

Preparation for Graft Copolymers of Sawdust/Vinyl Monomers and Their Application for Removal of Dye

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ABSTRACT: A kind of cationic exchanging resin of carboxyl sawdust (CSD) was fabricated through the hydrolysis of graft copolymers of sawdust with acrylonitrile (SAN) and sawdust with acrylamide (SAA) that were made by initiator $\text{Fe}^{2+}/\text{H}_2\text{O}_2$. A study of the graft copolymerization was conducted for initiator usage, vinyl monomer usage, and reaction temperature. The hydrolysis under basic/acid conditions was also studied for the yield and acid value of CSD followed to adsorb Basic Pink dye (BPD). Our results show the following: (1) graft copolymers (SAN and SAA) with a high rate of graft copolymerization are readily prepared by suitable usages of initiator and vinyl monomer under a certain temperature; (2) adsorption capacity of CSD is relative to pH of BPD solution and reaches the most adsorption capacity at $\text{pH} \approx 6$; (3) adsorption capacity of CSD increases along with the augment of its acid value; and (4) the adsorption capacity of the CSD toward BPD increases along with augment of initial concentration of the adsorbate and reaches about 500 mg/g. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 2390–2396, 2002

Key words: sawdust; acrylonitrile; acrylamide; graft copolymerization; hydrolysis; adsorption; dye

INTRODUCTION

The removal of heavy metal ions and toxic dye from sewage and industrial wastewater has been given much attention. The effective and economic removal of these, therefore, is an important task. Ion exchange and precipitation are efficient techniques for this. However, the manufacturing of ion-exchange resins in itself is usually associated with hazards and pollution. On the other hand, natural materials that are easily available can

achieve the goal at very little or no cost. Polymer-supported reactive reagents have been considered for the selective extraction processes of metal ions from aqueous solution.^{1–3} Because natural polymers, agricultural waste products, and byproducts have many advantages as a result of their highly porous structure and hydrophilic nature, they lead to a great adsorption capacity and high adsorption rate of metal ions. Thus, many studies concerning the use of agricultural waste products/byproducts for adsorption of metal ions have been fulfilled.^{4–8} However, the removal of dye by them has not been reported.

This article centers on the preparation of a kind of carboxyl sawdust (CSD) through graft co-

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polymerization of sawdust with vinyl monomers and hydrolysis. The work is further extended to include discussion of reaction conditions along with adsorption properties of a cationic dye—Basic Pink dye (BPD).

EXPERIMENTAL

Materials

Sawdust was used (particle size: $\phi \leq 2$ mm) supplied by Institute of Chemical Processing and Utilization of Forest Products, Nanjing, China. Acrylonitrile, acrylamide, NaOH, H_2O_2 , $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, acetone, and *N,N*-dimethylformamide (DMF) were chemically pure. BPD was purchased from local stores (industry grade).

Apparatus

A PerkinElmer Lambda-6 model ultraviolet-visible spectrophotometer was used for obtaining data.

Preparation for the Graft Copolymers

Graft Copolymer of Sawdust with Acrylonitrile (SAN). About 5.0 g of sawdust and a certain mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were added into a four-necked flask containing 100 mL of distilled water stirred at ambient temperature for 15 min, filtered, and then washed with distilled water for four times. The filter cake was put into the glass vessel with the addition of certain volumes of acrylonitrile and H_2O_2 , agitated, and kept at a certain temperature for a specific time period. The contents of the glass vessel were filtered after the reaction was over and washed with distilled water until the filter liquor was colorless and clean. The product was dried at 60–70°C, weighted, and immersed in DMF several times until the weight of the dried product was constant.

Graft Copolymer of Sawdust with Acrylamide (SAA). The preparation procedure for SAA was the same as SAN.

The rates of graft copolymerization and homopolymerization and graft mass on sawdust were calculated as follows

$$X = \frac{A - B}{M} \times 100\% \quad (1)$$

where X is the rate of graft copolymerization (%), A is the dry weight of graft copolymer after being immersed in DMF (g), B is the weight of sawdust before the reaction (g), and M is the monomer weight (g)

$$Y = \frac{C - A}{M} \times 100\% \quad (2)$$

where Y is the rate of homopolymerization (%), C is the weight of graft copolymer before being immersed in DMF (g), and A and M are the same as the formula in eq. (1)

$$Z = \frac{A - B}{B} \times 100\% \quad (3)$$

where Z is the graft weight on sawdust (%), and A and B are the same as the formula in eq. (1)

Hydrolysis of the Graft Copolymer: Method (A)

Approximately 2.0 g of SAN or 2.0 g of SAA was added into a 100-mL conical flask containing a certain volume of NaOH water solution and kept at a specific temperature for a while. It was then filtered and immersed in HCl solution for acidation, washed by distilled water until pH of the filter liquor was about 7, and dried at 60–70°C. The hydrolysis product was CSD.

Hydrolysis of the Graft Copolymer: Method (B)

About 2.0 g of SAN or 2.0 g of SAA was added into a 100-mL conical flask containing a certain volume of HCl water solution and kept at a certain temperature for a while, filtered, and washed by distilled water until the pH of the filter liquor was about 7 and dried at 60–70°C. The hydrolysis product was also CSD.

Determination for the Acid Value of CSD

About 0.500 g of CSD was placed into a conical flask with the addition of 10 mL 0.1 mol/L of NaOH and vigorously shaken for a while and then kept still at ambient for 1 h. The contents of the glass vessel were filtered and washed with distilled water until the effluent acquired pH $\approx$ 7. The filtrate was added by two to three drops indicator of methyl red and titrated with 0.1 mol/L HCl until the equivalent point was reached. In the meantime, a blank experiment was made. The

acid value of CSD was calculated by the following formula:

$$E = \frac{(V_1 - V_2)C_{\text{HCl}}}{m}$$

where E is the acid value of CSD (mmol/g), V_1 is the volume of HCl consumed by the blank solution (mL), V_2 is the volume of HCl consumed by the sample solution (mL), C_{HCl} is the concentration of HCl standard solution (mol/L), and m is the mass of the sample (g).

Adsorption Experiment for BPD

The Standard Cure. Approximately 1.000 g of BPD was placed into a 1000-mL flask followed by the addition of distilled water until the total volume of the contents in the flask was equal to 1000 mL. A series of solutions with different concentrations of BPD (from 0 to 200 mg/L) were made by dilution of the 1000-mg/L solution. The maximum adsorption wavelength of BPD ($\lambda_{\text{max}} = 553.0$ nm) was obtained by scanning in the range of 200–900 nm. The adsorption abundance of the samples was determined with the spectrophotometer in $\lambda_{\text{max}} = 553.0$ nm. The standard cure could be acquired through the concentration via the abundance of samples.

About 0.100 g of CSD was put into a 100-mL conical flask with the addition of BPD solution. The contents of the flask were kept at different temperatures for 2 h and then filtered. The solution before adsorption and the solution after adsorption were determined in $\lambda_{\text{max}} = 553.0$ nm for the adsorption abundance. The concentration of BPD in the solution was acquired from the preceding standard cure. All samples, of which concentration was more than 200 mg/L, were diluted 10 times before determination. The adsorption capacity of sample was calculated as follows

$$Q = \frac{V(C_0 - C_e)}{M}$$

where Q is the adsorption capacity of sample (mg/g), V is the volume of solution (100 mL), C_0 is the initial concentration of BPD (mg/L), C_e is the concentration of BPD after the adsorption equilibrium (mg/L), and M is the mass of CSD (0.100 g).

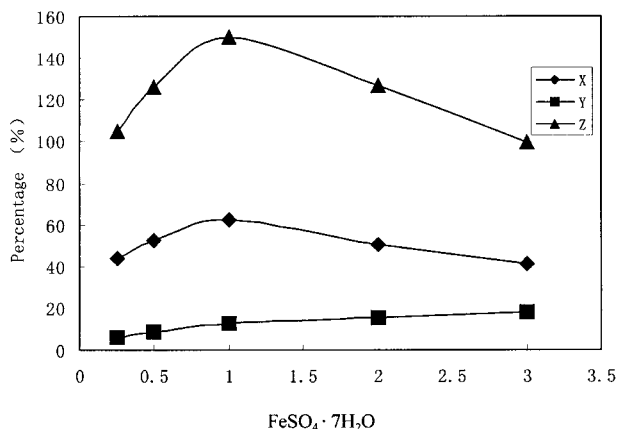


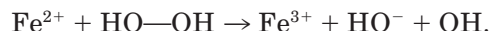
Figure 1 Effect of usage of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ on graft copolymerization for SAN.

RESULTS AND DISCUSSION

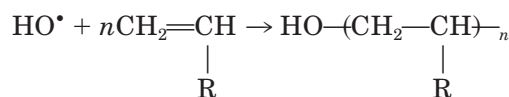
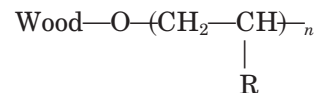
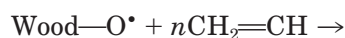
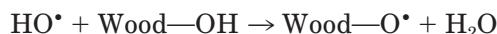
Factors Affecting Graft Copolymerization

Initiator Usage

$\text{Fe}^{2+}/\text{H}_2\text{O}_2$ is a kind of redox initiator that releases hydroxy radical $\text{HO}^\bullet$ through one-electron transportation as follows



Hydroxy radical initiates the graft copolymerization between sawdust and vinyl monomer. On the other hand, hydroxy radical also initiates the homopolymerization of vinyl monomers. The reaction procedures are shown as follows



In Figure 1, the rate of graft copolymer and the graft mass of sawdust increased with the usage

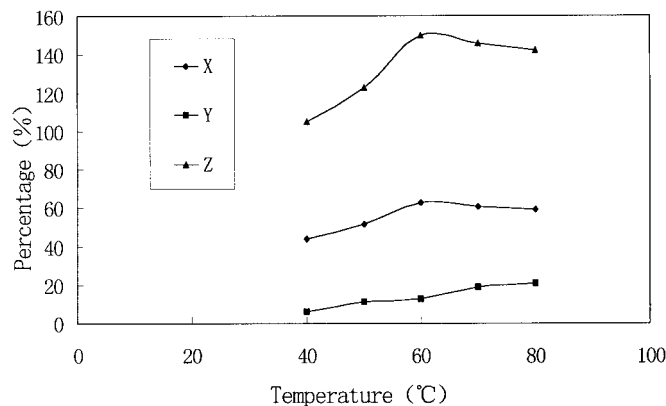


Figure 2 Effect of temperature on graft copolymerization for SAN.

increment of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and decreased when the usage was over 1 g, but the rate of homopolymer always increased. We assumed that the phenomena resulted from the content increment of Fe^{2+} in the water phase. The number of Fe^{2+} adsorbed on the surface of wood decides the number of active center on the surface of sawdust, of which the groups could adsorb cations. Thus, the increased usage of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ resulted in the enlargement of the graft rate. On the other hand, the number of Fe^{2+} in the liquid phase, which decided the quantity of free radical in aqueous, also increased with the increased usage of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. The enlargement of the quantity of free radical solved in the liquid phase resulted in the ascending homopolymer rate.

Reaction Temperature

As shown in Figure 2, the graft rate tended to decrease, whereas the temperature was over 60°C. The number of Fe^{2+} in the water phase

went up with the upgrade of temperature as a result of the desorption of Fe^{2+} from the surface of sawdust. Consequently, the free radicals that initialized the homopolymerization became more and more and resulted in an upward tendency of the homopolymerization rate that ultimately out-reached the graft rate. Hence, in a certain temperature the rate of graft copolymerization began with its downward tendency.

Usage of Acrylonitrile

In Figure 3, the optimal usage of acrylonitrile was 15 mL because of the reductions of the rate of graft copolymerization and the graft mass on sawdust.

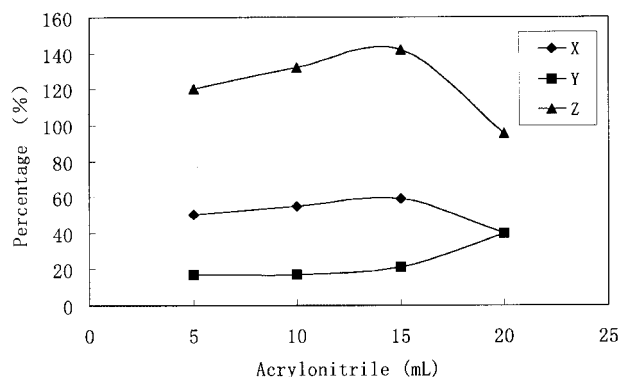


Figure 3 Effect of usage of acrylonitrile on graft copolymerization for SAN.

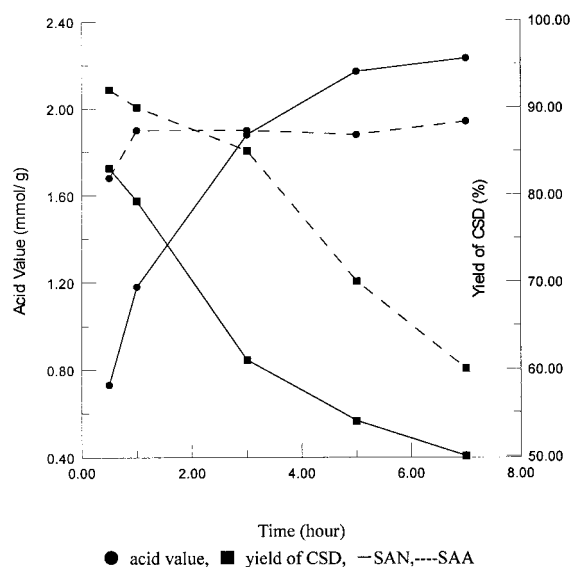


Figure 4 Effect of time of the hydrolysis on acid value and yield of CSD.

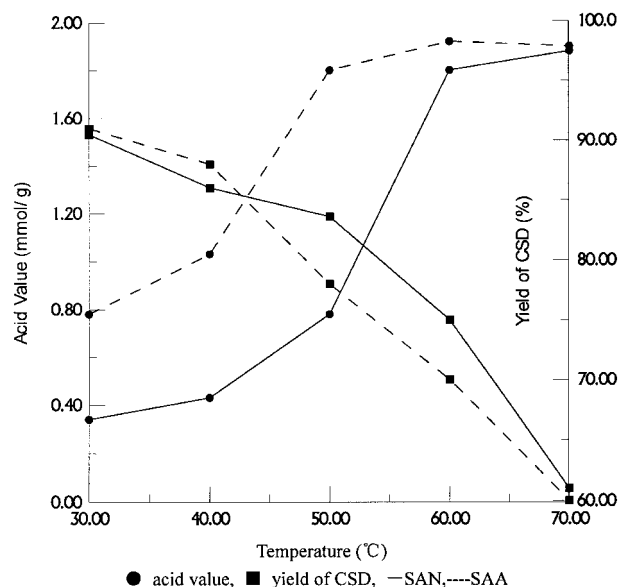


Figure 5 Effect of temperature of the hydrolysis on acid value and yield of CSD.

Factors Affecting the Acid Number and Yield of CSD

Two kinds of graft copolymers, SAN and SAA, were hydrolyzed under basic and acidic conditions, respectively. Factors affecting the acid value and yield of CSD are discussed as follows.

Hydrolysis under Basic Condition

With the prolonging of time, temperature upward, or the augment of NaOH concentration, the

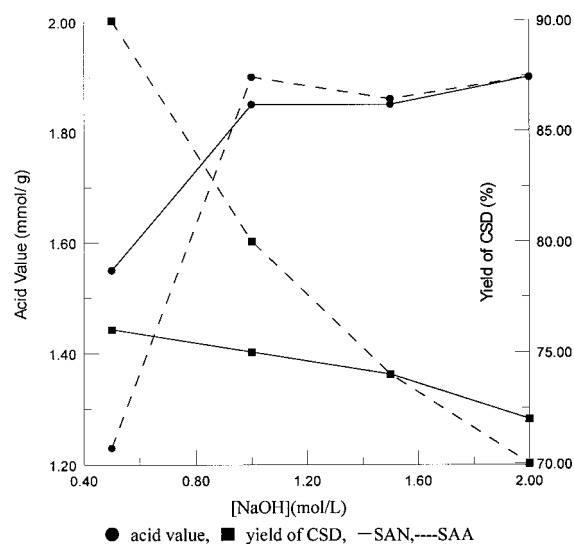


Figure 6 Effect of [NaOH] on acid value and yield of CSD.

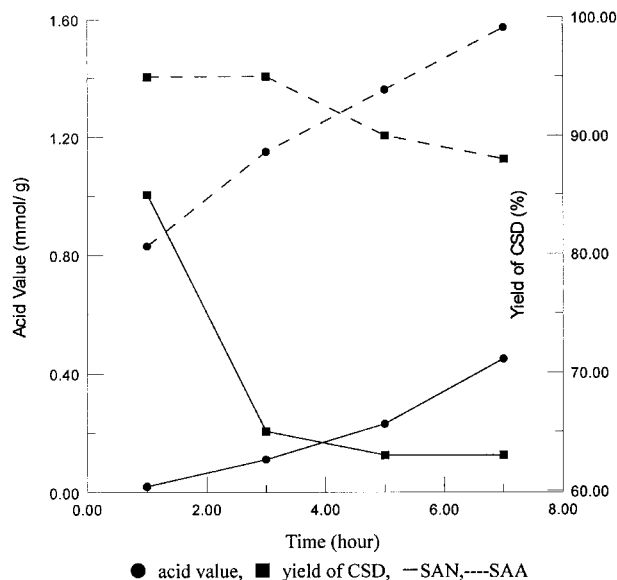


Figure 7 Effect of time of the hydrolysis on acid value and yield of CSD.

acid value of CSD became higher and higher (shown in Figs. 4, 5, and 6, respectively), but the yield of CSD became lower and lower because of the degradations of lignin and cellulose in the sawdust.

Hydrolysis under Acidic Condition

The acid value of CSD became higher and higher along with the prolonging of time, temperature upward, or the augment of HCl concentration

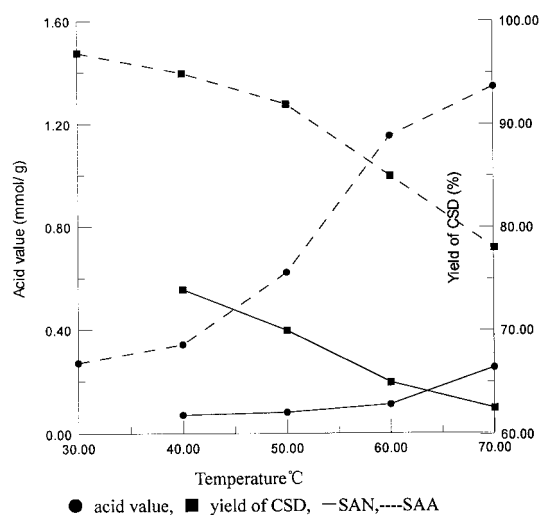


Figure 8 Effect of temperature of the hydrolysis on acid value and yield of CSD.

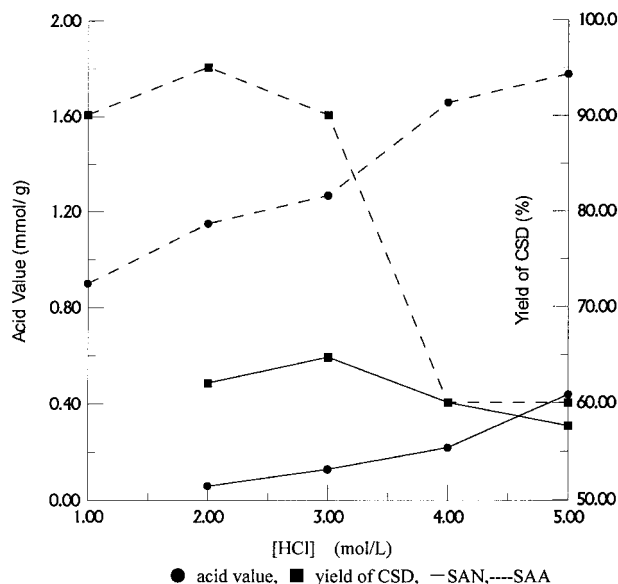


Figure 9 Effect of [HCl] on acid value and yield of CSD.

(shown in Figs. 7, 8, and 9, respectively), but the yield of CSD became lower and lower because lignin and cellulose of the sawdust were also degradable in the acid condition.

Adsorption Experiment of CSD to BPD

Effect of Temperature on the Adsorption Capacity

As was shown in Figure 10, the adsorption capacity of CSD toward BPD presented a downward tendency with the temperature rise. Generally, adsorption is a procedure concomitant to release heat. Therefore, the adsorption capacity of CSD at a higher temperature was less than that at a lower temperature.

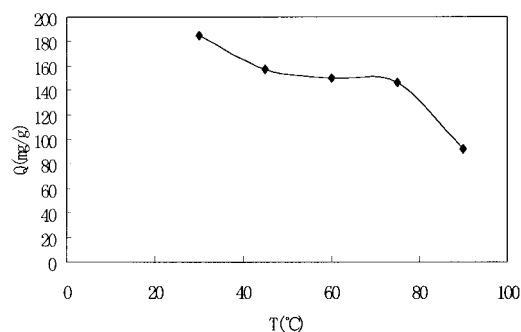


Figure 10 Effect of temperature on the adsorption capacity.

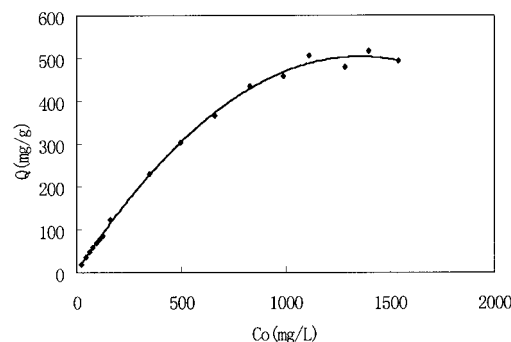


Figure 11 Effect of initial concentration on the adsorption capacity.

Effect of Initial Concentration on the Adsorption Capacity

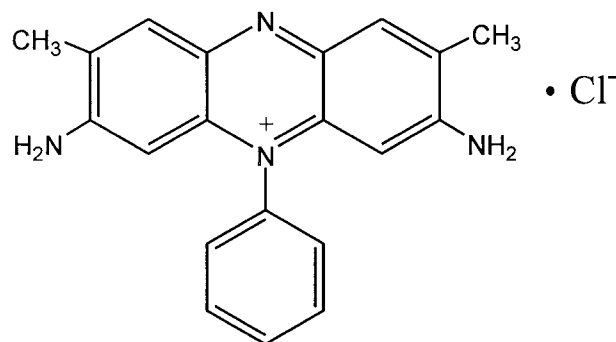
In Figure 11, the adsorption capacity of CSD increased with aggrandizement of initial concentration of BPD and was no higher when it reached about 500 mg/g, which indicated the saturation of the adsorption.

Effect of pH on the Adsorption Capacity

BPD is a cationic dye (Scheme 1) of which ionization equilibrium is influenced by the pH of the solution. On the other hand, the ionization equilibrium of the carboxyl of CSD is also affected by pH. The suitable pH for the adsorption of CSD was about 6 with respect to that of the adsorption capacity of CSD decreasing more than that of CSD in other pH conditions (shown in Fig. 12).

Effect of Acid Value of CSD on the Adsorption Capacity

In Table I, the adsorption capacity of CSD presents an upward tendency along with the accre-



Scheme 1 Molecular structure of BPD.

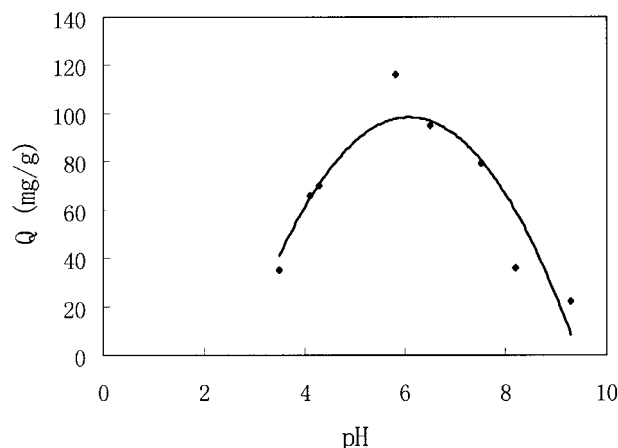


Figure 12 Effect of pH on the adsorption capacity.

tion of the acid value under the identical concentration of BPD.

Regenerated Ability of CSD

CSD samples, of which adsorption capacity was saturated in a specific concentration solution ($\text{Co} \geq 1000$ ppm), were immersed in 0.3 mol/L HCl for 3 h at room temperature, filtered, and washed by distilled water until the effluent pH was about 7. The regenerated CSD samples were put into different concentration solutions of BPD and determined for the adsorption capacity (shown in Table II).

The adsorption capacity of CSD after being reused the fourth time was about 81.0–87.2% of that at the first time.

CSD can also adsorb metal ions such as Cu^{2+} , Pb^{2+} , Zn^{2+} , Fe^{3+} , and so forth. More information about the adsorption behavior of CSD to metal ions will be presented in another article.

Table I Effect of Acid Number of CSD on the Adsorption Capacity

Acid Value (mmol/g)	0.02	0.11	0.45	0.83	1.16	1.57
Co (mg/L)	140	140	140	140	140	140
Ce (mg/L)	116	93	67	48	30	24
Q (mg/g)	24	47	73	92	110	116

Table II Regenerated Ability of CSD

Co (mg/L)	78	257	281	718	1490
Q_1 (mg/g)	63	171	189	378	506
Q_4 (mg/g)	52	141	153	309	441
Q_4/Q_1 (%)	82.5	82.5	81.0	81.7	87.2

Q_1 , Q_4 were the adsorption capacities of CSD used first and reused fourth, respectively.

CONCLUSIONS

A kind of CSD was prepared by hydrolysis of SAN and SAA, which were made through graft copolymerization of sawdust with acrylonitrile/acrylamide and examined for its adsorption properties toward BPD.

The following conclusions are obtained:

1. Graft copolymers (SAN and SAA) with a high rate of graft copolymerization are readily prepared by suitable usages of initiator and vinyl monomer at a certain temperature.
2. The adsorption capacity of CSD is related to pH of BPD solution and reaches the most adsorption capacity at $\text{pH} \approx 6$ (about 500 mg/g).
3. The adsorption capacity of CSD increases along with the augment of its acid value.

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