

Utilization of powdered peanut hull as biosorbent for removal of anionic dyes from aqueous solution

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Abstract

An untried, low cost, locally available biosorbent was investigated for its anionic dye removal capacity from aqueous solution. Powder prepared from peanut hull was used for biosorption of three anionic dyes, amaranth (Am), sunset yellow (SY) and fast green FCF (FG). The effects of various experimental parameters (e.g. initial pH and dye concentration, sorbent dosage, particle size, ion strength, contact time) were examined and optimal experimental conditions were decided. At initial pH 2.0, three dyes studied could be removed effectively. The isothermal data for biosorption followed the Langmuir and Freundlich models. The biosorption processes conformed to the pseudo-first-order rate kinetics. The results in this study indicated that powdered peanut hull was an attractive candidate for removing anionic dyes from dye wastewater.

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1. Introduction

Because of their ease of use, inexpensive cost of synthesis, stability and variety of color compared with natural dyes, synthetic dyes have been increasingly used in the textile, paper, rubber, plastics, cosmetics, pharmaceutical and food industries [1–3]. Today there are more than 10,000 dyes available commercially [4], most of which are difficult to biodegrade due to their complex aromatic molecular structure and synthetic origin [5]. The extensive use of dyes often poses pollution problems in the form of colored wastewater discharge into environmental water bodies. Even small quantities of dyes can color large water bodies, which not only affects aesthetic merit but also reduces light penetration and

photosynthesis. In addition, some dyes are either toxic or mutagenic and carcinogenic [6]. In industries, the methods employed for treating dye wastewaters include coagulation and flocculation [7], oxidation or ozonation [8,9], membrane separation [10] and activated carbon sorption [11]. These technologies do not show significant effectiveness or economic advantage. Activated carbon is the most popular and widely used dye sorbent, but its relatively high price, high operating costs and problems with regeneration hamper its large-scale application. Activated carbon 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 need to find low cost, renewable, locally available materials for the removal of dye colors. Some agricultural byproducts have been investigated for this purpose. These sorbents can be used

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once and then disposed as fuel for power generation or as ferment substrate to produce high protein animal feed.

Many sorbents based on low cost agricultural byproducts had been used for dye sorption from wastewater, which included orange peel [12]; cassava peel [13]; banana pith [14]; plum kernels [15]; apple pomace, wheat straw [16]; cotton waste, rice husk, teakwood bark [17]; sawdust [18]; bagasse pith, maize cob [19]; palm fruit bunch [20,21]; coir pith [22]. But new, economical, locally available and highly effective dye sorbents were still needed.

The purpose of this work was to investigate the possibility of peanut hull as a biosorbent for removal of anionic dyes from aqueous solution. Peanut hull is an abundant and low cost agricultural waste residue and is easily available in large quantity in China. The dyes selected as sorbate were amaranth (Am), sunset yellow (SY) and fast green FCF (FG). Their chemical structures and general data are shown in Fig. 1 and Table 1, respectively. The effects of various operating parameters on biosorption such as initial pH and dye concentration, sorbent dosage, particle size, ion strength, contact time 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 obtained from a local market. The collected biomaterial was extensively washed with tap water to remove soil and dust, sprayed with distilled water and then dried in an oven at 80 °C to a constant weight. Dry biomass was crushed into powder, sieved to different particle sizes and then preserved in a desiccator for use.

2.2. Preparation of anionic dye solutions

Three anionic dyes (Am, SY and FG), in 80–85% purity, were used without further purification. The dye stock solutions were prepared by dissolving accurately weighed dyes in distilled water to the concentration of 200 mg/l. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

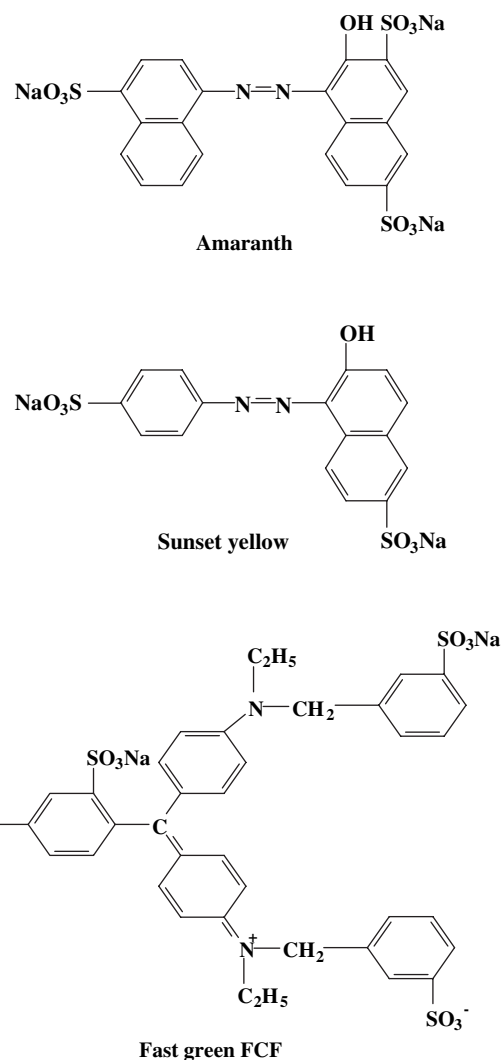


Fig. 1. The chemical structures of three anionic dyes used in this study.

2.3. Experimental methods and measurements

Biosorption experiments were carried out in a rotary shaker at 150 rpm and 20 ± 2 °C using 250 ml shaking flasks containing 100 ml of different concentrations and initial pH values of dye solutions. The initial pH values of the solutions were previously adjusted with 0.1 M HNO₃ or NaOH using pH meter. Different doses of sorbent were added to each flask and then the flasks were sealed to prevent change in volume of the solution during the experiments. After shaking the flasks for predetermined time intervals, the samples were taken

Table 1

The general data of three anionic dyes used in this study

Commercial name	Classification	C.I. no.	FW	λ_{\max} (nm)
Amaranth	Anionic monoazo	16,185	604.49	520
Sunset yellow	Anionic monoazo	15,985	452.37	490
Fast green FCF	Anionic triphenylmethane	42,053	808.86	620

out from the flasks and the dye solutions were separated from the sorbent by filtration with a 200 mesh stainless steel sieve and then centrifuged. Dye concentrations in the supernatant solutions were estimated by measuring the adsorbance at maximum wavelengths of dyes with a 752 W UV–Vis Grating Spectrophotometer (Shanghai, China) and computing from the calibration curves. The amount of dyes sorbed by the biomass was calculated using the following equation:

$$q = (C_0 - C_e)V/W$$

where q (mg/g) is the amount of dye sorbed by biomass, C_0 and C_e (mg/l) are the initial and equilibrium liquid-phase concentrations of the dye, respectively, V (l), the initial volume of dye solution, and W (g), the weight of the biomass.

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

3. Results and discussion

3.1. Effect of initial pH

Because the initial pH of solution can significantly influence biosorption of dyes, the effects of pH on dye biosorption by the powdered peanut hull was studied first. The value of pH used ranged from 2 to 11. As elucidated in Fig. 2, for all three dyes, the dye removal ratios were maximum at the initial pH 2. The ratios of dyes sorbed decreased as the initial pH was increased from 2 to 5, and, the dye removal ratios were kept

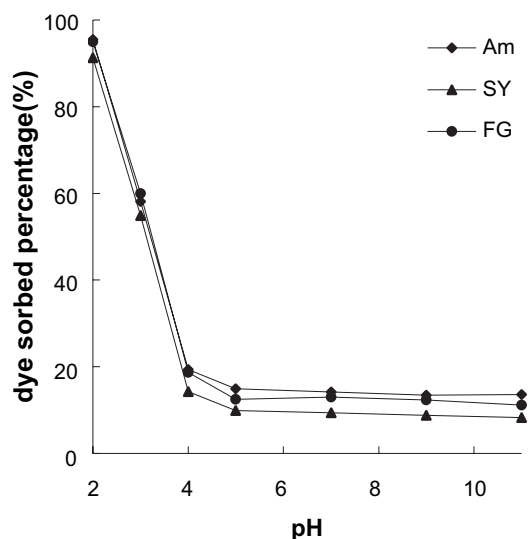


Fig. 2. Effect of initial pH on biosorption of Am, SY, FG by powdered peanut hull (dye concentration: 50 mg/l; sorbent dose: 5 g/l; particle size: 80–100 mesh; contact time: 36 h).

constant beyond pH 5. For this reason, pH 2 was selected for all other experiments.

3.2. Influence of initial dye concentration

The influence of dye concentration on biosorption percentages of dyes was estimated. As shown in Fig. 3, when the dye concentration was increased from 10 to 100 mg/l, the percentages of dyes sorbed decreased from 98.7 to 72.83% in Am, from 99.57 to 70.42% in SY and from 98.2 to 74.31% in FG.

With the data in Fig. 3, Langmuir and Freundlich equations were employed to study the sorption isotherms of dyes.

The Langmuir equation is shown as follows:

$$C_e/q_e = 1/(aQ_m) + C_e/Q_m$$

where C_e (mg/l) is the concentration of the dye solution at equilibrium, q_e (mg/g) is the amount of dye sorbed at equilibrium, Q_m is the maximum sorption capacity and a is the Langmuir constant. The Q_m and a values were calculated from the slopes ($1/Q_m$) and intercepts ($1/aQ_m$) of linear plots of C_e/q_e versus C_e .

The Freundlich equation was linearized as follows:

$$\ln Q_e = \ln K + (1/n) \ln C_e$$

where Q_e is the amount of dye sorbed at equilibrium, C_e is the concentration of the dye solution at equilibrium, K and $1/n$ are empirical constants and their values were obtained from the intercepts ($\ln K$) and slopes ($1/n$) of linear plots of $\ln Q_e$ versus $\ln C_e$.

Table 2 gives the Q_m and a values in Langmuir equation, the K and $1/n$ values in Freundlich equation and the correlation coefficients of the two equations. The maximum sorption capacities (Q_m) were 14.90 mg,

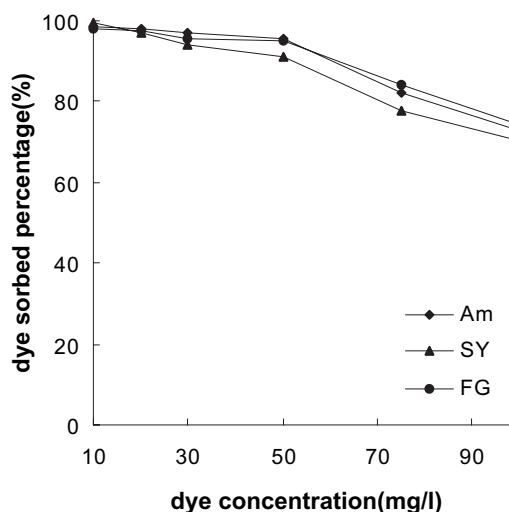


Fig. 3. Influence of dye concentration on biosorption of Am, SY, FG by powdered peanut hull (sorbent dose: 5 g/l; particle size: 80–100 mesh; contact time: 36 h; pH: 2.0).

Table 2

The Q_m and a values in Langmuir equation, the K and $1/n$ values in Freundlich equation and the correlation coefficients of equations

Dye	Langmuir			Freundlich		
	Q_m (mg/g)	a	R^2	K	$1/n$	R^2
Amaranth	14.90	0.766	0.9952	5.320	0.353	0.9254
Sunset yellow	13.99	0.495	0.9745	4.941	0.299	0.9802
Fast green FCF	15.60	0.571	0.9965	4.894	0.396	0.9381

13.99 mg and 15.60 mg dye per gram of the biosorbent for Am, SY and FG, respectively. From the results in Table 2, it could be concluded that the sorption isotherms of all three dyes followed the Langmuir and Freundlich models.

3.3. Effect of sorbent dose

The effects of sorbent dose on the removal ratios of dyes are shown Fig. 4. The percentages of dyes sorbed increased as the sorbent dose was increased over the range 1.0–10.0 g/l. The biosorption ratios of dyes increased from 33.64 to 98.64%, from 24.72 to 98.26% and from 38.16 to 99.12% in Am, SY and FG, respectively. Increase in biosorption with the sorbent dose could be attributed to increased surface area and the availability of more sorption sites. Except SY, the ratios of dyes sorbed had approached maximum values when sorbent dose of 5.0 g/l was used. So, in other parameter experiments, a peanut hull biomass of 5.0 g/l was chosen.

3.4. Influence of sorbent particle size

Fig. 5 shows the effects of sorbent particle size on biosorption percentages of dyes. The ratios of dyes sorbed increased as the sorbent particle size decreased,

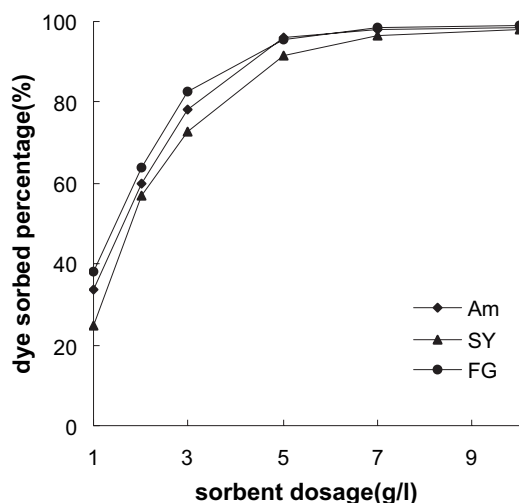


Fig. 4. Effect of sorbent dose on biosorption of Am, SY, FG by powdered peanut hull (dye concentration: 50 mg/l; particle size: 80–100 mesh; contact time: 36 h; pH: 2.0).

but the ratios of dyes sorbed had approached the maximum values in all three dyes when the sorbent particle size in 80–100 mesh. For convenience of liquid–solid phase separation, the sorbent particle in 80–100 mesh was used in all other parameter experiments.

3.5. Effect of ion strength

The effects of ion strength on biosorption of dyes were tested by the addition of sodium chloride to the solution. The concentration of NaCl used ranged from 0 to 0.5 M. As seen in Fig. 6, increasing the ion strength of solution caused decrease in biosorption percentages of dyes. This could be attributed to inhibition for the nearness of dye molecules and sorption sites. From the results in Fig. 6, it could be concluded that the smaller the dye molecular weights, the larger the effects of ion strength on dye biosorption.

3.6. Biosorption kinetics

Fig. 7 illustrated the biosorption kinetics of dyes. The removal rates of dyes were very rapid during the initial stages of the biosorption processes. After a very rapid biosorption, dye uptake capacities increased with time and reached equilibrium values at about 36 h for all

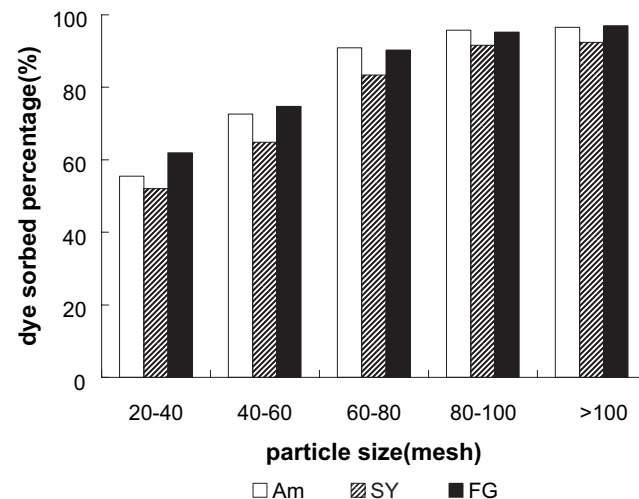


Fig. 5. Influence of particle size on biosorption of Am, SY, FG by powdered peanut hull (dye concentration: 50 mg/l; sorbent dose: 5 g/l; contact time: 36 h; pH: 2.0).

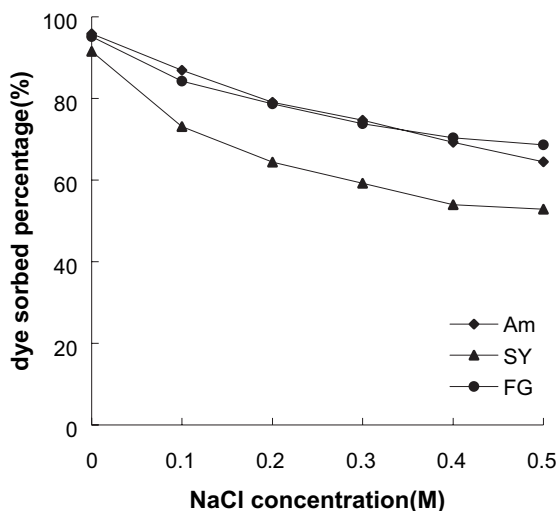


Fig. 6. Effect of ion strength on biosorption of Am, SY, FG by powdered peanut hull (dye concentration: 50 mg/l; sorbent dose: 5 g/l; particle size: 80–100 mesh; contact time: 36 h; pH: 2.0).

three dyes. After that, dye uptake became much less significant.

The kinetic data were treated with the following Lagergren's pseudo-first-order rate equation:

$$\log(q_e - q_t) = \log q_e - k_{ad}t/2.303$$

where q_e and q_t (mg/g) refer to the amount of dye sorbed at equilibrium and time t (min), respectively, and k_{ad} is the rate constant. The rate constant k_{ad} could be calculated from the slopes of the linear plots of $\log(q_e - q_t)$ versus t . The Lagergren plots of dye biosorptions are shown in Fig. 8. The high values of correlation coefficients showed that the data conformed well to the pseudo-first-order rate kinetic model.

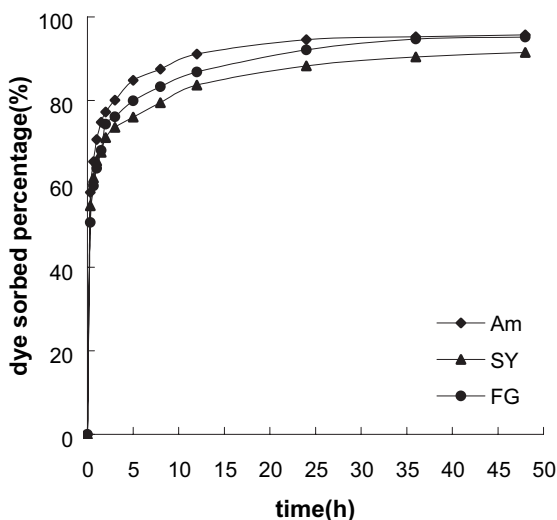


Fig. 7. Biosorption kinetics of Am, SY, FG by powdered peanut hull (dye concentration: 50 mg/l; sorbent dose: 5 g/l; particle size: 80–100 mesh; pH: 2.0).

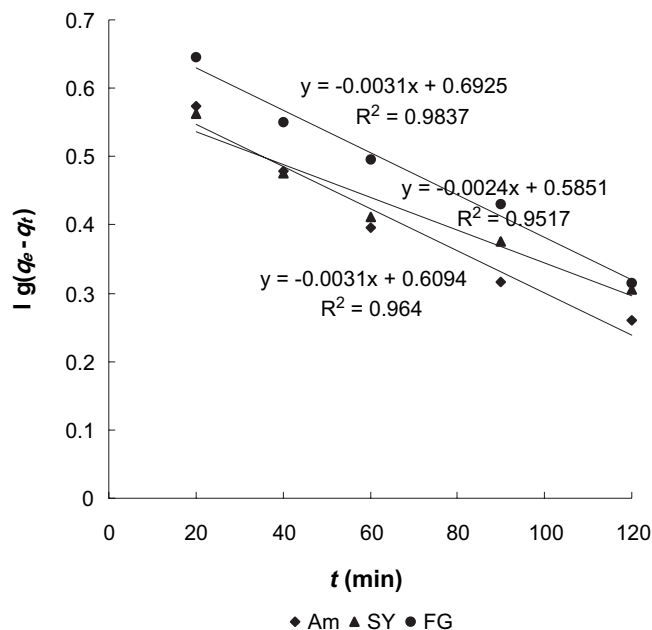


Fig. 8. Lagergren plots for biosorption of Am, SY, FG by powdered peanut hull.

4. Conclusions

The present study showed that the powdered peanut hull is a promising biosorbent for the removal of anionic dyes from aqueous solution, since the raw material peanut hull was easily available in large quantity and the treatment method of biomaterial seemed to be economical. At initial pH 2, three dyes studied could be removed effectively. The isothermal data of biosorption followed both Langmuir and Freundlich models. The sorption capacities were found to be 14.90 mg, 13.99 mg and 15.60 mg dye per gram of the biosorbent for Am, SY and FG, respectively. The biosorption processes conformed to the pseudo-first-order rate kinetics.

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