Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.981223

57 (2016) 3152–3159
February

Taylor & Francis
Taylor & Francis Group

Synthesis of acrylic-acid-modified shorea sawdust and application in adsorbing toxic organic materials

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Received 24 April 2014; Accepted 20 October 2014

ABSTRACT

Shorea sawdust grafted with poly(acrylic acid) (SD-g-PAA) is synthesized and characterized as an adsorbent of toxic organic compounds. SD-g-PAA copolymers are prepared using Fenton's reagent (Fe^{+2}–H_2O_2) as the redox initiator. The graft copolymerization is examined to determine the effects of temperature, concentrations of $Fe^{+2}_{(aq)}$ and $H_2O_{2(aq)}$, and AA/SD ratio. The obtained maximum grafting percentage of the grafted copolymer is 13.0 ± 0.2%. The grafted copolymer is characterized using Fourier transform infrared spectroscopy and solid-state ^{13}C NMR. A representative SD-g-PAA copolymer is neutralized to a sodium salt (SD-g-PANa) and used in the adsorption of malachite green (MG), methyl violet (MV), and paraquat (PQ). The monolayer adsorption capacities of these substances are 233.7, 312.9, and 164.8 mg/g adsorbent, respectively. The high adsorption capacity of SD-g-PANa for toxic matter indicates its potential in the treatment of wastewater that contains MG, MV, or PQ.

Keywords: Acrylic acid; Shorea sawdust; Graft copolymerization; Adsorption; Toxic materials

1. Introduction

Adsorption is an efficient method for removing pollutants from industrial effluent [1]. Compared to alternative technologies, adsorption is attractive due to its relative simplicity of design, operation and scale-up, high capacity, favorable rate, and low cost [2]. Although, activated carbon remains the most widely used adsorbent, its relatively high cost restricts its use somewhat [3]. This has led to the development of natural materials as alternative adsorbents. Many researchers have studied the feasibility of using low-cost substances such as rice husk [4], perlite [5], zeolite [6], chitin and its derivatives [7,8], bottom ash and de-oiled soya [9–16], hen feathers [17], wheat husk [18], and waste carbon slurry [19] as adsorbents for pollutants from wastewaters. Activated carbon prepared from waste rubber [20] or fertilizer waste [21] can be used to adsorb acid blue 113 or heavy metal ions.

Sawdust is the main waste of the furniture industry. It is rarely reused. Indian rosewood sawdust has been used in the removal of basic dye [22], and polyaniline coated sawdust and Meranti wood sawdust have been used to adsorb metal ions [23,24]. Rattan or wood sawdust were used to prepare the activated carbon and served as adsorbents of methylene blue [25,26]. Shorea sawdust has not been applied for practical use.

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In this work, poly(acrylic acid)-grafted shorea sawdust (SD-g-PAA) is synthesized and applied as an adsorbent of methyl violet (MV), malachite green (MG), and paraquat (PQ) in aqueous solution. MV is a triphenylmethane dye that is used as an antiallergen and bactericide. It may cause severe skin, eye, and respiratory tract irritation in humans [27]. It increases the organic content in the wastewater of textile and printing industries. MG is a cationic dye that is widely used as a fungicide in the aquaculture industry to control fish parasites. It has also been found to exhibit carcinogenic, genotoxic, and mutagenic properties [28]. PQ has been extensively used as an herbicide. During the past decade, studies on PQ have focused on the mechanism of PQ-induced Parkinson's disease [29,30] or evaluation of the antidotal feasibility of lysine acetylsalicylate [31]. A short summary of the adsorption results for MG, MV, and PQ is given in Table 1.

2. Materials and methods

2.1. Materials

SD sieved through 30–40 meshes was obtained from a furniture factory in southern Taiwan. PQ (24% w/w, 10 mL of which can be fatal if swallowed), purchased from Comlet Chemicals Co. (Taichung, Taiwan), was diluted to a suitable concentration for use. AA, MV, MG, ferrous ammonium sulfate, hydrogen peroxide, ammonium chloride, sodium dithionite, and acetone were of analytical grade or better and used as received.

2.2. Graft copolymerization

Graft copolymerization was performed in a 50-mL flask with a magnetic stirrer in a temperature-controlled water bath. 1 g of SD was stirred in 40 mL of $Fe^{+2}_{(aq)}$ aqueous solution (concentration ranged from 0.2×10^{-3} to 10×10^{-3} M) in a flask, which was purged gently with nitrogen for around 30 min at the reaction temperature. AA monomer and $H_2O_{2(aq)}$ were separately added to the flask in a series to initiate a 1 h reaction. The copolymerization products were filtered, washed thoroughly with deionized water, and extracted using acetone in a Soxhlet apparatus for 48 h to obtain the pure PAA-grafted SD copolymer (SD-g-PAA), free of the PAA homopolymer. The grafting percentage was evaluated gravimetrically [32,33].

2.3. Characterization of grafted copolymer

Fourier transform infrared (FT-IR) analysis of copolymer samples was performed using a Perkin-Elmer FT-IR spectrometer in the wavenumber range of 4,000–400 cm^{-1}. Solid-state ^{13}C NMR (nuclear magnetic resonance) spectra were obtained using a 400-MHz Bruker Advance NMR spectrometer. Each spectrum was obtained by averaging 8,600 scans. The experiment was conducted with the sample spinning at a rate of 6.2 kHz. A 5.0-μs pulse, corresponding to a 90° P1 angle, was chosen. A contact time of 1 ms and a delay of 5 s were set. All spectra were recorded at a sample temperature of 25°C.

Table 1
The results of various reported studies on the adsorption of MG, MV, and PQ by various adsorbents

Toxic material	Adsorbents	Monolayer capacity, q_m mg/g adsorbent	References
Malachite green	Rattan sawdust	62.71	[37]
	Treated ginger waste	84.03 (30°C)	[38]
	Treated ginger waste	163.9 (40°C)	[38]
	Treated ginger waste	188.6 (50°C)	[38]
	Pine wood decayed by fungi Poria cocos	42.63	[39]
	activated carbon derived from borassus		
	Aethiopum flower biomass	48.48 (300 K)	[40]
Methyl violet	Halloysite nanotubes	113.64	[41]
	Halloysite nanotube-Fe_3O_4 composite	80.64	[42]
	Granular activated carbon	95	[43]
	Polyacrylamide	1,136	[44]
Paraquat	Activated carbon	90–100	[45]
	Methacrylic acid-modified rice husk	317.7	[4]
	acrylic acid-modified middle		
	Deacetylated chitosan	396.7	[32]

2.4. Neutralization of grafted copolymer

The prepared SD-g-PAA copolymer was placed in a conical flask that contained 0.1 M $NaOH_{(aq)}$. The solution was stirred for 1 h before being filtered; it was then washed in distilled water until it became neutral. It was then dried at 50°C under vacuum until a constant weight was measured. The neutralized product was the sodium salt of PAA-grafted sawdust (SD-g-PANa), which was used to adsorb toxic organic compounds from aqueous solution.

2.5. Adsorption of toxic compounds

Adsorption experiments were carried out in a 1-L resin kettle at 37.5°C for 2 h. The agitation rate was controlled to be around 600 rpm to prevent the liquid film diffusion. The adsorption solution composed 0.5 g of SD-g-PANa powder, with a particle size of 0.39–0.51 mm, as the adsorbent. The pH values of adsorption solutions were 4.10 ± 0.50, 4.50 ± 0.50, and 4.70 ± 0.05 for MG, MV, and PQ, respectively, without using any chemical reagent. Each sample (0.2 mL) was removed using a micropipette at various times to measure the concentration of toxic organic materials.

2.5.1. Adsorption of MG and MV

The initial concentrations for the adsorption experiment were 75, 100, 125, 150, 175, and 200 ppm for MG and 100, 150, 200, 250, 300, and 350 ppm for MV. 0.2-mL samples were extracted using a micropipette at various times and analyzed using a Spectrumlab 22PC spectrophotometer at $\lambda_{\max}$ values of 617 and 585 nm for MG and MV, respectively.

2.5.2. Adsorption of PQ

The initial concentrations of PQ were 48, 72, 96, 120, 144, and 168 ppm. 0.2-mL samples were extracted using a micropipette at various times. The collected samples were then added to a sodium dithionite/saturated ammonium chloride solution and analyzed using a Spectrumlab 22PC spectrophotometer at a $\lambda_{\max}$ value of 394 nm.

3. Results and discussion

3.1. Graft copolymerization

The graft copolymerization of AA and SD was studied at various ratios of AA/SD, reaction temperatures (*T*), and concentrations of $Fe^{+2}_{(aq)}$ ($[Fe^{+2}_{(aq)}]$) and $H_2O_{2(aq)}$ ($[H_2O_{2(aq)}]$). Experiments were performed by varying one factor at a time, with the remaining factors held constant. Fig. 1(a) shows the effect of the AA/SD ratio, ranged from 1.0 to 5.0, on the grafting percentage. The grafting percentage of the copolymer increases clearly with increasing AA/SD at lower levels and mildly at higher levels. The optimal AA/SD ratio is 2.0 based on economic and environmental considerations. Fig. 1(b) shows the effect of temperature on the grafting percentage in the temperature range of 50–75°C. The maximum grafting percentage was obtained at 60°C. This result can be attributed to the competition between the graft copolymerization and homo-polymerization of the AA monomer in the reaction solution. The same trend of grafting percentage was obtained (maximum at around 1×10^{-3} M $[Fe^{+2}_{(aq)}]$) when $[Fe^{+2}_{(aq)}]$ was varied, while the other reaction variables were held constant, as shown in Fig. 1(c). At higher $[Fe^{+2}_{(aq)}]$, an increase of $[Fe^{+2}_{(aq)}]$ parallels a decrease in graft copolymer because $Fe^{+2}_{(aq)}$ destroys OH radicals and increases the $Fe^{+3}_{(aq)}$ concentration [34]. Fig. 1(d) reveals that the grafting percentage initially increases with $[H_2O_{2(aq)}]$ and then decreases significantly for $[H_2O_{2(aq)}]$ of over 0.2 M. This result can be attributed to further increases in $[H_2O_{2(aq)}]$ not favoring grafting due to the side reactions of the $H_2O_{2(aq)}/Fe^{+2}_{(aq)}$ redox system. To obtain the highest grafting percentage ($13.0 \pm 0.2\%$), the optimal reaction conditions are an AA/SD ratio of 2.0, a temperature of 60°C, 1×10^{-3} M $[Fe^{+2}_{(aq)}]$, and 0.2 M $[H_2O_{2(aq)}]$.

3.2. Characterization of grafted copolymer

FT-IR investigations were performed to elucidate the complex interaction between SD and PAA. Fig. 2(a) shows the spectrum of SD. The broad band between 3,000 and 3,700 cm^{-1} indicates the presence of OH groups on the surface of SD. FT-IR analysis of SD-g-PAA is shown in Fig. 2(b). The peaks at about 1,730 and 1,058 cm^{-1} are assigned to the stretching vibration of C=O and C–O from carboxylic groups, respectively [35]. All of these results reveal that the AA monomer was grafted onto the main chain of SD.

Fig. 3 shows the solid-state ^{13}C NMR spectra of SD and SD-g-PAA. Fig. 3(a) reveals solid-state ^{13}C NMR signals of C1–C6 in the cellulose molecule. The spectrum of SD-g-PAA exhibits an extra peak at 38.7 ppm, which corresponds to the C_β of PAA, and a middle signal at about 174.9 ppm, which is associated with the carbonyl carbon of PAA [36]. This result confirms that PAA was grafted onto SD.

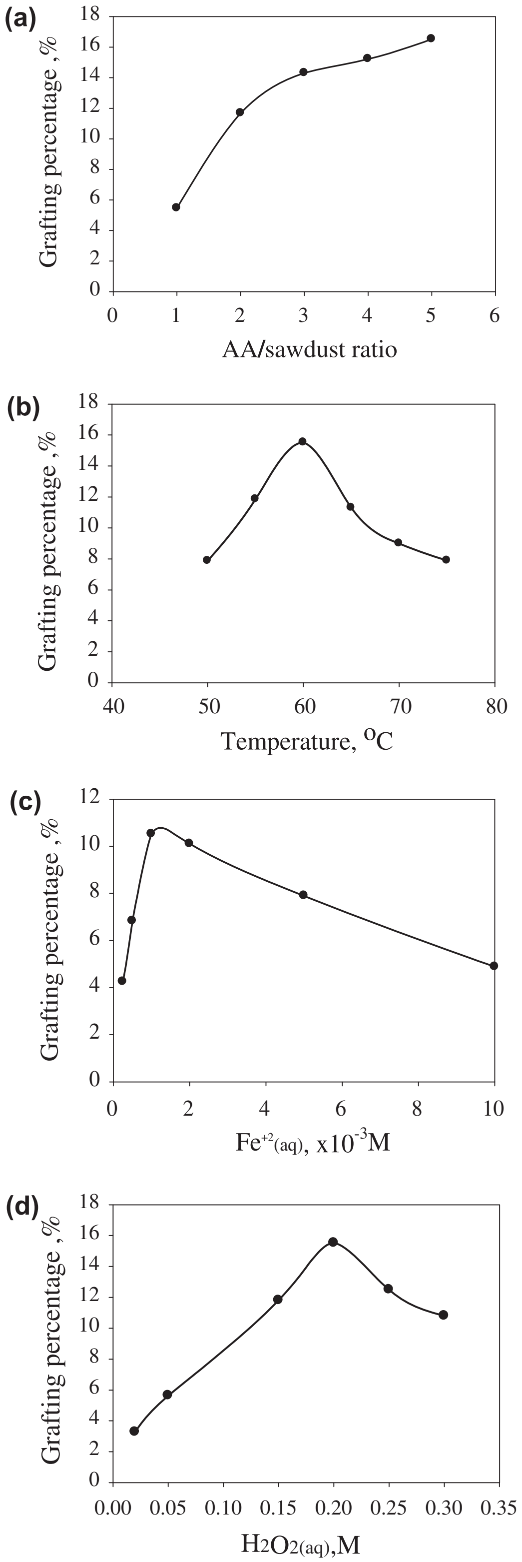

Fig. 1. Grafting percentages of SD-g-PAA at various (a) AA/sawdust ratios, (b) temperature, (c) [$Fe^{+2}_{(aq)}$], and (d) $H_2O_{2(aq)}$ concentrations.

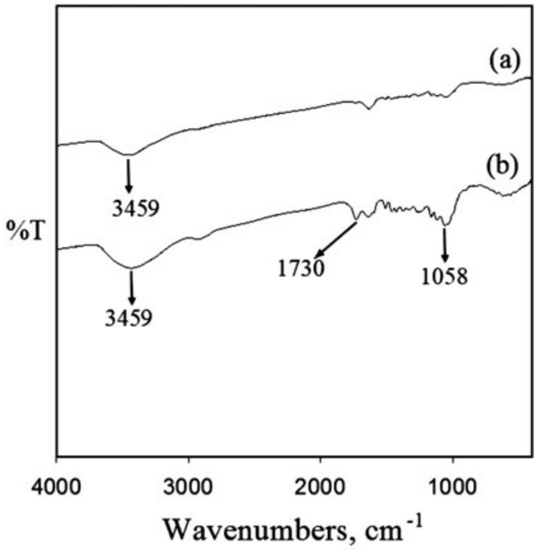

Fig. 2. FT-IR spectra of (a) SD and (b) SD-g-PAA.

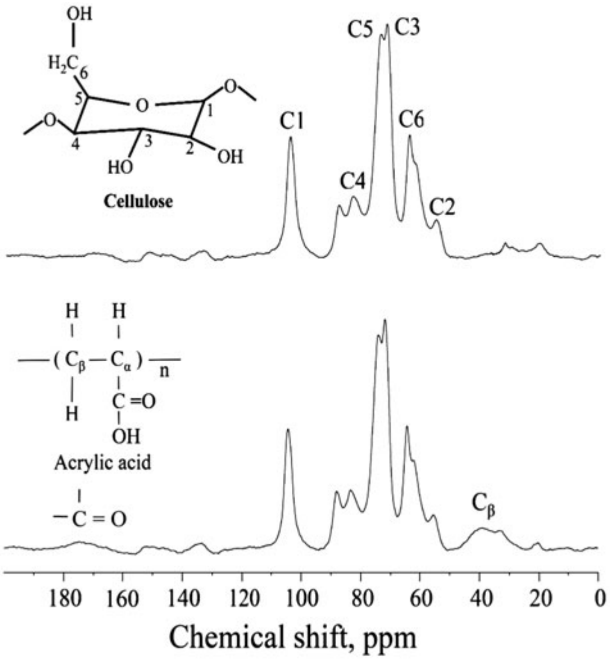

Fig. 3. Solid-state ^{13}C NMR spectra of (a) SD and (b) SD-g-PAA.

3.3. Adsorption of toxic organic compounds in aqueous solution

The SD-g-PAA copolymer with a 13.0% grafting percentage was neutralized in 0.1 M $NaOH_{(aq)}$ to prepare SD-g-PANa and used to adsorb MG, MV, and PQ, respectively. The equilibrium adsorptions (q_e) and equilibrium concentrations (C_e) of individual toxic organic compounds in aqueous solution were recorded at 2 h for various initial concentrations. Table 2 lists the original adsorption data of PQ, MV, and MG.

3.3.1. Adsorption of MG

Fig. 4(a) plots the adsorption experiment data and the Langmuir (LM) and Freundlich (FD) correlations of MG. The LM and FD isotherms and their relationship coefficient, r, are given as follows:

$$\text{LM} \qquad q_e = (233.7 \times 1.149C_e)/(1 + 1.149C_e) \quad r = 0.9939 \tag{1}$$

$$\text{FD} \qquad q_e = 157.0 \times {C_e}^{1/10.54} \quad r = 0.8837 \tag{2}$$

Since the r value of the LM isotherm (0.9939) is higher than that of the FD isotherm (0.8837), the LM model fitted the experimental results more closely than the FD model. The monolayer adsorption capacity calculated from the LM isotherm is 233.7 mg/g-adsorbent. This result is better than those obtained for rattan sawdust [37], treated ginger waste [38], decayed pine wood [39], and activated carbon derived from *borassus aethiopum* flower biomass [40]. However, the preparation of activated carbon from natural resources requires a high-temperature or strong-acid process. The synthesis and application of SD-g-PANa adsorbent are more environmentally friendly. The results reveal that SD-g-PANa is a potential adsorbent of MG for wastewater treatment in the aquaculture or coloring industries.

Table 2
Original adsorption data of PQ, MV, and MG

Toxic material	C_0, ppm	C_e, ppm	q_e, ppm
Paraquat	48	14.59	67.00
	72	25.09	93.82
	96	38.79	114.4
	120	57.07	125.9
	144	81.64	127.6
	168	104.2	127.7
Methyl violet	100	4.84	190.3
	150	18.36	263.3
	200	53.8	292.4
	250	97.7	304.6
	300	145.8	308.4
	350	195	310.0
Malachite green	75	1.523	147.0
	100	3.482	193.0
	125	13.09	223.8
	150	37.76	224.5
	175	61.04	227.9
	200	85.94	228.1

C_0: initial concentration of toxic material.

C_e: adsorption equilibrium concentration of toxic material in aqueous solution.

q_e: adsorption equilibrium concentration of toxic material in adsorbent.

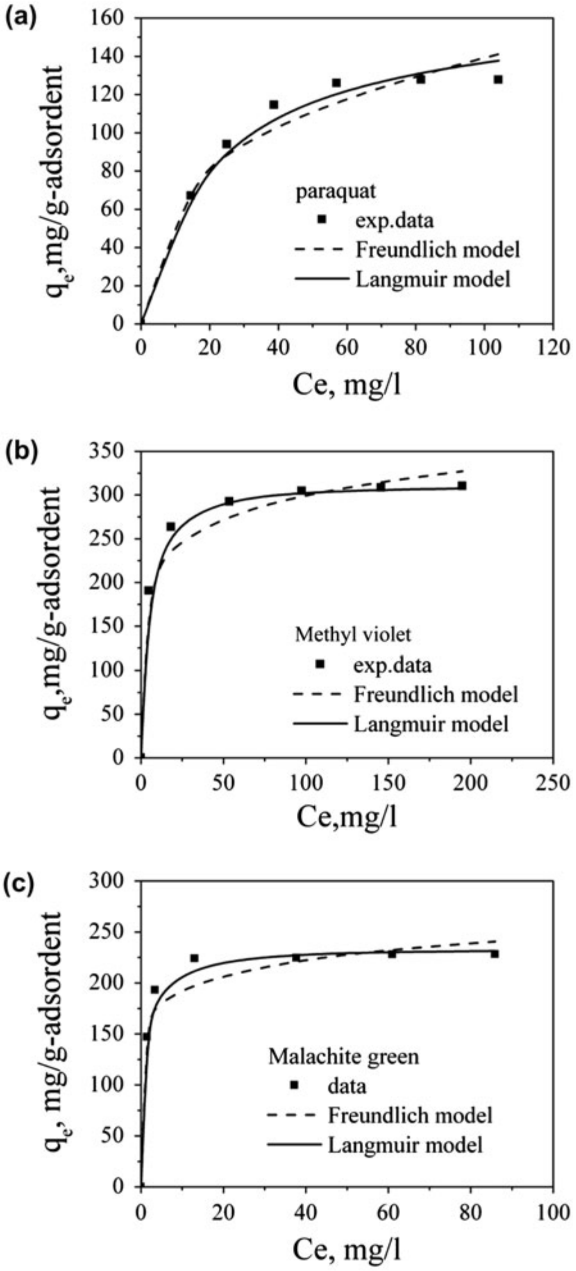

Fig. 4. LM and FD isotherms for adsorption of (a) PQ, (b) MV, and (c) MG by SD-g-PANa adsorbent.

3.3.2. Adsorption of MV

Fig. 4(b) shows the adsorption experiment data and the LM and FD correlations of MV. The LM and FD isotherms and their relationship coefficient, r, are given as follows:

$$\text{LM} \quad q_e = (312.9 \times 0.3192C_e)/(1 + 0.3192C_e) \quad r = 0.9992 \tag{3}$$

$$\text{FD} \quad q_e = 167.1 \times C_e^{1/7.849} \quad r = 0.9473 \tag{4}$$

The LM model fitted the experimental results better than the FD model (higher r value). The calculated monolayer adsorption capacity is 312.9 mg/g-adsorbent. This result is higher than those obtained for halloysite nanotubes [41,42] and granular activated carbon [43], but lower than that for polyacrylamide [44]. The value of n in the FD isotherm is 7.849, which indicates that the adsorption of MV using SD-g-PANa is favorable at lower initial concentrations. The results reveal that SD-g-PANa is a potential adsorbent of MV for wastewater treatment in the coloring or printing industries.

3.3.3. Adsorption of PQ

SD-g-PANa was used to adsorb PQ in aqueous solution. The adsorption was rapid in the first few minutes reaching equilibrium in around 20 min. Fig. 4(c) shows the adsorption experiment data and the LM and FD correlations of PQ. The LM and FD isotherms and their relationship coefficient, r, are given as follows:

$$\text{LM} \quad q_e = (164.8 \times 0.04893C_e)/(1 + 0.04893C_e) \quad r = 0.9870 \tag{5}$$

$$\text{FD} \quad q_e = 31.54 \times C_e^{1/3.101} \quad r = 0.9318 \tag{6}$$

The LM model fitted the experimental results better than the FD model. The calculated monolayer adsorption capacity is 164.8 mg/g-adsorbent. This result is about 1.6 times higher than that for an activated carbon cartridge, and 2.7 times higher than that for Fuller's earth [45]. The results reveal that SD-g-PANa is a potential adsorbent of PQ for PQ-poisoned patients for clinical emergency rescue.

The free energy change (ΔG) was evaluated to verify the mechanism of adsorption. The LM constant can be used to calculate the change in free energy, using the following equation [46].

$$\Delta G = -RT \ln K$$

where R is the gas constant, T is the absolute temperature, and K is the adsorption constant. The calculated ΔG values were −18.19, −14.88, and −10.04 kJ/mol for MG, MV, and PQ, respectively. These results reveal that the adsorptions of MG, MV, and PQ are more favorable at lower concentration.

4. Conclusion

PAA-grafted SD can be prepared via grafting copolymerization using Fenton's reagent as the redox initiator. The main factors affecting the grafting percentage of copolymer product are the reaction temperature, ratio of AA/SD, and the concentrations of $Fe^{+2}_{(aq)}$ and $H_2O_{2(aq)}$. The highest grafting percentage of AA onto SD (13.0%) was obtained when the copolymerization reaction was conducted with an AA/SD ratio of 2.0, a temperature of 60°C, 1×10^{-3} M [$Fe^{+2}_{(aq)}$], and 0.2 M [$H_2O_{2(aq)}$]. Carboxylic groups grafted onto the surface of SD can be neutralized to a salt with dilute $NaOH_{(aq)}$ and readily utilized to adsorb MV, MG, and PQ ions from aqueous solution. The rapid uptake and high adsorption capacity make the PAA-modified SD a highly promising alternative adsorbent of many toxic organic compounds. The LM isotherms are more accurate than FD isotherms. The monolayer adsorption capacities are 233.7, 312.9, and 164.8 mg/g-adsorbent for MG, MV, and PQ, respectively. Therefore, PAA-modified SD is a potential adsorbent in the wastewater treatment of various industries.

Acknowledgments

The authors would like to thank Comlet Chem. Ind. Co. Ltd for supplying the raw materials.

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