Various kinds of synthetic dyestuff appear in the effluents of wastewater in some industries such as dyestuffs, textiles, leather, paper-making, plastics, food, rubber, and cosmetics [1]. These dyes threaten human health because most of them are toxic and potentially carcinogenic [2]. Removal of these dyes from wastewater is an important practical problem [3]. A range of wastewater treatment technologies have been investigated for removal of these dyes, such as biodegradation [4], ultrasound irradiation [5], and photo-degradation [6]. However, these techniques have not been effective due to the essentially non-biodegradable nature of most dyes, which are stable to light and oxidation [7]. Adsorption is one of the effective separation techniques to remove dilute pollutants as well as offering the potential for regeneration, recovery, and recycling of the adsorbed material [8]. Many studies have been made on various adsorbents using activated carbon, peat, chitin, silica, fly ash, clay, mesoporous materials, and other adsorbents that have been investigated to remove dyes from aqueous solutions with varying success [9-12]. The study of dye adsorption onto a cost-effective adsorbent is significant in the industrial wastewater treatment system because it provides valuable insights into the mechanisms and the optimum operation parameters of adsorption processes [13].

Bentonite, a kind of argillaceous material, has been proven to be a promising material for the removal of contaminants from wastewater. This outstanding capability is due to the presence of the mineral montmorillonite [14]. However, the adsorption capacity of natural bentonite for organic molecules is low due to the hydrophilic nature of the mineral surfaces. Many methods have been employed...
to modify the surface property of natural bentonite, such as sodium modification [1], baking [15], acid activation [16], and magnesium chloride modification [17]. Recently, many interests have focused on organic ammonium salt modification, which could convert the hydrophilic surface property of natural bentonite to hydrophobic characteristic, resulting in modified bentonite having high adsorptive capacity [18]. In addition, without flocculants, absorbed bentonite cannot settle and is difficult to be separated from the water. However, there has been little work on the combination of bentonite and flocculants.

In this work, cetyltrimethylammonium chloride (CTAC)-modified bentonite combined with polyacrylamide (PAM) flocculant is used for the removal of a commonly used azo dye – Reactive Brilliant Red K-2BP (K-2BP) from aqueous solutions. The results might be helpful for finding a cost-effective method to remove synthetic dyes from dye wastewater.

Materials and Methods

Materials

The natural bentonite used in this study was obtained from clay found in Shanghai, China. The composition of this natural clay was: 67.82% SiO₂, 15.86% Al₂O₃, 1.83% Fe₂O₃, 4.43% CaO, 0.93% MgO, 1.01% K₂O, 0.13% Na₂O, 0.013% TiO₂, 0.06% P₂O₅, and trace MnO₂. The ignition loss of natural bentonite at 1,273 K was also found to be 7.91%. Its cation exchange capacity (CEC) is about 85.00 meq/100g and pH value is approximately 8.5, determined as literature method [19]. All chemicals (at least reagent grade) and dyestuffs (commercial grade) were purchased from Aldrich (USA) and used without further purification.

Preparation of Modified Bentonite

CTAC-bentonite is prepared as follows: Natural bentonite (200 g) was stirred for 24 h with CTAC modified reagent. This was followed by several washings with distilled water and filtrations to remove the excess modified reagent and other exchangeable cations from the clay. The clay was then re-suspended and filtered until a negative chloride test was obtained with 0.1 M AgNO₃. Then the bentonite was place in an oven at 120ºC until dry. The dried bentonite was in the form of clumps, thus crushing by mortar and pestle was required before the sample was passed through a 200 mesh analysis. Na-bentonite and HCl-bentonite are prepared using a similar method. Baking-bentonite is prepared as follows: Natural bentonite (200 g) was stirred for 24 h with CTAC modified reagent. The X-ray diffraction (XRD) patterns of natural bentonite and CTAC-bentonite were analyzed using a Rigaku Miniflex instrument with cobalt Kα radiation. The X-ray tube was operated at 30 kV and 15 mA beam current. The clays were examined over the range 3-70º 2θ at a scan speed of 2º 2θ/min.

Results and Discussion

Comparison of Different Modified Bentonite

The removal effect of K-2BP from aqueous solution by different modified bentonite were investigated at the conditions of 400 mg/L bentonite, 1.5 mg/L PAM, pH 8.0 and temperature 25ºC, and the results were summarized in Table 1. As shown in Table 1, after being modified, the removal efficiency of bentonite was increased in the order of CTAC-bentonite>Baking-bentonite>Na-bentonite>HCl-bentonite.
The increases in removal efficiency of modified bentonite were related to change of clay structure. In the acid treatment process, as protons penetrated into the clay layers, many impurities would be removed. Thus, the pore canals were dredged and it is favorable for the diffusion of dye molecule. In addition, Al\(^{3+}\) or Mg\(^{2+}\) ions were replaced by H\(^{+}\) ions [20]. It is well known that the ionic size of Al\(^{3+}\) or Mg\(^{2+}\) are greater than that of H\(^{+}\) in natural bentonite, so the acid modification resulted in a greater surface area, which is beneficial to the improvement of adsorption [21].

In the NaCl treatment process, Na\(^{+}\) with more exchangeability compensated the unbalanced charge from the 2:1 layers of smectite owing to isomorphous substitutions [22]. Meanwhile, bentonite was separated to thinner single crystal plate by solvent between layers, increasing the inner surface area. Thus, Na-bentonite had better adsorption capability than natural bentonite.

With thermal treatment up to 450ºC, the dehydration could reduce the resistance and not destroy the crystallinity and porosity of bentonite [23], which enhanced the adsorption capability of bentonite.

During the CTAC treatment process, natural bentonite, which was inherently hydrophilic due to hydration of metal ions, transformed into hydrophobic forms by ion-exchanging long-chain CTAC cations for metal ions on the clays [24]. Hence, bentonite modified by CTAC gives organophilic clay. Fig. 1 shows the XRD patterns of natural bentonite and CTAC-bentonite. As shown in Fig. 1, the CTAC modification led to an increase in \(d_{(001)}\) spacing from 15.42 to 18.75 Å, indicating that CTAC cations were intercalated in the interlayer space of the bentonite. And the \(d_{(001)}\) value of CTAC-bentonite was between 17.7 and 21.7 Å, which suggested the organic cations between the silicate layers formed a bilayer [25]. This result was similar with another report [14]. This bilayer formation results in an increase in adsorption capacity of clay for K-2BP, which is due to the alkyl chains in the interlamellar spaces of CATC-bentonite function as organic solvent in partitioning and electrostatic attraction with positively organoclay surfaces and anionic dye molecules [18].

**Effect of AT and Temperature**

Fig. 2 shows the CR\% at 25, 35, and 50ºC as a function of AT. As can be seen with the increase of temperature from 25 to 50ºC, the final CR\% increases slightly from 96% to 99% and the equilibrium time reduces from approximately 40 to 30 min. This observation reveals that the adsorption capacity of bentonite increases slightly and the adsorption process is slightly endothermic. This may be caused by the increased tendency of adsorbate ions to be adsorbed from the solution into the dye-clay interface [26].

In order to study the adsorption kinetics, we have calculated the amount of adsorbed using the following Equation:

\[
q_t = \frac{(C_0 - C_t)W}{m}
\]  

...where \(q_t\) was the amount of adsorbed (mg/g), \(C_0\) and \(C_t\) the concentrations (mg/L) of initial and treated solution (respectively), \(V\) the solution volume (L), and \(m\) the mass of adsorbent (g).

Low concentration of K-2BP is in accord with the Lambert-Beer law and has direct ratio relations with the absorbance. Therefore, the adsorption percentage and CR\% were calculated as Equation (4):

\[
\eta = CR\% = \frac{C_0 - C_t}{C_0} \times 100\% = \left(\frac{A_0 - A_t}{A_0}\right) \times 100\% \quad (4)
\]

...where \(\eta\) was the adsorption percentage, \(A_0\) and \(A_t\) the absorbance (Abs) of initial and treated solution.
Thus, $q_t$ could be calculated as:

$$q_t = \frac{\eta C_0 V}{m}$$  \hspace{1cm} (5)

Ho [27] developed a pseudo-second order kinetic expression for the sorption system of dye onto fly ash. This model has since been widely applied to a number of direct dye/adsorbent sorption systems [1, 28]. The pseudo-second-order reaction model based on sorption equilibrium capacity may be expressed as:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2$$  \hspace{1cm} (6)

The integrated form of Equation (6) becomes:

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

...where, $q_e$ is the amount of K-2BP adsorbed at equilibrium (mg/g), $q_t$ the amount of K-2BP adsorbed at time $t$ (mg/g) and $k_2$ is the rate constant of pseudo-second order sorption (g/mg min).

The initial sorption rate can be obtained as $q_t/t$ approaches zero:

$$h = k_2 q_e^2$$  \hspace{1cm} (8)

...where, $h$ is the initial sorption rate (mg/g min).

Parameters of pseudo-second order sorption are listed in Table 2. The kinetic plots are shown in Fig. 3. As it can be seen, pseudo-second-order model achieved a good fitting, indicating that the process was a chemical adsorption process between K-2BP and CTAC-bentonite.

Effect of pH Value

Because dye wastewater from the textile industry sometimes varies in acidity, it is important for researchers to investigate the effect of initial pH value on the removal of K-2BP. The results are shown in Fig. 4. With increases in pH value, the CR% curve had an uptrend. Under a strong acid system (pH<4), lowest CR% was gained. When increasing pH value from 4 to 8, the CR% increased steadily. Between pH 8 and pH 10, the CR% remained stable. At pH 11, the CR% was nearly up to 100%.

The lower amount of CR% in acidic solution is due to the protonation of the surface groups on bentonite. Thus, electrostatic repulsion exists between the positively charged surface and the positively charged dye molecule [13]. However, in alkaline solution, the situation is contrary. With reduction in electrostatic repulsion, the adsorption of K-2BP will be enhanced. In addition, the hydrolysis of K-2BP in alkaline conditions is also beneficial to the adsorption.

Table 2. Parameters of pseudo-second-order kinetic.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$k_2$ (g/mg min)</th>
<th>$q_e$ (mg/g)</th>
<th>$h$ (mg/g min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T=20ºC</td>
<td>0.0037</td>
<td>99.01</td>
<td>35.97</td>
<td>0.9984</td>
</tr>
<tr>
<td>T=35ºC</td>
<td>0.0055</td>
<td>101.01</td>
<td>55.86</td>
<td>0.9993</td>
</tr>
<tr>
<td>T=50ºC</td>
<td>0.0070</td>
<td>101.01</td>
<td>70.92</td>
<td>0.9994</td>
</tr>
</tbody>
</table>

Fig. 3. Kinetic plots of pseudo-second order sorption model: (a) 25ºC, (b) 35ºC, and (c) 50ºC.

Effect of Flocculant

We studied the effect of PAM and carboxymethyl cellulose (CMC) on ST and the results were plotted in Fig. 5. Without flocculants, the adsorbed bentonite could not settle. However, after adding flocculants, the bentonite could quickly settle. As shown in Fig. 5, PAM had much better flocculation effect than CMC. The average ST value of PAM was approximately 8.3 min and that of CMC was approximately 57.8 min. In addition, the shortest ST value
(2 min) of PAM was obtained at the dosage of 1.5 mg/L and that of CMC was obtained at 2 mg/L. Excess or scant floc- culant dosage would increase ST.

Recently, the use of synthetic polyelectrolytes such as PAM and CMC as flocculants for suspended solids removal in wastewater treatment has grown rapidly [29]. The advan- tage of polymeric flocculants is their ability to produce large, dense, compact, and stronger flocs with good settling characteristics. It can also reduce the sludge volume. Furthermore, the polymer performance is less dependent on pH. The flocculation performance of flocculants primarily lies on the type of flocculant and its molecular weight, ionic nature and content [30].

La Mer and Healy [31] described the action of polymeric flocculation agents whereby the polymer destabilizes a colloidal suspension by adsorption of particles and subse- quent formation of particle-polymer-particle bridges. The optimum flocculation conditions are obtained, when half of the solid surface is covered by the polymer. Excess poly- mers covering the solid particles will steady the suspension and reduce flocculation. Therefore, 1.5 mg/L and 2.0 mg/L were the optimum dosage for PAM and CMC, respectively, and excess or scant dosage would reduce the flocculation.

PAM are non-ionic and linear polymer and favorable for the flocculation of negative colloids. However, CMC are anionic polyelectrolycs and not easily adsorbed to electro-negative bentonite to form bridge [31]. Thus, the flocculation of CMC was much weaker than that of PAM.

Conclusions

In summary, the CTAC modification method could potentially enhance the removal efficiency of K-2BP from aqueous solution by bentonite. PAM is an effective floccu- lant to settle adsorbed bentonite with short ST (2 min) and low dosage (1.5 mg/L). Alkaline conditions are favorable for the adsorption of K-2BP. However, temperature influence is weak. Considering the high efficiency and low cost, CTAC-bentonite/PAM could extend broadly in dye waste- water treatments.

Acknowledgements

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Abbreviations

AT – adsorption time
CEC – cation exchange capacity
CMC – carboxymethyl cellulose
COD – chemical oxygen demand
CODR% – COD reduction percentage
CR% – color removal percentage
CTAC – cetyltrimethylammonium chloride
K-2BP – Reactive Brilliant Red K-2BP
PAM – polyacrylamide
SSR – sludge settling ratio
ST – sedimentation time
XRD – X-ray diffraction

References


