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Sorption of Acid Dyes by Chemically Modified Peanut Hulls

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Dyes, while comprising only a very small fraction of the total organic load in wastewater, render themselves easily recognizable substances in the aqueous environment. At present there are no general and economically suitable methods for the removal of dyes from textile effluents. Though dyes can be removed by activated carbon, the cost of treatment is high. Treatment of textile wastewater involving microorganisms has proven unsatisfactory in many textile plants. The use of low cost biological materials in removing color has attracted considerable attention. Some of the materials that have been studied include maize cob and bagasse pith (Nasser and El-Geundi 1991) wood (Poots et al. 1976) moss (Lee and Low 1987) rice hulls (Nawar and Doma 1989) and non-living biomass of water hyacinth roots (Low et al. 1995). Although many of these materials were efficient in removing basic dyes, they were less so for acid dyes which are negatively charged in aqueous solution. The greater affinity of these materials for basic dyes is due mainly to the coulombic attraction between the negative surface of the sorbents and the positively charged ions of the dissociated dyes. As the latter dyes are losing popularity in textile industry, the potential of using these materials to clean up textile waste is very limited. Hence there is a need to seek new materials or to modify low-cost biological materials so that they could be used to remove acid dyes. Quarternization of sugar cane bagasse through the use of N-(3-chloro-2-hydroxypropyl)-trimethylammonium chloride for the removal of acid dyes has been reported by Laszlo (1996). However, the lack of mechanical strength of this material necessitates a cross-linking step and hence increases its production cost, Peanut (*Arachis hypogea*) hull is obtained in great abundance in Malaysia. It is generally discarded or burnt as a fuel. It contains mainly cellulose and lignin (Woodroof 1983). In our continued effort to exploit low cost biomaterials for the removal of pollutants from aqueous environment, we investigated the suitability of quaternized peanut hull in the removal of acid dyes from synthetic solution and textile effluent.

MATERIALS AND METHODS

Peanuts were purchased from open market. The hull was ground to pass through a 1.0 mm-sieve. It was steeped in dilute nitric acid solution (1% v/v) overnight before being washed several times with distilled water. It was dried at

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80° C and the material was labeled as natural peanut hull (NPH). A portion of NPH was chemically modified according to the method reported by Laszlo (1996) with some modifications. NPH was treated in an alkaline solution of N-(3-chloro-2-hydroxyproply)trimethylammonium chloride at 70°C for 4 hr with intermittent stirring. The reaction mixture was then washed with distilled water until the pH of the filtrate was near neutral. It was then dried before experimentation. The quaternized peanut hull was labeled as QPH.

The sorption capacities of NPH and QPH for various acid and basic dyes were investigated. Subsequent sorption experiments were conducted using Acid Blue 25 as it was sorbed most favorably by QPH.
The effect of pH on dye sorption was investigated by equilibrating the sorbate-sorbent mixture at different initial pH values of 2-12 by the addition of 0.1 M HCl or NaOH before the addition of pre-weighed sorbent.

All sorption experiments were conducted by agitating a known weight of sorbent with various aqueous solutions of the dye at 150 rpm at 27±2°C for a specific time. The sorbent-solution mixture was then centrifuged at 4000 rpm for 5 min and the supernatant was analyzed for its dye concentration using a Shimadzu 160 double-beam UV/visible spectrophotometer with 1.0 cm light path cuvette at the appropriate λ_{max} for each dye. Per cent uptake (% uptake) is defined as $[(C_o-C_t)/C_o]x100$ where C_o and C_t are the initial and at time (t) of the concentrations of the dye solutions respectively. All the experiments were conducted in duplicate and the results shown are the average values of the duplicates. In general the relative standard deviation was less than 5%. Controls without sorbent were carried out simultaneously to ensure that sorption did not occur on the surface of containers.

The textile effluent was obtained from Kemunting Textile Industries, Perak, Malaysia.

RESULTS AND DISCUSSION

The quaternization of the peaunt hulls is believed to involve the carboxylic groups of the peanut hull as shown below:

$$S_h\text{-}CO_2Na + ClCH_2CH(OH)CH_2N^+(CH_3)_3Cl^- \rightarrow S_h\text{-}CO_2CH_2CH(OH)CH_2N^+(CH_3)_3Cl^- + NaCl$$

where Sh represents the surface of the hull.
The ability of QPH and NRH to remove various dyes is shown in Figure 1. It shows that sorption was favorable for acid dyes as compared to basic dyes. The uptakes for the basic dyes, MB and BB3 were less than 2 %. The acid dyes produce an anionic colored component in aqueous solution and is attracted to the cationic binding sites of QPH which is attributed to the presence of the quaternary ammonium group. The low uptake of basic dyes is due to the coulombic repulsion between the cationic colored component of the dyes and the positive charge of the QPH. Sorption enhancement for acid dyes through quaternization of

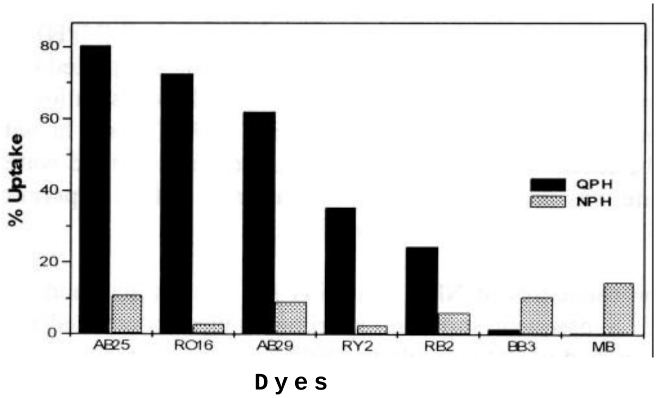

Figure 1. Comparative sorption capacity of QPH and NPH for various dyes. Condition: 0.05 g sorbent in 20 mL of 500 mg/L dye solution at 150 rpm for 8 hr. AB25 – Acid Blue 25; RO16 – Reactive Orange 16; AB28 – Acid Blue 28; RY2 – Reactive Yellow 2; RB2 – Reactive Blue 2; BB3 – Basic Blue 3 and MB – Methylene Blue.

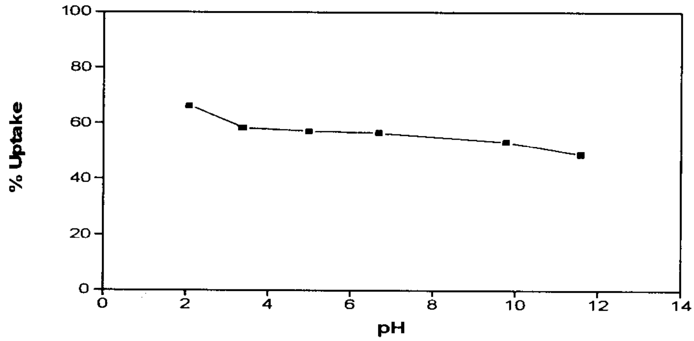

Figure 2. Sorption of AB 25 by QPH as a function of pH. Condition: 0.05 g of sorbent in 20 mL of 750 mg/L dye solution at 150 rpm for 8 hr.

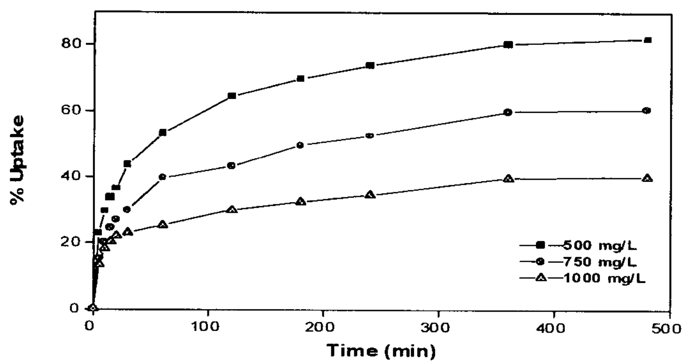

Figure 3. Effect of various initial concentrations on the uptake of AB25 by QPH. Condition: 0.05 g of sorbent in 20 mL dye solution at 150 rpm.

NPH is evident from this study. Hence, all subsequent experiments were carried out using QPH.

The effect of pH on the uptake of AB25 is shown in Figure 2. Uptake was more favorable under acidic conditions, The uptake increased in the pH range of 5.0 to 2.1. The sorption process may be considered as an ion-exchange between the Cl of the quaternary ammonium salt and the anionic component of the acid dye. As the pH value of the dye solution increases the concentration of the OH^- ion increases accordingly and this leads to competition for binding sites on the sorbent. Hence sorption decreases. As the effect of pH on the uptake of AB25 by QPH was not very great, it would be more economical to carry out subsequent experiments without pH adjustment. It was, accordingly, conducted at the pH of the dye solution which was 5.0.

The effect of different initial dye concentrations on the uptake of AB25 by QPH is shown in Figure 3. The plots followed the general pattern of higher percentage uptake with decreasing concentrations. Pseudo-equilibrium was attained after 4 h.

In order to optimize the amount of sorbent used in a given solution, the effect of sorbent dosage as a function of uptake was investigated and the results are shown in Table 1. For AB25 solution optimum amount of QPH for near complete removal of the dye occurred at 0.07 g.

Table 1. Effect of sorbent dosage on the sorption of AB25 by QPH. Condition: sorbent of various dosages in 20 mL of 500 mg/L AB25 solution agitated for 8 hr

Dosage (g)	Uptake (%)
0.01	14.23
0.03	42.04
0.05	80.31
0.06	93.31
0.07	99.11
0.09	99.85
0.12	100
0.15	100

In order to determine the maximum sorption capacity of QPH for AB25 sorption isotherm was constructed over the concentration range of 40 –1050 mg/L. The sorption data were fitted into a Langmuir isotherm of the form:

$$C_e/N_e = 1/(N^*b) + C_e/N^*$$

where C_e is the concentration of the dye at equilibrium (mg/L), N_e the amount of dye sorbed at equilibrium (mg/g), b, a constant related to the energy of sorption and N^* the maximum sorption capacity of the modified peanut hull for a particular dye at a known temperature. Such a isotherm is shown in Figure 4 and the maximum sorption capacity for RB25 is 175.44 mg/g. This value compares favorably to those obtained for commercial activated carbon (120 mg/g), natural

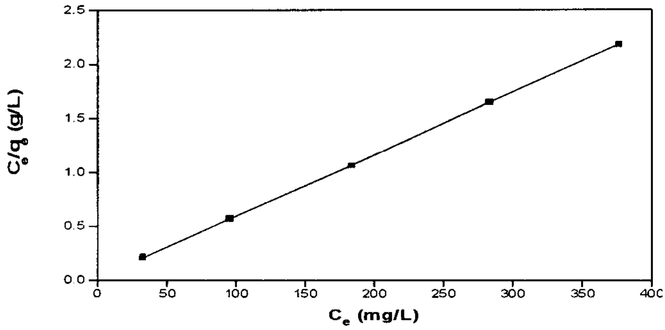

Figure 4. Langmuir isotherm for the sorption of AB25 on QPH.

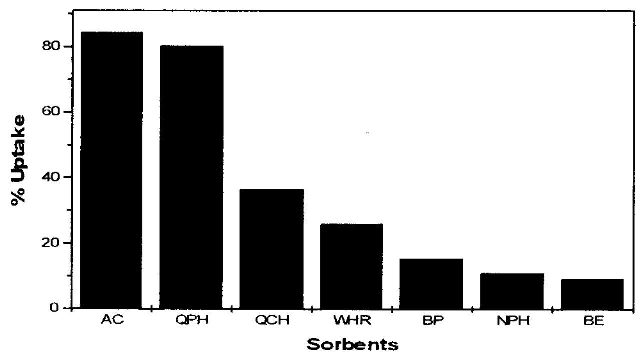

Figure 5. Comparative sorption capacity of various sorbents for AB25 Condition: 0.05 g sorbent in 20 mL of 500 mg/L solution at 150 rpm for 8 hr. AC- activated carbon; QPH- quaternized peanut hull; QCH- quaternized coconut hull; WHR- water hyacinth root; BP- banana pith; NPH- natural peanut hull and BE- bleaching earth.

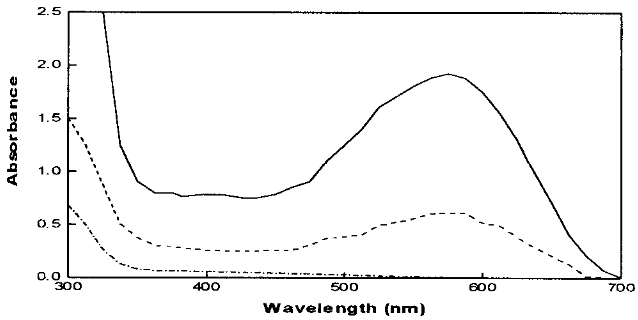

Figure 6. The absorption spectra of textile waste before and after treatment with QPH (—) - 0 min; (----) – 30 min and (-·· ·· -) 120 min.

clay (39.6 mg/g), maize cob (41.1 mg/g) and bagasse pith (23.2 mg/g) (Nassar and El-Geundi 1991).

A comparative study on the sorption capacity of QPH with various commonly available sorbents for AB25 is shown in Figure 5. The sorption capacity of QPH is comparable to that of activated carbon AB25. Through chemical modification the sorption capacity of peanut hull was greatly enhanced.

The usefulness of the QPH-dye system was evaluated by treating QPH with a sample of textile effluent. The waste consisted of a variety of reactive, disperse, direct and sulfur-vat dyes and pigments. The λ_{max} of the waste was 583 nm. The visible spectrum of the sample before and after sorption intervals of 30 and 120 min are shown in Figure 6 . Almost all the dyes were removed indicating that QPH is a suitable sorbent for the removal of dyes under batch conditions.

The results show that quaternized peanut hulls could be a useful sorbent for acid dyes in aqueous solution under batch conditions. However, its commercial applications to dye removal in textile waste can only be ascertained after its effectiveness in column study has been investigated. Such a study is currently being undertaken.

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