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Short communication

Removal of cationic dyes from aqueous solution by adsorption on peanut hull

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Abstract

The potential feasibility of peanut hul particle for removal of three cationic dyes (methylene blue, brilliant cresyl blue and neutral red) from aqueous solution was investigated. The effects of various experimental parameters were examined and optimal experimental conditions were decided. Above the value of initial pH 4, three dyes studied could be removed effectively. The isothermal data fitted the Langmuir model or Freundlich model. The adsorption processes followed the pseudo-first-order rate kinetics. The results in this study indicated that peanut hull was an attractive candidate for removing cationic dyes from dye wastewater.

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1. Introduction

Dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade [1]. Today there are more than 10,000 dyes available commercially [2]. Dyes are widely used in textiles, paper, rubber, plastics, leather, cosmetics, pharmaceutical and food industries. The extensive use of dyes often poses pollution problems in the form of colored wastewater discharged into environmental water bodies. It not only affects aesthetic merit but also reduces light penetration and photosynthesis. In addition, some dyes are either toxic or mutagenic and carcinogenic [3]. The conventional methods for treating dyes containing wastewaters are coagulation and flocculation [4], oxidation or ozonation [5,6], membrane separation [7] and activated carbon adsorption [8]. But these technologies do not show significant effectiveness or economic advantage. Activated car-

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bon is the most popular and widely used dye sorbent but there are certain problems with its use. It is expensive and the higher the quality the greater the cost. Furthermore, regeneration using solutions produces a small additional effluent, while regeneration by refractory technique results in a 10-15% loss of sorbent and its uptake capacity. Therefore, there is a growing interest in using low cost, easily available biomaterials for the adsorption of dye colors.

Some low cost botanic materials had directly been used as sorbent for dye adsorption from wastewater [9–20]. As the largest producer of synthetic dyes and developing nation in the world, new, economical and highly effective treatment technologies of dye wastewater were urgently needed in China.

In this paper, the feasibility of peanut hull particle as sorbent for removal of cationic dyes from aqueous solution was investigated. Peanut is an oil plant which is extensively cultured in China. The annual peanut output of China is 5 million ton and an estimated total of 1.4 million ton of peanut hull is produced annually. Most of this agricultural

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waste is arbitrarily discarded or set on fire. These disposals must result in environmental pollution. The exploitation and utilization of this bioresource must bring obvious economic and social benefit to us.

The dyes selected as sorbate were methylene blue (C.I.52015, FW = 373.9, $\lambda_{max} = 670$ nm), brilliant cresyl blue (C.I.51010, FW = 317.8, $\lambda_{max} = 630$ nm) and neutral red (C.I.50040, FW = 288.8, $\lambda_{max} = 530$ nm). The effects of various operating parameters on adsorption such as sorbent dosage, particle size, contact time, initial dye concentration and pH were monitored and optimal experimental conditions were decided.

2. Materials and methods

2.1. Preparation of peanut hull sorbent

The peanut hull used in this study was collected from a local market. The collected biomaterial was extensively washed with tap water to remove soil and dust, sprayed with distilled water then dried in an oven at 80 °C to a constant weight. Dry peanut hull was crushed into powder and sieved to different particle sizes, then preserved in the desiccator for use.

2.2. Preparation of cationic dye solutions

Three cationic dyes (MB, BCB and NR), in commercial purity, were used without further purification. The dye stock solutions were prepared by dissolving accurately weighted dyes in distilled water to the concentration of 500 mg/l. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

2.3. Experimental methods and measurements

Adsorption experiments were carried out in a rotary shaker at 150 rpm and 20 °C using 250 ml shaking flasks containing 100 ml different concentrations and initial pH values of dye solutions. The initial pH values of the solutions were previous adjusted with 0.1 M HNO₃ or NaOH using pH meter. Different doses of sorbent were added to each flask. After shaking the flasks for predetermined time intervals, the samples were withdrawn from the flasks and the dye solutions were separated from the sorbent by filtration then centrifugation. Dye concentrations in the supernatant solutions were estimated by measuring adsorbance at maximum wavelengths of dyes with a 752 W Grating Spectrophotometer (Shanghai, China) and computing from the calibration curves.

The experiments were conducted in duplicate and the negative controls (with no sorbent) were simultaneously carried out to ensure that adsorption was by peanut hull biomass and not by the container.



Fig. 1. Effect of sorbent dose on adsorption of MB, BCB, NR by peanut hull (dye concentration: 100 mg/l; particle size: 60–80 mesh; contact time: 12 h; pH 5.0).

3. Results and discussion

3.1. Effect of sorbent dose

The effects of sorbent dose on the removal ratios of dyes were shown Fig. 1. The percentages of dyes sorbed increased as the sorbent dose was increased over the range 0.5–2.0 g/l. The adsorption ratios of dyes increased from 34.75 to 89.51%, from 79.14 to 96.47% and from 36.82 to 96.62% in MB, BCB and NR, respectively. Above 2.0 g/l of sorbent dose, the adsorption equilibriums of dyes were reached and the removal ratios of dyes held almost no variety. So, the peanut hull biomass of 2.0 g/l was chosen for subsequent experiments.

3.2. Influence of initial dye concentration

The influences of dye concentration on adsorption percentages of dyes were estimated. As shown in Fig. 2, when



Fig. 2. Influence of dye concentration on adsorption of MB, BCB, NR by peanut hull (sorbent dose: 2 g/l; particle size: 60–80 mesh; contact time: 12 h; pH 5.0).

The Q_m a	nd a values in Langn	uir equation, th	e K and $1/n$ values, in Freund	lich equation and the corre	lation coefficient	s of equations	
Dye	Langmuir equa	tion $(C_e/q_e = 1/($	$aQ_m) + C_e/Q_m)$	Freundlich equation $(\ln Q_e = \ln K + (1/n) \ln C)$			
	$\overline{Q_m (\mathrm{mg/g})}$	а	R^2	K	1/n	R^2	
MB	68.03	0.157	0.9952	9.11	0.5279	0.9460	

^a $R^2 \ll 1$, the Freundlich model was not fitted.

87.72

Table 1

BCB

NR

the dye concentration was increased from 10 to 200 mg/l, the percentages of dyes sorbed decreased from 95.97 to 62.11% in MB and from 95.35 to 78.76% in NR, but the ratio of BCB sorbed kept basically unchangeable and fluctuated between 95.07 and 96.79%.

0.232

0.9796

With the data in Fig. 2, Langmuir equation and Freundlich equation were employed to study the adsorption isotherm of dyes.

Table 1 shows Q_m and *a* values in Langmuir equation, the *K* and 1/n values in Freundlich equation and the correlation coefficients of two equations. From the results in Table 1, it could be concluded that the adsorption isotherm of MB fitted the Langmuir model and Freundlich model, but the adsorption isotherms only fitted the Freundlich model in BCB and Langmuir model in NR.

3.3. Effect of initial pH

The effects of initial pH on adsorption percentages of dyes were researched over a range of pH values from 2 to 11. But for NR, the experiments were only conducted from pH 2 to 6 for avoiding dye precipitation. As elucidated in Fig. 3, for all three dyes, the dye removal ratios were minimum at the initial pH 2. The ratios of dyes sorbed increased as the initial pH was increased from pH 2 to 4, then the dye removal ratios were not significantly altered (P > 0.05) beyond pH 4. For this reason, the pH 5 was selected for the other experiments.



Fig. 3. Effect of initial pH on adsorption of MB, BCB, NR by peanut hull (dye concentration: 100 mg/l; sorbent dose: 2 g/l; particle size: 60–80 mesh; contact time: 12 h).

Table 2

12.00

14.70

The dye removal percentages of different particle size (dye concentration: 100 mg/l; sorbent dose: 2 g/l; contact time: 12 h; pH 5.0)

0.9803

0.7713ª

1.0038

0.5791

Dye	Particle si	Particle size (mesh)						
	20-40	40-60	60-80	80-100	>100			
MB	62.17	80.15	89.33	90.54	91.32			
BCB	92.06	94.73	96.22	96.26	96.32			
NR	65.93	92.23	96.73	97.14	97.79			

3.4. Effect of sorbent particle size

Table 2 showed the effects of sorbent particle size on adsorption percentages of dyes. The ratios of dyes sorbed increased as the sorbent particle size was decreased. The ratios of dyes sorbed had neared the maximum values in all three dyes when the sorbent particle size in 60–80 mesh. For convenience of liquid–solid phase separation, the sorbent particle in 60–80 mesh was used in all other parameter experiments.

3.5. Adsorption kinetics

Fig. 4 illustrated the adsorption kinetics of dyes. The removal rates of dyes were very rapid during the initial stages of the adsorption processes. After a very rapid adsorption, dye uptake capacities increased with time and reached equilibrium values at about 12 h for all three dyes.

The kinetic data in Fig. 4 were treated with Langergren's pseudo-first-order rate equation. The data of Langergren plots of dye adsorptions were shown in Table 3.



Fig. 4. Adsorption kinetics of MB, BCB, NR by peanut hull (dye concentration: 100 mg/l; sorbent dose: 2 g/l; particle size: 60–80 mesh; pH 5.0).

Table 3 The log q_e and $k_{ad}/2.303$ values and the correlation coefficients of Langergren's pseudo-first-order rate equation

Dye	Langergren equation $(\log (q_e - q_t) = \log q_e - k_{ad} t/2.303)$				
	$\log q_e$	$k_{\rm ad}/2.303$	R^2		
MB	1.1763	0.0113	0.9726		
BCB	0.6427	0.0054	0.9739		
NR	1.2849	0.0064	0.9809		

The high values of correlation coefficients showed that the data conformed well to the pseudo-first-order rate kinetic model.

4. Conclusions

This study showed that peanut hull particle could effectively remove MB, BCB and NR from aqueous solution. The optimal pH for favorable adsorption of dyes was 4 and above. The percentages of dyes sorbed increased then reached maximum values as the sorbent dose was increased. The ratios of dyes sorbed increased as the sorbent particle size was decreased. The adsorption equilibriums were reached at about 12 h. The isothermal data fitted the Langmuir model or Freundlich model. The adsorption processes followed the pseudo-first-order rate kinetics.

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