Modification of Bleached Eucalyptus Kraft Pulp by p-DMA-co-ECH and Its Application for the Removal of Acid Scarlet G in Aqueous Solution

Zhen Wang,* Nana Bo, Yu Liu, Guihua Yang, Gaojin Lv, and Ying Liu

Poly-epichlorohydrin-dimethylamine (p-DMA-co-ECH) was synthesized and was used to modify bleached eucalyptus kraft pulp (BEKP). The modified pulp (designated PDMAECH pulp) was characterized by zeta potential, FTIR, NMR, and SEM. Both the PDMAECH pulp and the BEKP were used as adsorbents to remove Acid Scarlet G (ASG) from aqueous solution. The effects of operational parameters on the efficiency of dye removal, including pH, adsorbent dosage, initial dye concentration, and contact time, were investigated. Results showed that modification could change the surface characteristics and effectively enhance the adsorption capacity. The optimum pH for ASG removal with the modified bleached eucalyptus kraft pulp (PDMAECH pulp) was found to be 4.0, and for BEKP it was 2.0. Under the optimized conditions, the maximum capacities for ASG adsorption were also investigated. The adsorption processes of both adsorption reactions were spontaneous and exothermic, and the adsorption capacities decreased with an increase in temperature. Freundlich and Langmuir models were used to analyze the obtained experimental data. The Langmuir model was found to be a better fit for the experimental data for both adsorbents. Kinetic studies showed that the rate of adsorption of ASG on both adsorbents obeyed a pseudo-second-order kinetics model. The desorption process for PDMAECH pulp was also explored.

Keywords: Bleached Eucalyptus kraft pulp; Poly-epichlorohydrin-dimethylamine; Adsorption; Acid Scarlet G

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INTRODUCTION

Azo dyes are extensively used in the textile, paper printing, food, leather, cosmetics, and pharmaceutical industries (Chang et al. 2001). The discharge of industrial wastewater containing dyes causes serious environmental problems because of their high toxicity and possible accumulation in the environment. The majority of these dyes are synthetic in nature and are usually composed of aromatic rings, which makes them carcinogenic, mutagenic, inert, and non-biodegradable when discharged into waste streams. Therefore, the removal of such colored agents from aqueous effluents is of significant environmental, technical, and commercial importance (Allen et al. 2004).

Adsorption has proved to be an effective process for color removal from dye wastewater. Diverse cellulose-based materials have been found to be effective for the removal of azo dyes from aqueous solution.
Classes of cellulose-based sorbent considered in previous literature have included the biomass of living and dead micro-organisms, agricultural wastes, activated carbons prepared from agricultural waste biomass, composites with chitosan, and biosorbents in general (Hubbe et al. 2012). Among all the adsorbents mentioned above, the most popular adsorbent for the removal of dyes is activated carbon (derived from biomaterials), due to its excellent adsorption ability, but it suffers from three major disadvantages: high cost, difficulties in regeneration, and the loss of adsorption efficiency after regeneration (Srivastava et al. 2007). Meanwhile, most low-cost adsorbents have generally low adsorption capacities and require large amounts of adsorbent. Therefore, there is a need to find absorbents that are new, economical, easily available, and highly effective. Therefore, there is a considerable need for cheap adsorbents.

The effectiveness of microbial decolorization depends on the adaptability and the activity of selected microorganisms. Wide range of microorganisms including bacteria (Beveridge 1999; Saratale et al. 2010), fungi (Levin et al. 2010), yeasts (Aksu and Dönmez 2003), actinomycetes, and algae capable of degrading azo dyes have been reported (Ozer et al. 2006).

There are specific alternative agricultural by-products used intensely as azo dye adsorbents such as peanut hull (Gong et al. 2005; Tanyildizi 2011), coir pith (Namasivayam et al. 2001), bagasse (Valix et al. 2004), bamboo (Mui 2010), rice husk (Han et al. 2008), wood sawdust (Jain and Sikarwar 2008), orange peel (Sivaraj et al. 2001), beech wood sawdust (Dulman and Cucu-Man 2009), and rice husk (Lakshmi et al. 2009). Due to the unique polycationic structure, chitosan has been found to possess high removal capacities for anionic dyes such as acid, reactive, and direct dyes (Annadurai et al. 2008; Crini et al. 2008).

Bleached eucalyptus kraft pulp (designated BEKP) is a common pulp in South America and Southeast Asia and is produced annually in large quantities. As a complex material, BEKP is composed of cellulose, lignin, and hemicelluloses. Because the acidic groups exist in the structure of cellulose, lignin, and hemicelluloses, the pulp fiber suspensions are negatively charged in aqueous solution. These acidic groups mainly include (1) carboxylic acid, whose pKa value is about 4.5, (2) the phenolic hydroxyl group, whose pKa value is about 10.2, and (3) the aliphatic hydroxyl group, whose pKa value is about 13.7. Due to its negatively charged surface, pulp is known to strongly bind to heavy metal ions (Gupta and Ali 2000; Aksu and Isoglu 2005) and cationic dyes (Khattri and Singh 1999; Ho et al. 2005).

Few studies have dealt with the removal of anionic dyes using modified pulp. In this study, the adsorption of anionic dyes, namely Acid Scarlet G (ASG), onto polyelectrolyte-modified pulp was investigated. Anionic dyes were chosen as the model system because the overwhelming majority of synthetic dyes currently used are highly water-soluble anionic dyes. P-DMA-co-ECH was synthesized and used as a polyelectrolyte to modify the surface of BEKP. The product was characterized and was used as an adsorbent for the removal of anionic dye (ASG) from aqueous solutions. All the experiments in this study were carried out in a batch system to evaluate the effects of different operational variables, such as the pH of the solution; initial dye concentration, contact time, the most suitable isotherm models, and kinetics equations were also investigated.
EXPERIMENTAL

Chemicals and Materials

Acid Scarlet G (ASG) is an anionic dye with a molecular weight of 509.4 g mol⁻¹ (C₁₈H₁₃N₃Na₂O₅S₂). The ASG used in this work was of analytical grade (Chengdu Best Chemicals Company, China). The chemical structure of the dye is shown in Fig. 1.

![Fig. 1. The molecular structure of Acid Scarlet G](image)

Experimental solutions of ASG were prepared by diluting the stock solution (1000 mg L⁻¹) with distilled water. The dried material was ground in a laboratory mill. Bleached eucalyptus kraft pulp was obtained from Zhongmaoshengyuan Co., Ltd., (Weifang City, China). No other chemical or physical treatments were used prior to the adsorption experiments. The pH of the dye solutions was adjusted to a given level by the addition of HCl or NaOH solution and measured using a pH meter.

Preparation of PDMAECH-pulp

The synthesis process for p-DMA-co-ECH-modified BEKP (designated PDMAECH pulp) was carried out in two steps; the first step was p-DMA-co-ECH synthesis. An aliquot of 118 mL (1.5 mol) of epichlorohydrin was placed in a 500-mL three-neck round-bottom flask equipped with a condenser and electromagnetic stirring at room temperature, followed by dropwise addition of 127 mL of dimethylamine (1.0 mol) for the graft reaction. Next, 5 mL of ethylenediamine was added, and the mixture was stirred at 70 °C for 5 h. The product was collected and used in the following reactions. The PDMAECH pulp was produced in the second synthesis process.

![Fig. 2. Synthetic reactions of PDMAECH pulp (with glucuronic acid xylan as an example)](image)
The synthetic reaction of p-DMA-co-ECH is summarized in Fig. 2 (with glucuronic acid xylan as an example). Ethylenediamine was used as a crosslinking agent during this process (Choi et al. 2001). As in most softwood pulps, most of the carboxylic acid groups of BEKP come from polygalacturonic acids (Dronnet et al. 1996), which mainly exist in the state of 4-O-methyl-α-D-glucuronic acid xylan (Naran et al. 2009). Polysaccharides and their modified products have a primary role in the adsorption of cationic species from aqueous solutions (Wing 1997). Furthermore, other groups such as phenolic hydroxyls and aliphatic hydroxyls can also bind cations in solution.

For treatment of the fibers, 10 g of oven-dried BEKP was dispersed into 2 L of water to swell for 30 min. Under stirring, 60 mL of p-DMA-co-ECH was added slowly to the pulp at 60 °C. Then, the solution was adjusted to a pH of 9 using 0.1 N NaOH, and the dispersion was stirred at 60 °C and reacted for 5 h. The products were separated from the mixture by vacuum filtering and were washed several times with deionized water. The final products were dried at 80 °C in an oven. These products were used in all the sorption experiments.

Characterization of Bleached Eucalyptus Kraft Pulp and PDMAECH Pulp

The Boehm titration method (Goertzen et al. 2010) was used to determine the amount of acidic or basic functional groups on the surface of the BEKP.

Zeta potential measurements were carried out using a microelectrophoresis apparatus (JS94H, Shanghai Zhongchen Digital Technical Apparatus Co., Ltd., China). The zeta potentials of PDMAECH pulp and BEKP were determined in a pH range of 2.0 to 11.0.

The functional groups present in the BEKP and PDMAECH pulp samples were investigated using the FTIR technique (Perkin-Elmer “Spectrum BX” spectrometer). The spectrum was scanned from 400 to 4000 cm⁻¹.

Scanning electron microscopy (SEM) of the samples was performed using a JEOL JSM-6480LV scanning electron microscope. The samples were coated with platinum before the SEM micrograph was obtained.

Solid-state $^{13}$C NMR spectra were acquired at room temperature on a Bruker AV 400 spectrometer operating at 100.62 MHz and equipped with a 4 mm probe-head. All $^{13}$C spectra were recorded under magic angle spinning (MAS) conditions at a spinning speed of 5 kHz. CP experiments were performed using a 2 s recycle delay and a 1000 μs contact time.

Adsorption Experiments

To study the effect of PDMAECH pulp and BEKP dosage on ASG removal, different quantities (0.05 to 2.0 g) of PDMAECH pulp (or BEKP) were placed in several 100-mL Erlenmeyer flasks with 50 mL of 50-mg L⁻¹ ASG solutions. The flasks were shaken at 120 rpm for 60 min in a thermostat. The concentration of ASG in solution was measured on an ultraviolet (UV) spectrophotometer (Mode-722, China) at a specific wavelength for ASG (510 nm).

In the pH effect experiment, the initial solution pH (2.0 to 9.0) was first adjusted, and then 0.1 g of PDMAECH pulp (or BEKP) was added to several 100-mL Erlenmeyer flasks with 50 mL of 50-mg L⁻¹ ASG solutions. Then, the equilibrium pH and residual ASG concentrations in the solutions were determined. Batch sorption experiments were carried out at three different temperatures (293, 303, and 313 K) to determine the impact of temperature on the sorption process. An aliquot of 0.1 g of PDMAECH pulp (or
BEKP) was immersed in several 100-mL Erlenmeyer flasks with 50 mL of ASG solution at different concentrations (50 to 400 mg L\(^{-1}\)). All adsorption experiments were carried out under optimum pHs for both BEKP and PDMAECH pulp, except in the experiment related to the effect of pH.

**Desorption Experiments**

The PDMAECH pulp was selected in the desorption tests. Desorption studies of the adsorbed ASG were carried out by shaking the spent PDMAECH pulp in 50 mL of 1 M HCl for a period of 2 h. After complete recovery of the anions, the adsorbent was filtered and washed with distilled water. The regenerated adsorbent samples were reused in the subsequent experiments. The sorption and regeneration cycles were repeated three times, and a comparison of the value with those observed in the initial sorption step was used to compute the percentage recovery values.

**RESULTS AND DISCUSSION**

**Characterization of Bleached Eucalyptus Kraft Pulp and PDMAECH-pulp**

*Determination of surface chemistry*

Due to the dissociation of the surface adsorbent, the amount of acidic and basic groups on the surface can be expected to have a significant effect on the adsorption process. The Boehm titration method was used to determine the surface chemistry and the amount of functional groups such as phenolic, lactonic, and carboxylic acid groups of the pulp (Mohamad et al. 2012).

The experimental results of the titration method are presented in Table 1. Obviously, the total amount of acidic groups (0.4765 mmol g\(^{-1}\)) is much higher than that of the basic groups (0.0147 mmol g\(^{-1}\)), indicating the BEKP surface is acidic, resulting from the presence of major acidic groups.

**Table 1. Results of Boehm Titration of BEKP**

<table>
<thead>
<tr>
<th>Active sites</th>
<th>BEKP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total acidic sites (mmol g(^{-1}))</td>
<td>0.4765</td>
</tr>
<tr>
<td>Carboxylic (mmol g(^{-1}))</td>
<td>0.1235</td>
</tr>
<tr>
<td>Lactone (mmol g(^{-1}))</td>
<td>0.0818</td>
</tr>
<tr>
<td>Phenolic (mmol g(^{-1}))</td>
<td>0.2312</td>
</tr>
<tr>
<td>Total basic sites (mmol g(^{-1}))</td>
<td>0.0147</td>
</tr>
</tbody>
</table>

Figure 3 shows the zeta potentials of PDMAECH pulp and BEKP at different pH values. The results indicate that the zeta potentials of BEKP remained negative throughout the range of pH values. In contrast, with the BEKP, the zeta potential of PDMAECH pulp was positive in the designated pH range, which indicates the existence of positively charged functional groups in the framework of PDMAECH pulp. However, a gradual decrease in the zeta potential of PDMAECH pulp was observed with increasing pH; this could be attributed to the pH-dependent functional groups existing in PDMAECH pulp, such as phenolic hydroxyl and carboxyl groups. These groups will exhibit a greater negative charge when the pH is increased, which results in a decrease in the positive charge of the PDMAECH pulp.
Fig. 3. Effect of pH on the zeta potential changes of BEKP and PDMAECH pulp

FTIR analysis of PDMAECH pulp

The FT-IR spectra of BEKP and PDMAECH pulps are shown in Fig. 4. The FT-IR spectra reveal a broad peak around 3370 cm⁻¹, which can be attributed to the O-H in the hydroxyl functional group. The FTIR spectra of the BEKP shows bands at 1748 cm⁻¹, which are attributed to the carbonyl functional group in ketones, aldehydes, and carboxylic acids. Two overlapped bands around 1654 cm⁻¹ and 1425 cm⁻¹ in the FTIR spectra can be assigned to the asymmetric and symmetric stretch modes of the COO⁻ group, respectively. The 1056 cm⁻¹ band can be attributed to C-O stretching vibrations (Castro et al. 2010). As illustrated in Fig. 4, the peak intensity of the carbonyl group was diminished in the FT-IR spectrum after modification. Moreover, a new peak appeared at 1370 cm⁻¹, indicating that the amino groups have been grafted into the PDMAECH pulp structure (Xu et al. 2009).

Fig. 4. FTIR analysis of (a) BEKP and (b) PDMAECH pulp

Solid-state ¹³C NMR spectra of BEKP and PDMAECH pulp

Figure 5 shows the solid-state ¹³C NMR spectra of BEKP and PDMAECH pulp. The spectra of cellulose/hemicellulose chains in BEKP are dominated by the set of resonances in the region between 60 and 120 ppm (Newman and Redgwell 2002). As seen in
Fig. 5a, a set of five distinct peaks were present. The intense peaks at 105, 84, and 64 ppm are assigned to C-1, C-5, and C-6 carbons in cellulose chains. The intense peaks at 73 and 75 ppm are overlapping signals due to the C-2, C-3, and C-5 carbons of all polysaccharides (Baraka et al. 2007; Xu et al. 2011).

Solid-state $^{13}$C NMR spectra of PDMAECH pulp are shown in Fig. 5b. Enlargement of amine carbon peaks (30 to 60 ppm) can be observed in the spectrum of PDMAECH pulp as compared to the spectrum of BEKP, which is the result of the presence of the carbons of -CH$_2$N- and -NCH$_3$. The central chemical shifts for the peaks of -CH$_2$N- and -NCH$_3$ are located at 52 ppm and 35 ppm, respectively. Meanwhile, these signals are accounted together with the carbons of lignin and hemicelluloses, which make it difficult to quantify each component (Baraka et al. 2007).

**SEM analysis of PDMAECH pulp**

SEM micrographs of PDMAECH pulp samples before and after dye adsorption are shown in Fig. 6.

Fig. 5. Solid-state 13CNMR Spectra of (A) BEKP and (B) PDMAECH pulp

Fig. 6. SEM micrograph of PDMAECH pulp before (a, c) and after (b, d) ASG adsorption
Figures 6(a) and (c) are the micrographs before adsorption, while Figs. 6(b) and (d) are the micrographs after adsorption. The micrographs clearly indicate that the PDMAECH pulp had a smooth surface before ASG adsorption (Fig. 6(a) and (c)); the surface becomes multilayered and appears irregular after the adsorbent-loaded ABR (Fig. 6(b) and (d)), which confirms that the surface of the adsorbent is covered with dye molecules.

**Effect of pH**

As can be seen in Fig. 7, the ASG removal efficiency of PDMAECH pulp was much higher than that of BEKP. For the BEKP, the surface was dominated by negatively charged sites that were largely carboxylate groups together with some weaker acidic groups of heteropolysaccharides (Dronnet *et al.* 1997). At higher pH values, a negatively charged surface site on the biosorbent does not favor the adsorption of dye anions due to electrostatic repulsion. The increase of OH⁻ ions with increasing pH also causes a competition with the dye anions for the adsorption sites, resulting in a decrease in biosorption. As the pH of the system decreases, the number of negatively charged sites on the biosorbent surface declines and the electrostatic repulsion also drops. Thus, some of the negatively charged sites are changed into positively charged sites, so the dye uptake increases due to the electrostatic attractions between the negatively charged dye anions and the positively charged sorbent surface.

![Figure 7](image-url)

**Fig. 7.** Effect of pH on the adsorption of ASG onto BEKP and PDMAECH pulp (initial dye concentration: 50 mg L⁻¹; temperature: 293K; shaker speed: 180 rpm; contact time: 180 min.)

For the PDMAECH pulp, more protons will be available at a lower pH, thereby increasing electrostatic attractions between negatively charged dye anions and positively charged adsorption sites, causing an increase in dye adsorption. The high adsorption capacity observed can be attributed to the strong electrostatic interaction between the -N⁺(CH₃)₂(CH₂)(CHOH)(CH₃) and -N⁺H₂(CH₂)₂-N⁺H₂ of PDMAECH pulp and dye anions, respectively. When the pH of the solution was increased, the positive charge on the pulp or solution interface decreased and the adsorbent surface appeared to be neutral or negatively charged. Also, when there are no exchangeable anions on the outer surface of the adsorbent at higher pH values, the adsorption can be expected to decrease (Wu *et al.* 2004).
Effect of Dosage and Contact Time on the Sorption Process

The effects of BEKP and PDMAECH pulp dosage on the sorption of ASG were studied by varying the concentration of the sorbent from 0.5 to 20 g L\(^{-1}\) while keeping the other experimental conditions constant. The percentage removal of ASG vs. BEKP and PDMAECH pulp dosages is shown in Fig. 8.

An increase in the removal efficiencies of ASG was observed with increasing dosages of both adsorbents. This can be attributed to the availability of more surface functional groups at higher adsorbent dosages. Figure 8 shows the two adsorbents’ removal efficiencies for ASG (50 mg L\(^{-1}\)). Nearly 96.6% of ASG removal was achieved using only 2 g L\(^{-1}\) of PDMAECH pulp, as compared with 9.1% for BEKP at this dosage. This suggests that the adsorption capacity of PDMAECH pulp was much higher than the BEKP and demonstrates that the modification process can enhance the adsorption capacity effectively.

Fig. 8. Effect of dosage on the sorption of ASG (initial dye concentration: 50 mg L\(^{-1}\); temperature: 293K; shaker speed: 180 rpm; original solution pH: 4.0 for PDMAECH pulp and 2.0 for BEKP)

Fig. 9. Effect of contact time for the adsorption of ASG onto PDMAECH pulp at various dosages (initial dye concentration: 100 mg L\(^{-1}\); temperature: 293K; shaker speed: 180 rpm; original solution pH: 4.0)
As indicated in Fig. 8, the amount of ASG per unit weight of the adsorbents \( (q_e) \) decreased with an increase in dosages. When the ASG removal reached the utmost limit, the increase of adsorbents dosage would result in the decrease of the \( q_e \) because the capacity is normalized by added adsorbents.

To continue to explore the influence of PDMAECH pulp dose on the equilibrium time, a series of different sorbent dosages was selected (results combined in Fig. 8) and the experiment was carried out. Results shown in Fig. 9 indicate that the equilibrium time was different for different PDMAECH pulp dosages: when the dosage was lower than 1.5 g L\(^{-1}\), the modified pulp required a long period of time to reach equilibrium (120 min). However, a significant decrease in equilibrium time for ASG sorption (40 min) was observed when the PDMAECH pulp dosage was increased to 2.0 g L\(^{-1}\), when the equilibrium time was steady. Based on shortening the sorption equilibrium time, a PDMAECH pulp dosage of 2 g L\(^{-1}\) was chosen as the optimum and was used in the subsequent experiments.

**Adsorption Isotherm Analysis**

Adsorption isotherms disclose how adsorbates interact with adsorbents, and they are important in optimizing the use of the adsorbents. In our work, three typical isotherm models were analyzed: the Langmuir, Freundlich, and Redlich-Peterson (R-P) isotherms (Tsai et al. 2006):

\[
q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \\
\text{Langmuir:} \tag{1}
\]

\[
q_e = K_F C_e^{1/n} \\
\text{Freundlich:} \tag{2}
\]

\[
q_e = \frac{K_R C_e}{1 + a_R C_e^g} \\
\text{Redlich-Peterson:} \tag{3}
\]

where \( C_e \) is the equilibrium dye concentration in solution (mg L\(^{-1}\)), \( q_{\max} \) is the monolayer capacity of the sorbent (mg g\(^{-1}\)), \( K_L \) is the Langmuir constant (L mg\(^{-1}\)), \( K_F \) is the Freundlich constant (L g\(^{-1}\)), \( K_R \) (mg g\(^{-1}\)), \( C_e^g \), and \( a_R \) are the Redlich-Peterson constants. The validity of models was determined by calculating the standard deviation (S.D., %) using (Wu 2007):

\[
S.D. = \sqrt{\frac{\sum [(q_{exp} - q_{cal})/q_{exp}]^2}{n - 1}} \times 100 \tag{4}
\]

where the subscripts \( exp \) and \( cal \) refer to the experimental and the calculated data, and \( n \) is the number of data points.

The values of the isotherm constants were calculated using non-linear regression analysis, and the results are listed in Table 2. As can be seen from the table, a low value of \( \chi^2 \) and a high value of \( R^2 \) for the Redlich-Peterson isotherm indicated a very good mathematical fit for the Langmuir and Redlich-Peterson models for both BEKP and PDMAECH pulp. The fit of the data suggests that the Langmuir model gave slightly
closer fittings than those of the Freundlich and Redlich-Peterson models. This can be attributed to the fact that the adsorption follows a monomolecular layer adsorption mechanism.

**Table 2. Isotherm Constants for Sorption of ASG**

<table>
<thead>
<tr>
<th></th>
<th>BEKP</th>
<th>PDMAECH pulp</th>
</tr>
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<tbody>
<tr>
<td>Langmuir model</td>
<td></td>
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</tr>
<tr>
<td>T (K)</td>
<td>$q_{\text{max}}$</td>
<td>$K_L$</td>
</tr>
<tr>
<td>293</td>
<td>9.5</td>
<td>0.02035</td>
</tr>
<tr>
<td>303</td>
<td>8.93</td>
<td>0.02462</td>
</tr>
<tr>
<td>313</td>
<td>8.01</td>
<td>0.0293</td>
</tr>
<tr>
<td>Freundlich model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T (K)</td>
<td>$K_F$</td>
<td>$n$</td>
</tr>
<tr>
<td>293</td>
<td>2.29</td>
<td>4.37</td>
</tr>
<tr>
<td>303</td>
<td>2.13</td>
<td>4.35</td>
</tr>
<tr>
<td>313</td>
<td>2.27</td>
<td>4.91</td>
</tr>
<tr>
<td>Redlich-Peterson model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T (K)</td>
<td>$K_R$</td>
<td>$a_R$</td>
</tr>
<tr>
<td>293</td>
<td>0.265</td>
<td>0.969</td>
</tr>
<tr>
<td>303</td>
<td>0.220</td>
<td>1.000</td>
</tr>
<tr>
<td>313</td>
<td>0.221</td>
<td>1.017</td>
</tr>
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</table>

**Thermodynamic Parameters**

Thermodynamic parameters provide in-depth information about the inherent energetic changes associated with sorption; the thermodynamic parameters, such as the change in standard free energy ($\Delta G^0$), enthalpy ($\Delta H^0$), and entropy ($\Delta S^0$) were calculated to elucidate the process of sorption. The Langmuir isotherm was applied to calculate the thermodynamic parameters via Eqs. (5) and (6) (Ajmal et al. 1998; Huang et al. 2007)

\[
\Delta G^0 = -RT \ln (K_L) \quad (5)
\]

\[
\ln (K_L) = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (6)
\]

where $K_L$ is the Langmuir equilibrium constant (L mol$^{-1}$), $R$ is the universal gas constant (8.314 J mol$^{-1}$K$^{-1}$), and $T$ (K) is the absolute temperature. The enthalpy change was determined by plotting $\ln (K_L)$ vs. $1/T$. The thermodynamic parameters are listed in Table 3. The negative values of $\Delta G^0$ indicate that the sorption of the anionic dyes onto PDMAECH pulp (or BEKP) was spontaneous and thermodynamically favorable. The increase in the value of $\Delta G^0$ with increasing temperature indicates that the sorption process was more favorable at higher temperatures.

Generally, the change in free energy for physisorption is between -20 and 0 kJ mol$^{-1}$, but that for chemisorption ranges between -80 and -400 kJ mol$^{-1}$ (Jaycock and Parfitt 1981). As can be seen from Table 3, the adsorption process for BEKP was very close to physisorption, but the adsorption process for PDMAECH pulp was between the
range of physisorption and chemisorption. Furthermore, the negative value for free energy indicates that both the adsorption reactions were spontaneous.

The small negative value of the standard enthalpy change for both adsorbents indicates that the adsorption was physical in nature, involves weak forces of attraction, and was also exothermic, thereby demonstrating that the process was energetically stable. At the same time, the low value of $\Delta H^0$ implies that there was loose bonding between the adsorbate molecules and the adsorbent surface (Singh 2000). In addition, the positive value of $\Delta S^0$ suggests an increase in the degree of freedom at the solid-liquid interface during the sorption process, which reflects increased randomness at the solid/solution interface and dye affinity for PDMAECH pulp (or BEKP). Similar results were observed for the sorption of Acid Red 57 on surfactant-modified sepiolite (Ozcan and Ozcan 2005).

### Table 3. Thermodynamic Parameters for Adsorption of ASG onto Different Adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>T(K)</th>
<th>$\Delta G^0$(KJ/mol)</th>
<th>$\Delta H^0$(KJ/mol)</th>
<th>$\Delta S^0$(J K$^{-1}$mol$^{-1}$)</th>
<th>$R^2$</th>
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</thead>
<tbody>
<tr>
<td>BEKP</td>
<td>293</td>
<td>-23.41</td>
<td>-13.88</td>
<td>32.56</td>
<td>0.996</td>
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<tr>
<td></td>
<td>303</td>
<td>-23.77</td>
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<td></td>
<td>313</td>
<td>-24.06</td>
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<td></td>
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<tr>
<td></td>
<td>293</td>
<td>-31.70</td>
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<td></td>
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</tr>
<tr>
<td>PDMAECH pulp</td>
<td>303</td>
<td>-32.38</td>
<td>-10.98</td>
<td>70.70</td>
<td>0.996</td>
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<tr>
<td></td>
<td>313</td>
<td>-33.12</td>
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### Adsorption Kinetics

Sorption kinetics, which demonstrates the solute uptake rate, represents essential information about the reaction pathways and therefore determines their potential applications. To analyze the sorption rate of ASG onto PDMAECH pulp (or BEKP), the pseudo-first-order equation and pseudo-second-order equation were evaluated based on the experimental data. The kinetic analysis was carried out at 313K.

**Pseudo-first-order kinetic model**

The rate constant was determined by the pseudo-first-order kinetic model as proposed by Lagergren (1898),

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$  \hspace{1cm} (7)

where $q_e$ and $q_t$ are the amounts of adsorbate adsorbed (mg g$^{-1}$) at equilibrium and at any time, respectively, and $k_1$ is the rate constant of pseudo-first-order adsorption (min$^{-1}$). The adsorption rate constant $k_1$ and equilibrium adsorption capacity $q_{e,cal}$, along with correlation coefficients $R^2$, are listed in Table 4. As shown in Table 4, the experimental $q_{e,exp}$ value did not agree with the calculated one obtained from the linear plots. The results indicated that the adsorption of ASG onto PDMAECH pulp probably did not follow the pseudo-first-order kinetics model, and the reaction mechanism did not follow a first-order reaction. The same trend was found for BEKP.
Pseudo-second-order kinetic model

The pseudo-second-order kinetic model based on equilibrium adsorption can be represented in the following equation (Singh et al. 2005)

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}
\]

where \( k_2 \) is the equilibrium rate constant for the pseudo-second-order adsorption model (g mg\(^{-1}\) min\(^{-1}\)). The calculated values of \( k_2 \) and \( q_e \), along with the correlation coefficient \( R^2 \), are listed in Table 4. The results show that the second-order rate constant \( k_2 \) decreased as the original ASG concentration was increased.

Table 4. Comparison of Pseudo-First-Order and Pseudo-Second-Order Adsorption Rate Constants and Calculated and Experimental \( q_e \) Values for ASG Adsorption

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>( C_0 ) (mg L(^{-1}))</th>
<th>( q_{e, exp} ) (mg g(^{-1}))</th>
<th>( k_1 ) (g mg(^{-1}) min(^{-1}))</th>
<th>( q_{e, cal} ) (mg g(^{-1}))</th>
<th>( R^2 )</th>
<th>S.D.</th>
<th>( k_2 ) (g mg(^{-1}) min(^{-1}))</th>
<th>( q_{e, cal} ) (mg g(^{-1}))</th>
<th>( R^2 )</th>
<th>S.D.</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEKP</td>
<td>50</td>
<td>4.58</td>
<td>0.031</td>
<td>2.95</td>
<td>0.952</td>
<td>20.6</td>
<td>0.0157</td>
<td>4.92</td>
<td>0.998</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>5.49</td>
<td>0.037</td>
<td>3.98</td>
<td>0.983</td>
<td>15.8</td>
<td>0.0125</td>
<td>6.14</td>
<td>0.997</td>
<td>6.8</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>5.88</td>
<td>0.038</td>
<td>4.37</td>
<td>0.982</td>
<td>14.9</td>
<td>0.0119</td>
<td>6.44</td>
<td>0.996</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>6.47</td>
<td>0.035</td>
<td>4.56</td>
<td>0.965</td>
<td>17.1</td>
<td>0.0100</td>
<td>7.03</td>
<td>0.997</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>59.4</td>
<td>0.029</td>
<td>20.18</td>
<td>0.952</td>
<td>38.1</td>
<td>3.04×10(^{-4})</td>
<td>49.70</td>
<td>0.999</td>
<td>9.4</td>
</tr>
<tr>
<td>PDMAECH-pulp</td>
<td>80</td>
<td>79.5</td>
<td>0.037</td>
<td>42.78</td>
<td>0.983</td>
<td>26.7</td>
<td>1.57×10(^{-3})</td>
<td>76.39</td>
<td>0.999</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>86.0</td>
<td>0.036</td>
<td>47.56</td>
<td>0.982</td>
<td>25.8</td>
<td>1.49×10(^{-3})</td>
<td>86.28</td>
<td>0.999</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>89.8</td>
<td>0.037</td>
<td>50.65</td>
<td>0.965</td>
<td>25.2</td>
<td>1.47×10(^{-3})</td>
<td>92.25</td>
<td>0.999</td>
<td>1.6</td>
</tr>
</tbody>
</table>

It may also be found from Table 4 that the calculated \( q_e \) values agreed well with those of experimentally obtained \( q_e \) for the pseudo-second-order model. Also, the correlation coefficient values for all ASG concentrations obtained by fitting the experimental data to Eq. (8) were close to 1.0. The pseudo-second-order model, which considers chemisorption involving valency forming through sharing or exchange of electrons between the adsorbate and adsorbent as the rate-limiting step, provided the best correlation with the experimental data (Wu et al. 2009). Thus, it can be concluded that the adsorption of ASG on PDMAECH pulp (or BEKP) follows a pseudo-second-order kinetic model.

Some modified mineral adsorbents, activated carbon, and other reported biomass adsorbents have been selected to compare their ASG adsorption capacities on the basis of reported literature (Shen et al. 2009; Zhou et al. 2012; Janos et al. 2003; Seredych and Bandosz 2007; Li et al. 2010; Wang et al. 2008; Guo et al. 2012). The results are presented in Table 5 in comparison to those of PDMAECH pulp. The ASG adsorption capacity of PDMAECH pulp (105.6 mg g\(^{-1}\)) was found to be higher than most of those adsorbents.

Comparing these results with the \( Q_{\text{max}} \) obtained from these adsorbents (in Tab.5), the PDMAECH pulp developed in this study can be considered as alternative materials for ASG removal in aqueous solution.
Table 5. $Q_{\text{max}}$ of ASG on Different Adsorbents

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>$Q_{\text{max}}$ (mg g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDMAECH pulp</td>
<td>105.6</td>
<td>In this work</td>
</tr>
<tr>
<td>Fly ash-Czech Republic</td>
<td>71.5</td>
<td>Janos et al. 2003</td>
</tr>
<tr>
<td>Organo-bentonite</td>
<td>116.5</td>
<td>Shen et al. 2009</td>
</tr>
<tr>
<td>Cellulose acetate-organo-montmorillonite</td>
<td>85.7</td>
<td>Zhou et al. 2012</td>
</tr>
<tr>
<td>Sewage sludge</td>
<td>73</td>
<td>Speredych and Bandosz (2007)</td>
</tr>
<tr>
<td>EPI-DMA/bentonite</td>
<td>45.54</td>
<td>Li et al. 2010</td>
</tr>
<tr>
<td>Sludge-based activated carbon</td>
<td>15.0</td>
<td>Wang et al. 2008</td>
</tr>
<tr>
<td>Chitosan modified bentonite</td>
<td>102.0</td>
<td>Guo et al. 2012</td>
</tr>
</tbody>
</table>

Desorption Tests

Desorption tests and the regeneration efficiencies of PDMAECH pulp for ASG were investigated. HCl solution (1 M) was used as an eluent, and the desorption efficiencies for ASG during three successive cycles were 76.3%, 62.5%, and 47.8%. The low desorption efficiencies may be due to the selectivity of the dye anion for elution. The weight loss of the adsorbent was also measured after three adsorption-desorption cycles. A weight loss with a range of 8 to 15% was observed in the desorption tests for the adsorbent after the elution of the HCl solution. It seems that the elution of the HCl solution caused the degradation of cellulose/hemicelluloses structures in PDMAECH pulp, which resulted in a decrease in the weight of the adsorbent. This result was consistent with the work of Osifo et al. (2008), who reported a weight loss (25%) of chitosan beads after five sorption-desorption cycles using HCl solution as an eluent.

CONCLUSIONS

1. This study investigated the effect of p-DMA-co-ECH modification on the surface characteristics and adsorption characteristics of BEKP. The dynamics of the adsorption of the anionic dye ASG onto PDMAECH pulp were also explored. Results showed that modification can change the surface characteristics and enhance the adsorption capacity effectively. The optimum pH for ASG removal by PDMAECH pulp was found to be 4.0, and for BEKP it was 2.0. Under the optimized conditions, a maximum of 105.6 mg g$^{-1}$ ASG removal by PDMAECH pulp could be achieved at 293 K, but a removal of only 9.5 mg g$^{-1}$ was achieved for BEKP. The adsorption of ASG onto PDMAECH pulp and BEKP was exothermic in nature.

2. The pseudo-second-order kinetics model agreed very well with the dynamic behavior of the adsorption of ASG onto both PDMAECH pulp and BEKP under different temperatures. The experimental data for both adsorbents fitted well to the Langmuir adsorption isotherm.

3. The enthalpy changes ($\Delta H^\circ$) for the adsorption process of PDMAECH pulp and BEKP were -10.98 kJ mol$^{-1}$ and -13.88 kJ mol$^{-1}$, respectively, which did not indicate very strong chemical forces between the adsorbed dye molecules and either of the adsorbents. The $\Delta G^\circ$ values were positive: therefore, the adsorption was not spontaneous, and the positive value of $\Delta S^\circ$ suggests an increased randomness at the solid/solution interface; no significant changes occur in the internal structure of the adsorbent through the adsorption of ASG onto PDMAECH pulp.
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