Cationized Sawdust as Ion Exchanger for Anionic Residual Dyes

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ABSTRACT: Using the same procedure as recently described for cotton fiber, the preparation of cationized wood sawdust was performed by treating alkali sawdust with epoxy propyl trimethyl ammonium chloride (EPTMAC) in a nonaqueous medium (dimethylformamide, DMF). The fixation of ammonium groups onto sawdust was monitored by weight uptake, nitrogen content determination, and infrared spectroscopy. EPTMAC-sawdust with a 0.5 wt % nitrogen content is then used as adsorbent for acid dyes (Acid Blue 25, Acid Yellow 99, Reactive Yellow 23, and Acid Blue 74). The adsorption capacity, determined by spectrometric measurement of the residual dye in the treated solution, decreases with increasing temperature. The modeling of the adsorption isotherms using Langmuir, Freundlich, and General relations allows the determination of isotherm constants. Globally, EPTMAC-sawdust has a behavior similar to EPTMAC-cotton, and its use for depollution of waste waters from dyeing industries presents advantages over cotton, such as a larger availability and a lower price. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 31–37, 2001

Key words: cationized sawdust; acid dyes; adsorption isotherm; exchange capacity

INTRODUCTION

Waste waters arising from dyeing industries constitute a potential pollution because of the toxicity and coloration of the dye molecules, which necessitates their elimination before throwing away in the environment. For many years, various adsorbing systems have been proposed for an effective treatment of these wastes. Among recent studies, the absorbents used can be classified in three categories: (i) mineral supports, such as activated carbon,[1] aluminum oxide,[2] vermiculite,[3] slag,[4] fly ash,[5,6] and magnesium chloride;[7] (ii) vegetal material, generally agricultural by-products (bagasse,[8] sugar cane,[9] palm-fruit bunch,[10] pith,[11] and peat[12]) or wood industries wastes (barks,[13] wood chips,[14] and sawdust[15]); and (iii) modified biopolymers for enhancement of adsorption: deacetylated chitin,[16] aminated wood sawdust,[17] and cotton and lignocellulosic material bearing various chemical functions.[18–20]

It has been previously shown that cationized cotton is an efficient adsorbent for acid dyes because of the quaternary ammonium sites fixed on the biopolymer.[20,21] In the present work, cationization of wood sawdust, a more abundant and less expensive material, is performed in the same manner for immobilization of the same acid dyes.

EXPERIMENTAL

The procedures followed for the preparation of epoxy propyl trimethyl ammonium chloride (EPT-

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Table I Degree of Grafting and Nitrogen Content of EPTMAC-Sawdust

Sample	Reaction Time (min)	%N	%G	
			Found	Calculated[a]
EPTMAC-sawdust	120	0.5	6	5.45

[a] Calculation based on %N.

MAC) treated sawdust (EPTMAC-sawdust) and for its use as dye adsorbent are very similar to that previously described for EPTMAC-cotton.[20]

Materials

Sawdust with a particle size range of 0.25 to 0.53 mm was supplied by "Société Parisienne des Sciures," France. The sawdust consists mainly of spruce (85%), poplar, pine, and fir. This industrial product is elaborated from raw sawdust for different filtration purposes and, for this reason, presents relatively constant composition and properties. It has also been submitted to alkaline hot water washing so that the hemicelluloses are partly extracted. All reagents [dimethylformamide (DMF), tri *n*-propylamine (TPA), and EPTMAC] were supplied by Aldrich (Sigma-Aldrich Chimie Sarl, Saint-Quentin Fallavier, France) and used without further purification. The chemical structure and characteristics of the acid dyes used in the adsorption experiments are given in the previous work[20]: Acid Blue 25, Acid Yellow 99, Reactive Yellow 23, and Acid Blue 74 (referred to as AB 25, AY 99, RY 23, and AB 74 respectively).

Techniques

Preparation of EPTMAC-Sawdust

For purification of the initial material, sawdust was subjected to a repeated soxhlet extraction with ethanol followed by washing with distilled water and drying in air at room temperature. The EPTMAC-sawdust was prepared in two steps.[21] In the first step, purified sawdust was transformed into sodium hydroxide-treated wood (NaOH-wood) by treatment with aqueous sodium hydroxide (5 N) at room temperature for 2 h. After washing, neutralization with 1% acetic acid, and a second washing with distilled water, the powder was dried in air at room temperature for 2 days. The second step was carried out as follows: in a 500-mL three-necked flask fitted with a dropping funnel, a mechanical stirrer unit, and reflux condenser, were placed 100 mL of DMF, 3 mL of TPA, and 10 g of NaOH-wood. The mixture was heated in an oil bath at 90°C for 1 h, and then 10 mL of EPTMAC was added in a dropwise manner with stirring and maintaining the temperature at 90°C. After complete addition (~ 30 min), the temperature was increased to 120°C and maintained for 2 h. The sample was then filtered and washed thoroughly with a mixture of ethanol and methanol (50/50 v/v), then with acidified water (1% v/v HCl), and finally rinsed with distilled water and dried. The sample was then subjected to a repeated soxhlet extraction with ethanol to remove the unreacted EPTMAC and dried at 60°C for ~ 72 h until a constant weight was obtained.

Characterization of the EPTMAC-Sawdust

The degree of grafting, determined from the weight uptake percentage, is in good agreement with the value determined by the nitrogen content measurement (Table I). Wood sawdust treated with the same conditions as cotton gives rise to a lower nitrogen content: 0.5 instead of 1.85%.[20] This difference may be because of a lower hydroxyl content in wood (cellulose + lignin) and/or to a lower accessibility of these groups.

Infrared (IR) spectra of sawdust and EPTMAC-sawdust were obtained on a Perkin-Elmer 1760-X infrared Fourier (FTIR) spectrometer. The IR spectra of the control and modified sawdust are shown in Figure 1. It can be seen from the graph (b) that for the EPTMAC-sawdust sample, the C=O band at 1737 cm^{-1} due to xylan is already removed by treatment with alkali,[22] and addi-

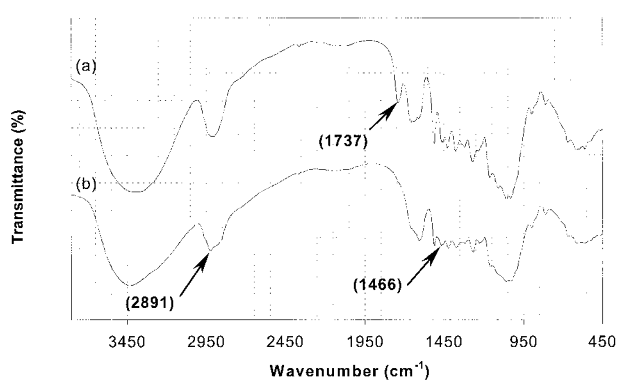

Figure 1 Infrared spectrum of (a) control sawdust and (b) EPTMAC-sawdust.

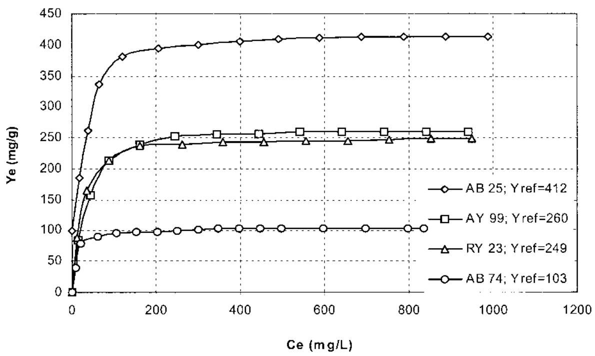

Figure 2 Adsorption isotherms of dyes on EPTMAC-sawdust (temperature = 20°C).

tional bands are obtained at 1466 and 2891 cm^{-1} that are due to C—H bonds of methyl groups, thus confirming the introduction of trimethyl ammonium groups onto the wood structure.

Adsorption

For the adsorption isotherms determination, a given mass of EPTMAC-sawdust was immersed in a series of different dye solutions of varying concentration. The modified wood (1 g) and the dye solution (100 mL) of initial concentration C_o were stirred mechanically in an Ahiba Nuance laboratory machine for a period of 2 h at the desired temperature. It was verified that this time is sufficient for the equilibration of the heterogeneous system. The concentration of the dye remaining in solution C_e was measured with an UVIKON 941 Plus spectrophotometer at the wavelength corresponding to its maximum of absorbance (λ_{max}), and the quantity of dye adsorbed on the sawdust, Y_e, was then deduced from the difference with C_o. Adsorption isotherms were studied at four different temperatures between 20 and 80°C.

RESULTS AND DISCUSSION

Treatment of Colored Waters by Modified Sawdust

As with cotton, untreated material does not adsorb any of the four tested dyes. On the contrary, high adsorption capacities are obtained for dyes AB 25 (412 mg/g) and RY 23 (249 mg/g) on treated sawdust, and these values are higher (~ +43%) than for treated cotton. For AY 99 (260 mg/g) and AB 74 (103 mg/g), the values obtained are somewhat lower (−20%) than that for cotton. The adsorption isotherms, Y_e versus C_e, for each of the four dyes on EPTMAC-sawdust (nitrogen content 0.5%) at 20°C are shown in Figure 2. A limit value Y_{ref} was obtained for each dye. For an equal 0.5% nitrogen content, a comparison between cationized cotton[20] and cationized sawdust as dye adsorbents is established in Table II. The registered difference can be attributed to various factors, including (i) wood has a more complex chemical structure than cotton, and (ii) all hydroxyl groups (alcoholic functions in cellulose and alcoholic-phenolic functions in lignin) can undergo the chemical modification in the conditions of treatment. However, at the same level of grafting, the density of quaternary ammonium groups in cellulosic moieties of wood is certainly higher than in pure cellulose, and it has been shown[20] that all OH are not accessible in this case.

Effect of Temperature

The temperature affects two major aspects of adsorption: the equilibrium position in relation with the exothermicity of the adsorption phenomenon and the swelling capacity of the adsorbent. Thus, adjustment of temperature may be required in the adsorption process. The effect of temperature on the adsorption of AB 25 on modified wood is shown in Figure 3. As generally observed, the adsorption capacity decreases with increasing temperature: the adsorption limit value at 80°C is ~ 60% of that observed at ambient temperature. This parameter appears to have a greater influence than in the case of cationized cotton, and a desorption process is therefore possible, as previously mentioned.[20,23]

Adsorption Isotherms

As with studies concerning cotton, sawdust adsorption data for the four dyes were treated with the Langmuir, Freundlich, and General relations.

Table II Comparison of Cationized Cotton and Cationized Sawdust as Dye Adsorbents[a]

	Y_{ref} (mg/g)	
Dye	Cationized Cotton[b]	Cationized Sawdust
AB 25	288	412
AY 99	326	260
RY 23	174	249
AB 74	126	103

[a] At 20°C; %N = 0.5.
[b] Reference 20.

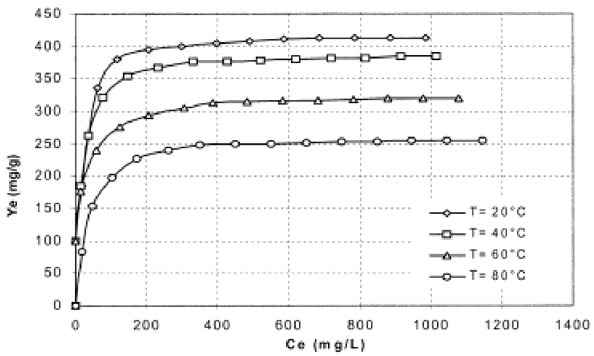

Figure 3 Effect of temperature on the adsorption isotherm of AB 25 on EPTMAC-sawdust (%N = 0.5).

All parameters are defined in the Nomenclature Section.

Analysis by Langmuir Isotherms

The Langmuir isotherms[24] are governed by the following equations:

$$Y_e = \frac{QbC_e}{1 + bC_e} \quad \text{or} \quad \frac{C_e}{Y_e} = \frac{1}{Qb} + \frac{C_e}{Q} \qquad (1)$$

Plotting C_e/Y_e versus C_e, according to eq. 1 produces straight lines with a relatively good correlation coefficient, showing that all data correctly fit the Langmuir relation (Figures 4 and 5). The Langmuir constants are summarized in Table III. There is a good agreement between the experimental value Y_{ref} (limit value of Y_e) and the calculated value Q.

The Langmuir equilibrium constant $K_L = Qb$, measured at different temperatures, allows the calculation of adsorption enthalpy through the Clausius–Clapeyron relation (Figure 6). The enthalpies associated with the adsorption of a initially solvated dye molecule onto the solid support are −37.6, −29.4, −42.0, and −36.2 kJ/mol for AB 25, AY 99, RY 23, and AB 74, respectively. These negative values indicate that heat is liberated during the adsorption process, which limits the adsorption of these dyes by EPTMAC-sawdust at high temperatures.

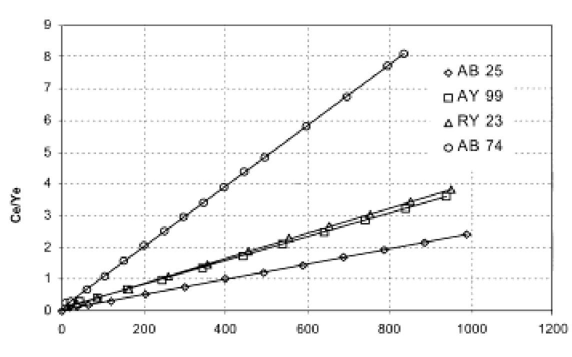

Figure 4 Langmuir isotherms for the four dyes on EPTMAC-sawdust (temperature = 20°C).

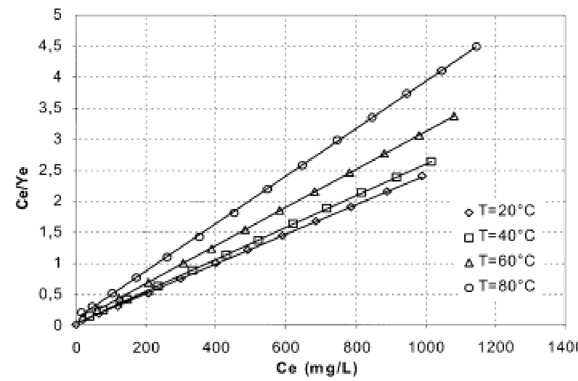

Figure 5 Effect of temperature on Langmuir isotherms for the adsorption of AB 25 on EPTMAC-sawdust.

Analysis by the Freundlich Isotherm

When heterogeneous surface energies are involved, the Freundlich equation[25] is used in the general form

Table III Langmuir Constants from Equation 1[a]

Dye	Temperature (°C)	Y_{ref} (mg/g)	Langmuir Constants Q (mg/g)	K_L[b] (L/g)	b (L/mg)
AB 25	20	412	416	27	0.06
	40	385	385	24	0.06
	60	320	322	16	0.04
	80	255	263	9	0.03
AY 99	20	260	270	11	0.04
	40	227	232	10	0.04
	60	180	185	7	0.03
	80	136	135	4	0.03
RY 23	20	249	256	14	0.05
	40	200	204	9	0.04
	60	165	169	7	0.04
	80	142	147	4	0.02
AB 74	20	103	104	9	0.08
	40	89	91	5	0.05
	60	69	71	4	0.04
	80	59	61	3	0.05

[a] %N = 0.5.
[b] Calculated slope of C_e/Y_e versus C_e.

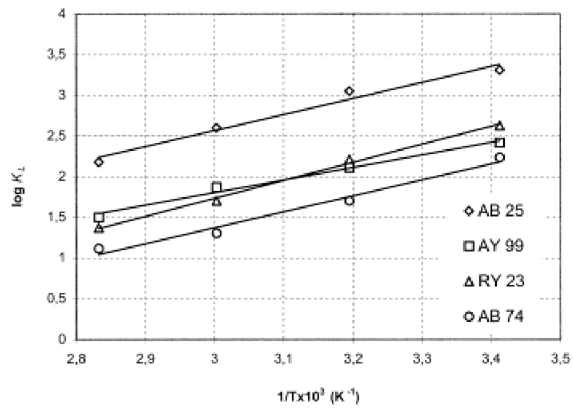

Figure 6 Log K_L versus reciprocal of temperature.

$$Y_e = PC_e^{1/n} \quad \text{or} \quad \log Y_e = \log P + \frac{1}{n}\log C_e \tag{2}$$

Typical Freundlich plots (log Y_e versus log C_e), which are assimilated to two straight lines according to Fritz and Schlunder,[26] are shown in Figure 7.

The Freundlich constants deduced from the first straight lines obtained in Figure 7 are summarized in Table IV. For all experiments, the exponent n is in the range $1.58 < n < 5.5$, showing that adsorption is favorable.

Analysis by the General Isotherm

The adsorption data correctly fit the Langmuir equation, as shown in Figures 4 and 5, whereas they are not in accordance with the Freundlich equation (Figure 7). A General isotherm taking into account both the Langmuir and Freundlich expressions has been postulated by Weber and Mattews[27] and is represented by the following equation:

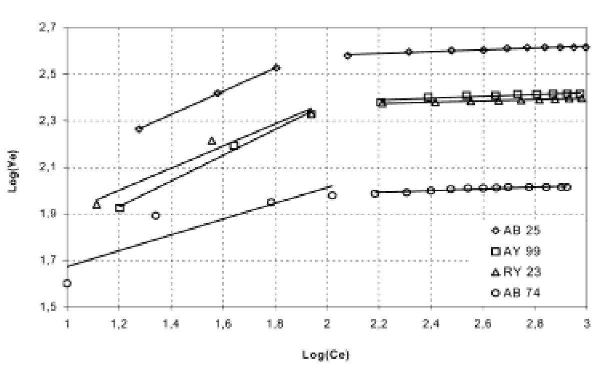

Figure 7 Freundlich analysis of the adsorption of four dyes on EPTMAC-sawdust (temperature = 20°C).

Table IV Freundlich Constants from Equation 2

Dye	Temperature (°C)	Freundlich Constants P	Freundlich Constants n
AB 25	20	93.70	4.20
	40	96.70	3.78
	60	98.60	4.6
	80	26.19	2.3
AY 99	20	24.8	2.15
	40	28.37	2.48
	60	26.52	2.85
	80	26.78	3.49
RY 23	20	26.98	2.10
	40	71.30	5.50
	60	25.17	2.78
	80	5.43	1.58
AB 74	20	16.80	2.3
	40	19.88	3.26
	60	15.90	3.44
	80	6.92	2.23

$$Y_e = \frac{iC_e}{1 + j(C_e)^m} \tag{3}$$

For practical design purposes in a system operating over a wide range of concentration, this "intermediate" isotherm is often a more realistic representation of the system. The results are presented in Table V. The results in Figure 8 indicate that the General isotherm best fits the experimental data in the entire range of concentration. The weaknesses of the Langmuir isotherm are highlighted in the region of monolayer coverage, and the Freundlich isotherm does not appear to be able to characterize the adsorbent/adsorbate system in the entire range of concentrations.

Effect of Isotherm Shape

Considering a Langmuir-type adsorption process, the isotherm shape can be classified by a term, "r", which is a dimensionless constant separation factor that is defined by the following relationship given by Hall et al.[28]

$$r = \left[\frac{1}{1 + bC_0}\right] \tag{4}$$

Weber and Chakravorti[29] consider that the isotherm shape can predict if the adsorption is "favorable" or "unfavorable."

Table V General Isotherms Constants for the Various Adsorption Systems

Dye	Temperature (°C)	General Isotherms Constants			Correlation Coefficient
		i (L/g)	j (L/mg)	m	
AB 25	20	17.86	0.03	1.02	0.984
	40	31.95	0.10	0.96	0.985
	60	209.62	1.28	0.89	0.992
	80	10.11	0.05	0.95	0.995
AY 99	20	9.94	0.04	0.99	0.996
	40	9.02	0.03	0.99	0.995
	60	5.08	0.02	1.03	0.999
	80	4.80	0.03	0.97	0.998
RY 23	20	13.12	0.05	0.98	0.996
	40	40.99	0.31	0.93	0.997
	60	5.49	0.03	1.02	0.999
	80	2.11	0.01	1.14	0.991
AB 74	20	8.27	0.07	1.02	0.993
	40	7.94	0.11	0.96	0.999
	60	5.18	0.09	0.96	0.999
	80	3.56	0.07	0.96	0.993

The values of "r" for each adsorbent/adsorbate system are given in Figure 9 and Table VI. All four systems show favorable adsorption; namely, $0 < r < 1$, with "r" near zero.

CONCLUSIONS

A strong basic ion-exchange wood powder was obtained by reacting alkali-treated sawdust with EPTMAC in DMF at 120°C for 2 h. The results indicate that EPTMAC-sawdust is an excellent adsorbent for anionic moieties. High adsorptive capacities were observed for the adsorption of acid dyes; namely, 412, 260, 249, and 103 mg dye $\cdot$ g^{-1} EPTMAC-sawdust for Acid Blue 25, Acid Yellow 99, Reactive Yellow 23, and Acid Blue 74, respectively. Freundlich's isotherm was unable to characterize the adsorbent/adsorbate system in this case. Theoretical Langmuir and General isotherms were compared with experimental data and good agreement was obtained. As observed for cotton, all isotherms show that cationized sawdust is favorable for the immobilization of pollutant dyes. However, a raising of temperature severely decreases the quantity of adsorbed dye.

Because of the availability and low cost of wood sawdust, its use as anionic exchanger seems promising for the cleaning up of dyeworks waste waters.

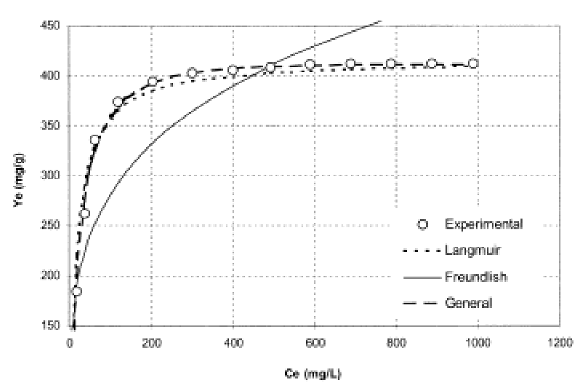

Figure 8 Comparison of theoretical isotherms with experimental data for the adsorption of AB 25 on EPTMAC-sawdust (temperature = 20°C).

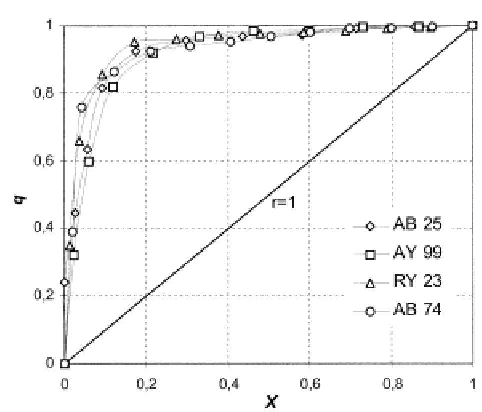

Figure 9 Dimensionless concentration isotherms as function of the separation factor for the four dyes (temperature = 20°C).

Table VI Separation Factors for the Various Adsorption Systems

Dye	Temperature (°C)	b (L/mg)	r
AB 25	20	0.06	0.001
	40	0.06	0.017
	60	0.04	0.025
	80	0.03	0.031
AY 99	20	0.04	0.032
	40	0.04	0.028
	60	0.03	0.035
	80	0.03	0.033
RY 23	20	0.05	0.020
	40	0.04	0.027
	60	0.04	0.030
	80	0.02	0.050
AB 74	20	0.08	0.025
	40	0.05	0.030
	60	0.04	0.040
	80	0.05	0.040

NOMENCLATURE

b constant related to the energy of adsorption (L/g)
C_e dye concentration in solution at equilibrium (mg/L)
C_o initial dye concentration in solution (mg/L)
ΔH enthalpy of adsorption (kJ/mol)
i constant in General isotherm (L/g)
j constant in General isotherm (L/mg)
K_L Langmuir equilibrium constant (L/g)
m constant in General isotherm
n adsorption intensity
P measure of adsorption capacity [mg(mg/L)$^{1/n}$/g]
q dimensionless solid-phase concentration at equilibrium
Q dye concentration at monolayer coverage (mg/g)
r dimensionless constant separation factor
X dimensionless liquid-phase concentration at equilibrium
Y_e dye concentration at equilibrium (mg/g)
Y_{ref} maximum solid-phase dye concentration

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