary shaker. The effect of contact time, initial dye concentrations and amount of adsorbent on the adsorption capacity were studied. The adsorption behaviour of PR on the beads was investigated using double-beam UV-Vis spectrophotometer at maximum absorption of 558 nm. The adsorption of dye increased with increasing initial dye concentration and adsorbent dosage. Nearly 50 h of contact time was found to be sufficient for the adsorption to reach equilibrium. The experimental data were analyzed using pseudo-first-order and pseudo-second-order kinetic models and the rate constants were evaluated. The Langmuir and Freundlich models adsorption were applied to describe the isotherm equilibrium and to determine its constants. Both models agreed well with the experimental data with an adsorption capacity of 2.67 mg of dye per g of beads with 88.8% removal efficiency.

Keywords: adsorption; kinetic studies; phenol red dye; epoxidized natural rubber (ENR)/polyvinyl chloride (PVC); beads; silica

INTRODUCTION

The removal of colour from aquatic systems caused by presence of synthetic dyes has become one of the major challenges nowadays to be resolved. Coloured wastewater generally comes from dye or pigment manufacturing, textile industries, pulp and paper mills and laboratories. In Malaysia, there are more than 1500 textile factories, many of which operate as cottage industries producing the local ‘batik’ textile (Siddiqui et al. 2011). The disposal of dyes into water system destructs the esthetic nature, poses a serious threat to human health and affects the food cycle in water ecosystems (Mishra and Tripathy, 1993). Colouring agent or dye is a visible pollutant and appears highly visible even at very low concentrations. Due to their chemical structure which usually contains complex aromatic structures, dyes are toxic, carcinogenic and resistant to fading on exposure to light, heat, water, microbes and many chemicals (Pagga and Taeger, 1994; Robinson et al., 2001).

Currently, the main methods of treatment for the dye-bearing wastewater are physical and chemical techniques. Among the various available physico chemical processes, adsorption technology is considered to be one of the most effective and proven technology for decolorization in water and effluent (Anjaneyulu et al., 2005). This has encouraged the development of adsorbents from a variety of materials having great potentials for the purpose. Low cost, simple preparation, high adsorption capacity are a few of many added values desired for the adsorbents.

The present work deals with the applicability of adsorption means in the removal of the dye phenol red from wastewaters. Phenol red is a highly watersoluble fabric dye belonged to the class of triphenylmethane dyes. It exists as a red crystal beside being stable in air and a weak acid since at 20°C, the pKa value has been found to be 8.00 (Anonymous, 2012). It is frequently used as a reagent dye for measuring the pH of water in a range of 6.8 (yellow) to 8.2 (bright pink). It is thus widely employed as a pH indicator in cell biology laboratories and for water testing applications. Toxicity data reveal that phenol red inhibits the growth of renal epithelial cells (Walsh-Reitz and Toback, 1992). Direct or indirect contact with the dye leads to irritation to the eyes, respiratory system and skin. Phenol red dyes are reported to cause mutagenic effects (Chung et al., 1981) and are toxic to muscle fibers (Baylor and Hollingworth, 1990). Hence, this
study is aimed to practically utilize a newly developed silica-filled ENR/PVC beads as adsorbent to remove this hazardous organic dye from wastewaters. The study focused on batch adsorption experiments by using various initial amounts of dye and adsorbent. The adsorption capacity and kinetic were also studied in order to discuss the potential of the beads as dye adsorber to be applied in various wastewater.

EXPERIMENTAL

Materials and Methods

The dye used in the study was phenol red, 4’-(3H-2,1-benzoxathiol-3-ylidene) bis-phenol, S,S-dioxide obtained from Sigma-Aldrich with chemical structure shown in Figure 1. Phenol red is also commonly known as phenol sulfonephthalein. An intense colour is due to the extended conjugation systems of the alternate double and single bond in the dye structure (Mittal et al., 2009). Some general physicochemical properties of phenol red are presented in Table 1. Phenol red dye stock solution was prepared in doubly distilled water and suitably diluted to the required initial concentrations. The phenol red aqueous solutions was maintained at pH 12 by adjusting them with the addition of sodium hydroxide (5% NaOH).

![Figure 1. Chemical structure of phenol red](image)

Table 1: Physicochemical properties of phenol red (PR)

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class</td>
<td>Triphenylmethane dyes</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C_{19}H_{18}O_{3}S</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>354.38</td>
</tr>
<tr>
<td>Solubility</td>
<td>Soluble in water (0.77 g/L)</td>
</tr>
<tr>
<td>Absorption maxima</td>
<td>558 nm</td>
</tr>
</tbody>
</table>

The adsorbent material in the present research work was prepared by internal mixing of 60/40 by weight percent of epoxidized natural rubber having 50 mol % of epoxidation (ENR50) and poly (vinyl chloride) (PVC) in a Brabender Plasticoder PL2000 to form a matrix blend. It was carried out at 160°C for total duration of 13 mins with rotor speed at 10 rpm for the first 3 min and 50 rpm for the subsequent 10 min. The blend was dissolved in tetrahydrofuran. Fumed silica (8 wt%) was then added into the solution and stirred consistently for a homogeneous solution. ENR 50 was provided by Malaysian Rubber Board. PVC resin and fumed silica (particle size of 0.007 µm) were supplied by Industrial Resin (M) Ltd. and Sigma-Aldrich, respectively. The ENR/PVC/silica solution was then added drop wise into a solidifying solution containing a 1:1 mixture of deionized water and ethyl alcohol to obtain composite beads. The gelled beads were filtered and rinsed thoroughly with deionized water prior to drying in an oven for 3 hours at 80°C. Tetrahydrofuran (THF) stabilized with 0.025% BHT and ethyl alcohol (95% v/v denatured) were purchased from Systerm. The adsorbents beads were finally stored in a desiccator.

Adsorption Studies

Adsorption behaviours were determined by conducting a primary analysis. The influence of crucial parameters such as effect of contact time, initial concentration, and amount of adsorbent were investigated by batch adsorption studies. These studies were performed by taking 60 mL of PR dye solution in close-lid 250-mL conical flasks. A predetermined amount of silica-filled ENR/PVC beads was added into each flask with intermittent shaking on a rotary shaker at temperature of 25±1°C. After 24 h these solutions were filtered and the amount of dye adsorbed was analyzed at λ_{max} 558 nm. The initial concentration and adsorbent dosage were varied and subsequently the variation in the amount of dye taken up by the adsorbent was analyzed. The dye absorption studies were carried out using double-beam UV-Vis spectrophotometer model Shimadzu 2650.

Kinetic Studies

An appropriate amount of silica-filled ENR/PVC beads were added to 60 mL of the dye solutions in close-lid 250-mL conical flasks. In each flask 1.0 g of the adsorbent beads were added prior to a continuous shaking on a rotary shaker at temperature of 25±1°C. These solutions were filtered after a particular time interval and spectrophotometric analysis was performed for the amount of dye uptake.

RESULTS AND DISCUSSION

Adsorption Studies

For these studies, the amount of dye adsorbed (q_e) onto the silica-filled ENR/PVC beads and the percentage of removal (R) were calculated using the following relationships:

\[ q_e = \left( C_0 - C_e \right) \frac{V}{W} \]  \hspace{1cm} (1)

\[ R = \left( \frac{C_0 - C_e}{C_0} \right) \times 100 \]  \hspace{1cm} (2)

where C_0 and C_e are the initial and equilibrium concentration (mg/L), respectively, V is the volume of the solution (L) and W is the amount of adsorbent (g).
Effect of Contact Time
The study on contact time was done to understand the amount of dye adsorbed at various time intervals by a fixed amount of the adsorbent. Figure 2 clearly illustrates that the dye adsorption increases with increase in the contact time. The amount of dye adsorbed rose rapidly within 6 h of contact time before increasing gradually reaching plateau stage for the subsequent hours. After almost 3 h of contact, the percentage of removal was 30.97%. The percentage of dye removal and adsorption capacity at contact time of 50 h were 88.8% and 2.67 mg/g, respectively. After this time no further increase in the adsorption was observed. This might be due to aggregation of the dye molecules at the adsorption sites on the adsorbents and increased path length of diffusion (Gupta et al., 2003). Hence 50 h was taken as the equilibrium time.

Effect of Initial Dye Concentrations
An initial dye concentration range of 10 to 100 ppm was selected and fixed amounts of the adsorbents were added to these solutions. It was found that the adsorption increases with the increase in dye concentration. Figure 3 shows the effect of initial concentration on the adsorption capacity of the dye. Nonetheless, adsorbate saturation of the adsorbent sites may occur on increasing concentration of the dye solution causing no further adsorption of the dye molecules.

Adsorption Isotherms
The adsorption of phenol red (PR) in aqueous solution onto silica-filled ENR/PVC beads was studied at a temperature of 25±1°C. This work deals mainly with two well-known isotherms, namely Langmuir and Freundlich isotherms.

Langmuir Isotherm
The Langmuir isotherm assumes that the surface of any adsorbent material contains a number of active sites where the adsorbate attaches itself. This attachment can either be physical or chemical. When the attachment is via van der Waals interactions, it is known as physisorption whereas when it is via covalent bond, it is known as chemisorption. There is also not much interaction between the adsorbate molecules and once a saturation value has been reached, no further adsorption would take place (Langmuir, 1916). The relationship between amount of dye adsorbed and adsorption capacity is described in the following equation:

\[ \frac{C_e}{q_e} = \frac{1}{q_m}C_e + \frac{1}{K_Lq_m} \]  

where \( q_e \) is the amount of phenol red adsorbed (mg/g), \( C_e \) is the equilibrium concentration of the adsorbate (mg/L), \( q_m \) is the maximum adsorption capacity (mg/g) and \( K_L \) is the energy of adsorption (L/mg). Figure 5 shows a linear plot of \( C_e/q_e \) versus \( C_e \) obtained for Langmuir isotherm in which \( R^2 \) value indicates reliability of the experimental data for the
adsorption of PR by silica-filled ENR/PVC beads. The values of Langmuir constant and $R^2$ are presented in Table 2. The important characteristic of the Langmuir isotherm can be expressed by means of dimensionless constant separation factor, which is calculated using the following equation:

$$R_L = \frac{1}{1 + \frac{K_L}{C_0}}$$  \hspace{1cm} (4)

where $K_L$ denotes the Langmuir constant and $C_0$ is the initial concentration (Weber and Chakravorti, 1974). At all initial concentrations within studied range, $R_L$ values presented in Table 3 have been found between 0 and unity (1), indicating thereby favorable processes for the adsorbent.

Table 2: Langmuir and Freundlich constants and $R^2$ values for adsorption of PR by silica-filled ENR/PVC beads (adsorbent dose = 1.0 g)

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_L$ (L/mg)</td>
<td>$q_m$ (mg/g)</td>
<td>$n$</td>
</tr>
<tr>
<td>Langmuir</td>
<td>0.356</td>
<td>2.623</td>
<td>-</td>
</tr>
<tr>
<td>Freundlich</td>
<td>-</td>
<td>3.014</td>
<td>0.753</td>
</tr>
</tbody>
</table>

The values of Freundlich constant and $R^2$ are presented in Table 2. Based on the results, the Langmuir isotherm fits the experimental data better than Freundlich isotherm for the adsorption behaviour in phenol red-ENR/PVC/Silica system.

Table 3: $C_o$ and $R_L$ values for adsorption of PR by silica-filled ENR/PVC beads (adsorbent dose = 1.0 g)

<table>
<thead>
<tr>
<th>$C_o$</th>
<th>$R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.219</td>
</tr>
<tr>
<td>30</td>
<td>0.086</td>
</tr>
<tr>
<td>50</td>
<td>0.053</td>
</tr>
<tr>
<td>60</td>
<td>0.045</td>
</tr>
<tr>
<td>80</td>
<td>0.034</td>
</tr>
<tr>
<td>100</td>
<td>0.027</td>
</tr>
</tbody>
</table>

**Freundlich Isotherm**

The Freundlich model (Osma et al., 2007) is given by the equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \hspace{1cm} (5)

where $q_e$ is the amount of dye adsorbed (mg/g), $C_e$ is the equilibrium concentration of the adsorbate (mg/L), $K_F$ and $n$, the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The model is based on the assumption that adsorption occurs on a heterogeneous adsorption surface having unequally available sites with different energies of adsorption (Weber and Chakravorti, 1974). Figure 6 illustrates the plot obtained for the Freundlich isotherm for the adsorption of PR by silica-filled ENR/PVC beads. The values of Freundlich constant and $R^2$ are presented in Table 2. Based on the results, the Langmuir isotherm fits the experimental data better than Freundlich isotherm for the adsorption behaviour in phenol red-ENR/PVC/Silica system.

Figure 6. Freundlich adsorption isotherm for adsorption of PR onto silica-filled ENR/PVC beads

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**Kinetic Studies**

Pseudo-first-order and pseudo-second-order rate equations were applied to adsorption of PR by silica-filled ENR/PVC beads (Lagergren and Svenska, 1898; Ho and McKay, 1998). The equations given below summarize the Lagergrens pseudo-first-order and pseudo-second-order rate equations, respectively:

$$\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303}$$  \hspace{1cm} (6)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (7)

where $q_e$ and $q_t$ denote the amounts adsorbed at equilibrium and at any time t in grams, respectively, and $k_1$ and $k_2$ are the rate constants. In the case of pseudo-first-order a graph was plotted between log ($q_e - q_t$) versus time where the slope of the graph gives the value of $k_1$, as depicted by Figure 7. In the case of pseudo-second-order, a graph was plotted between $t/q_t$ versus time where the intercept gives the value of $k_2$, as shown in Figure 8.
In both cases, straight-line graphs were obtained. Table 4 summarizes the values of $k_1$, $k_2$ constants and $R^2$ obtained from the equations. The $R^2$ value obtained in pseudo-first-order model was higher than that of pseudo-second-order model. Therefore, the values indicate that the ongoing reaction proceeds via pseudo-first-order mechanism rather than pseudo-second-order mechanism.

Figure 7. Plot of log ($q_e - q_t$) vs. time for the adsorption of PR by silica-filled ENR/PVC beads.

Figure 8. Plot of $t/q_t$ vs. time for the adsorption of PR by silica-filled ENR/PVC beads.

Table 4 Rate constants and $R^2$ values of pseudo-first-order and pseudo-second-order for adsorption of PR by silica-filled ENR/PVC beads

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first-order</td>
<td>0.00276</td>
<td>-</td>
<td>0.9606</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>-</td>
<td>0.000873</td>
<td>0.8945</td>
</tr>
</tbody>
</table>

CONCLUSION

The preceding experiments disclosed that silica-filled ENR/PVC beads demonstrate to be a potential adsorbent for the removal of phenol red dye from aqueous solution. These organic-inorganic adsorbent beads are novel, lightweight with good physical and thermal stability as well as high potential of adsorbing the dye from wastewater. Presence of porous structure and high surface area due to the size and spherical shape of the adsorbents, silica-filled ENR/PVC beads are possibly capable to surpass the commercially available materials. The effectiveness was proven by maximum adsorption capacity and the removal efficiency determined at 2.67 mg of dye per g of beads and 88.8%, respectively. The adsorption process was concluded to proceed by a pseudo-first-order mechanism. The Langmuir model of adsorption agreed well with the experimental data compared to Freundlich model. Thus, from the above discussion it has been established that silica-filled ENR/PVC beads can be potentially utilized as adsorbents for the removal of phenol red dye from wastewater.

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REFERENCE


