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

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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} ($C_{18}H_{13}N_3Na_2O_8S_2$). 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.

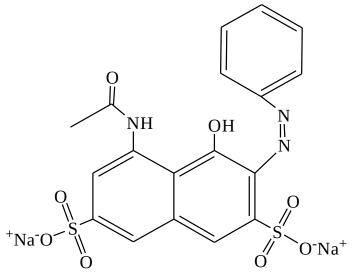

Fig. 1. The molecular structure of Acid Scarlet G

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.

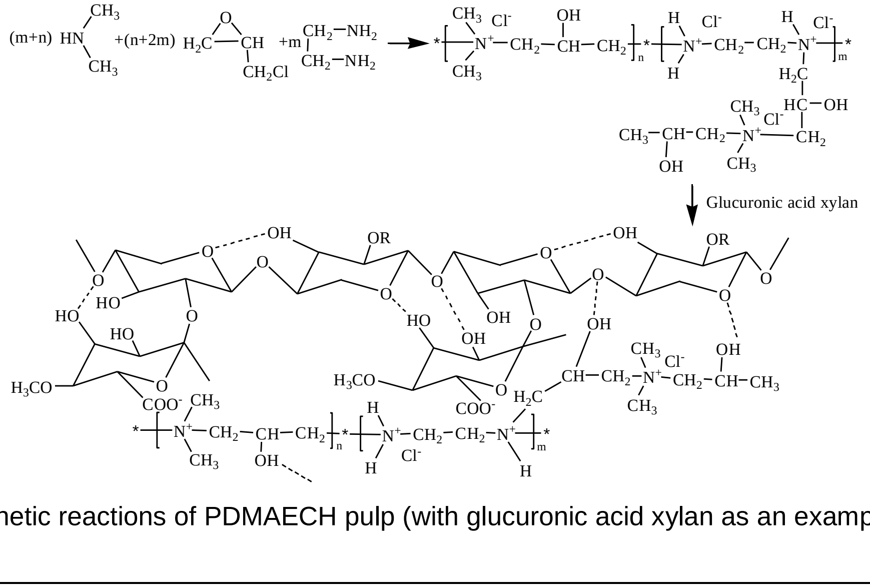

Fig. 2. Synthetic reactions of PDMAECH pulp (with glucuronic acid xylan as an example)

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 ºC. Then, the solution was adjusted to a pH of 9 using 0.1 N NaOH, and the dispersion was stirred at 60 ºC 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 ºC 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

Active sites	BEKP
Total acidic sites (mmol g^{-1})	0.4765
Carboxylic (mmol g^{-1})	0.1235
Lactone (mmol g^{-1})	0.0818
Phenolic (mmol g^{-1})	0.2312
Total basic sites (mmol g^{-1})	0.0147

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.

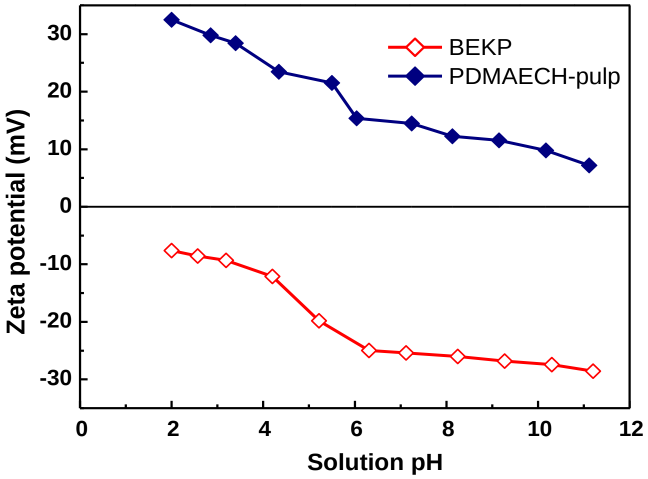

Fig. 3. Effect of pH on the zeta potential changes of BEKP and PDMAECH pulp

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).

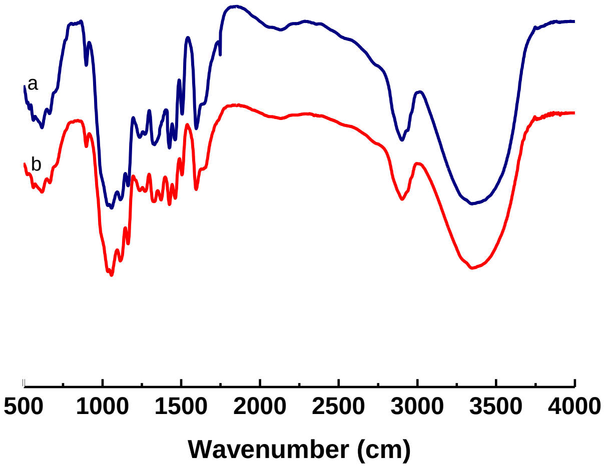

Fig. 4. FTIR analysis of (a) BEKP and (b) PDMAECH pulp

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

Figure 5 shows the solid-state ^{13}C 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).

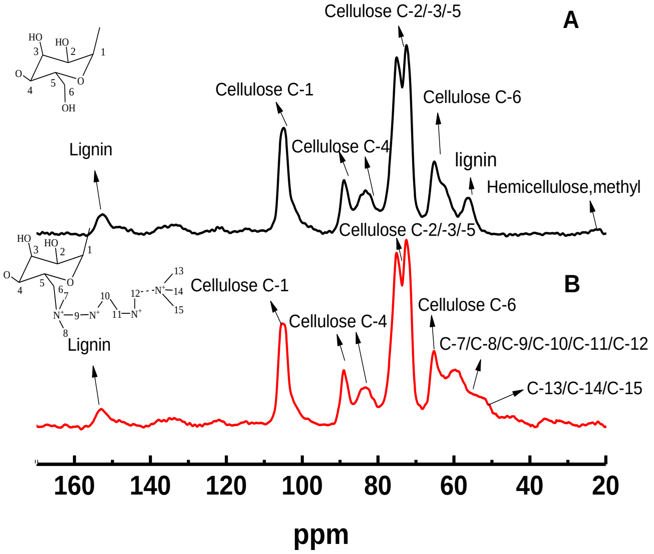

Fig. 5. Solid-state 13CNMR Spectra of (A) BEKP and (B) PDMAECH pulp

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_2N- and -NCH_3. The central chemical shifts for the peaks of -CH_2N- 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.

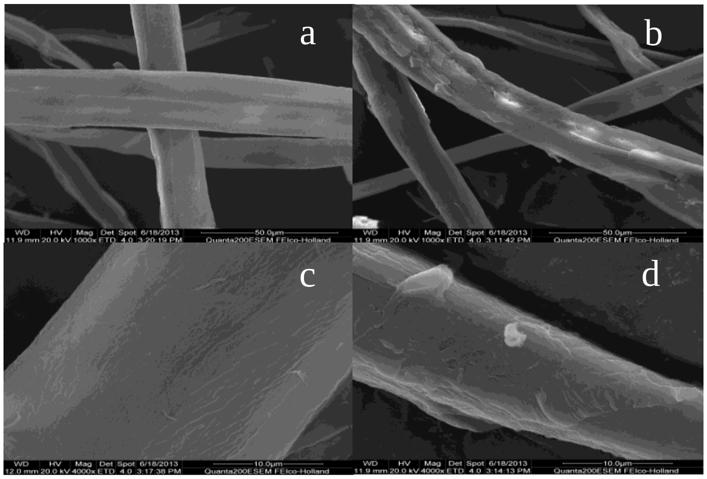

Fig. 6. SEM micrograph of PDMAECH pulp before (a, c) and after (b, d) ASG adsorption

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.

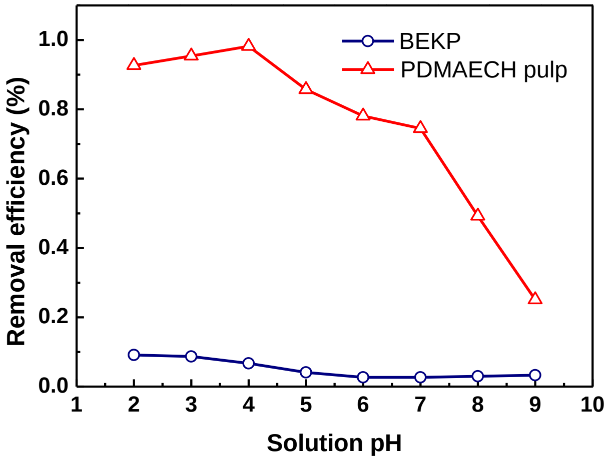

Fig. 7. Effect of pH on the adsorption of ASG onto BEKP and PDMAECH pulp (initial dye concentration: 50 mg L^{-1}; temperature: 293K; shaker speed: 180 rpm; contact time: 180 min.)

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 $-N^+(CH_3)_2(CH_2)(CHOH)(CH_3)$ and $-N^+H_2(CH_2)_2-N^+H_2$ 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.

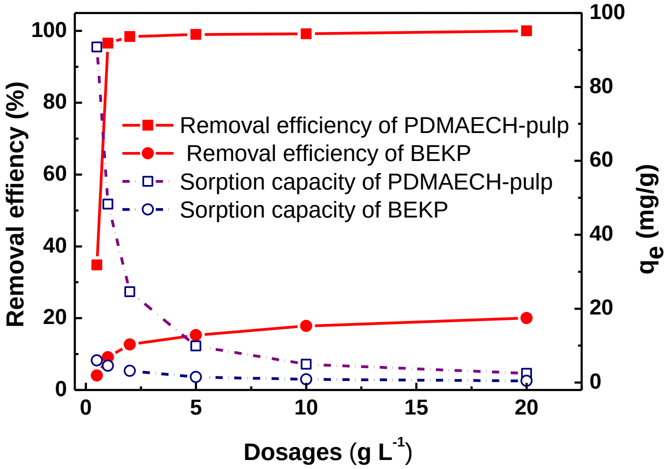

Fig. 8. Effect of dosage on the sorption of ASG (initial dye concentration: 50 mg L^{-1}; temperature: 293K; shaker speed: 180 rpm; original solution pH: 4.0 for PDMAECH pulp and 2.0 for BEKP)

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.

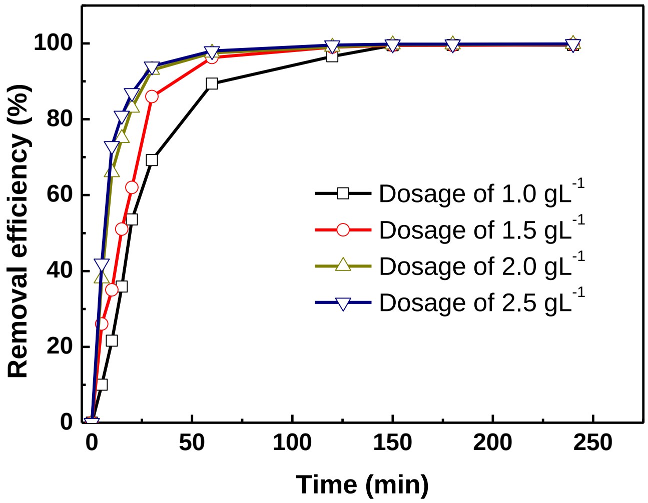

Fig. 9. Effect of contact time for the adsorption of ASG onto PDMAECH pulp at various dosages (initial dye concentration: 100 mg L^{-1}; temperature: 293K; shaker speed: 180 rpm; original solution pH: 4.0)

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):

Langmuir:
$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \tag{1}$$

Freundlich:
$$q_e = K_F C_e^{\frac{1}{n}} \tag{2}$$

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

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}), and 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):

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

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 X^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

BEKP							PDMAECH pulp					
Langmuir model												
T (K)	q_{max}	K_L		χ^2	R^2	S.D.	q_{max}	K_L		χ^2	R^2	S.D.
293	9.5	0.02035		0.02	0.987	7.2	105.6	0.66		0.244	0.999	5.8
303	8.93	0.02462		0.005	0.997	6.0	99.8	0.62		0.215	0.999	4.6
313	8.01	0.0293		0.002	0.998	13.9	91.5	0.48		0.49	0.998	4.7
Freundlich model												
T (K)	K_F	n		χ^2	R^2	S.D.	K_F	n		χ^2	R^2	S.D.
293	2.29	4.37		0.096	0.938	14.8	61.70	9.37		104.1	0.760	15.2
303	2.13	4.35		0.096	0.932	7.2	60.81	10.18		94.69	0.728	13.7
313	2.27	4.91		0.08	0.917	8.3	58.55	11.28		70.87	0.716	14.6
Redlich-Peterson model												
T (K)	K_R	a_R	g	χ^2	R^2	S.D.	K_R	a_R	g	χ^2	R^2	S.D.
293	0.265	0.969	0.034	0.023	0.985	8.0	72.51	0.995	0.703	0.066	0.999	5.7
303	0.220	1.000	0.025	0.006	0.996	6.4	73.65	1.002	0.729	0.217	0.999	6.8
313	0.221	1.017	0.025	0.002	0.998	14.1	78.77	1.004	0.847	0.511	0.998	10.1

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 (ΔG^{o}), enthalpy (ΔH^{o}), and entropy (ΔS^{o}) 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)

$$\Delta G^{0} = -RT\ln\left(K_L\right) \tag{5}$$

$$\ln\left(K_L\right) = \frac{\Delta S^{0}}{R} - \frac{\Delta H^{0}}{RT} \tag{6}$$

where K_L is the Langmuir equilibrium constant (L mol^{-1}), R is the universal gas constant (8.314 Jmol^{-1}K), 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 ΔG^{o} indicate that the sorption of the anionic dyes onto PDMAECH pulp (or BEKP) was spontaneous and thermodynamically favorable. The increase in the value of ΔG^{o} 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 ΔH^o implies that there was loose bonding between the adsorbate molecules and the adsorbent surface (Singh 2000). In addition, the positive value of ΔS^o 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

Adsorbents	T(K)	ΔG^0(KJ/mol)	ΔH^0(KJ/mol)	ΔS^0(J $K^{-1}mol^{-1}$)	R^2
BEKP	293	-23.41	-13.88	32.56	0.996
	303	-23.77			
	313	-24. 06			
PDMAECH pulp	293	-31.70	-10.98	70.70	0.996
	303	-32.38			
	313	-33.12			

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),

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

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)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{8}$$

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

Adsorbents	C_0	$q_{e,\,exp}$	Pseudo-first-order				Pseudo-second-order			
			k_1	$q_{e,\,cal}$	R^2	*S.D.*	k_2	$q_{e,\,cal}$	R^2	*S.D.*
BEKP	50	4.58	0.031	2.95	0.952	20.6	0.0157	4.92	0.998	4.3
	80	5.49	0.037	3.98	0.983	15.8	0.0125	6.14	0.997	6.8
	100	5.88	0.038	4.37	0.982	14.9	0.0119	6.44	0.996	5.5
	150	6.47	0.035	4.56	0.965	17.1	0.0100	7.03	0.997	5.0
PDMAECH -pulp	50	59.4	0.029	20.18	0.952	38.1	3.04×10^{-4}	49.70	0.999	9.4
	80	79.5	0.037	42.78	0.983	26.7	1.57×10^{-3}	76.39	0.999	2.3
	100	86.0	0.036	47.56	0.982	25.8	1.49×10^{-3}	86.28	0.999	0.2
	150	89.8	0.037	50.65	0.965	25.2	1.47×10^{-3}	92.25	0.999	1.6

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 $Q_{\max}$ 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_{max} of ASG on Different Adsorbents

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

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 (ΔH^o) 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 ΔG^o values were positive: therefore, the adsorption was not spontaneous, and the positive value of ΔS^o 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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