UTILIZATION OF CALCIUM ALGINATE BEADS AS ADSORBENT FOR REMOVAL OF DYES FROM TANNERY WASTEWATERS

by

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ABSTRACT

The presence of color due to dyes in the effluents from leather industry is a major concern in today's eco-sensitive world. In this present study, the removal of three most commonly used dyes in leather industry, viz. acid, direct and metal complex dye, by adsorption onto calcium alginate beads has been studied in dynamic-batch mode. The effect of initial dye concentration, alginate quantity, size of the beads, pH and temperature on dye removal was studied for batch conditions. Experiments with commercial tannery dye effluents have also been carried out and the results indicate the potential of calcium alginate beads as effective adsorbents for removal of dyes from commercial tannery effluent. Desorption studies were carried out, which indicate the reuse potential of the alginate beads. The measured adsorption kinetics was well described by a pseudo-second order kinetic model.

INTRODUCTION

The leather industry has gained a negative image owing to the pollution problems it causes. Leather processing involves various steps, which converts the putrescible hide/skin into non-putrescible, fashionable leather.[1] Dyeing is one such operation in leather processing, which imparts color to the leather. As a result of this operation, the effluent emerging from tanneries is highly colored. Color being the most discernable indicator of pollution in the aqueous environment, is the first to attract the attention. The presence of dyes in the effluent leads to not only aesthetic problems but also affects the photosynthesis process adversely.[2] Thus, the removal of dyes from tannery effluents is of significant importance from both ecological and commercial point of view.

Various physical and chemical methods have been explored for the removal of dyes from wastewaters.[3,4] The most commonly employed process for dye removal from wastewaters is through adsorption, especially with activated carbon.[5,6] However, the disadvantages associated with use of activated carbon are disposal of concentrated sludge and regeneration of the carbon, which is expensive. In this regard, the use of low cost biological materials seems potential alternatives for adsorption. The ability of various waste residues such as wheat straw, corncobs, barley husks, apple pomace, kudzu, orange peel, date pits for removal of dyes have been investigated.[7-9] The adsorption behavior of reactive dyes in aqueous solution on chemically cross linked chitosan beads has been studied.[10] Various biological processes have also been attempted for the removal of dyes.[11,12] However, these processes are highly sensitive to the characteristics of the effluent such as pH, temperature, chemical composition etc. Conventional biological processes are not effective for treating dyestuff because they are toxic to the organisms being used and result in problems of sludge bulking, pin point floc etc.[13] The dye binding capacity of sewage sludge has also been explored.[14] However, the limitations with respect to sludge quality, appropriate soil availability and difficulties encountered in its management and monitoring exist.

Alginate is a carbohydrate polymer, which is an attractive natural resource, possessing a potential to remove toxic pollutants. Many biopolymers are known to have a strong binding on metals and the use of alginic acid as adsorbents for the recovery of valuable metals or the removal of toxic metals has been studied.[15,16] Alginic acid is a biopolymer carrying carboxyl groups capable of forming complexes with metal ion. One of the useful characteristics of alginate is the ability to form hydrogels.[17] An aqueous solution of alginate is readily transformed into a hydrogel on addition of metallic divalent cations such as Ca^{2+}.[18] Alginate is often used for immobilization of biological entities.[19] Moreover, the important contribution of alginate of certain biological entities, such as algae, to the uptake of heavy metal ions has been reported.[20,21]

In the present investigation, the potential use of calcium alginate beads for removal of dyes from tannery effluents in dynamic-batch mode has been studied. Three most commonly used dyes in leather processing namely; acid dye, direct dye and metal complex dye have been chosen for the study. The effect of the initial dye concentrations and adsorbent dosages on the uptake of dyes has been investigated. The kinetics of the adsorption has been studied. Desorption studies have been

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Manuscript received September 30, 2005, accepted for publication November 30, 2005

carried out to assess the reusability of the dye loaded alginate beads. Studies on dye removal from commercial dye effluent of a tannery have been carried out to evaluate the ability of alginate beads to remove dyes from commercial tannery effluent in the presence of other chemicals used in leather processing.

EXPERIMENTAL

Materials

Sodium alginate (sodium polymannuronate) was obtained from Loba Chemie Pvt. Ltd. India. Calcium chloride and potassium hydroxide were procured from SD Fine Chemicals, India. Three commercially used dyes, acid brown (AB) direct blue (DB) and acid orange (AO) were selected and used for the dye removal experiments. The dyes were miscible in water giving a pH of 6.5±0.5, yielding a brown, dark blue and reddish orange color, respectively in aqueous solution. The dyes have the color index classification CI Acid brown 213 (acid dye), CI Direct blue 25 (direct dye) and CI Acid orange 76 (metal complex dye), respectively. The chemical structures of the 3 dyes are given in Fig. 1.

Preparation and characterization of adsorbent

A solution of 2% calcium chloride and 2% sodium alginate in deionized water was prepared separately. For preparation of beads, the 2% sodium alginate solution was added drop-by-drop by means of a peristaltic pump equipped with a micropipette tip into stirring calcium chloride solution. The water-soluble sodium alginate was converted into water-insoluble calcium alginate beads on treatment with calcium chloride. The diameters of the beads were varied using various sizes of micropipette tips. The beads were maintained in the solution for a period of 24 h at 4 °C. The beads were then washed with deionized water several times to remove unbound $CaCl_2$ from bead surface. A known number of beads, about 250, were taken and the total volume was measured by adding them to a cylinder with a known volume of distilled water. The particle diameter was experimentally estimated and found to be 2.5±0.1 mm (the values are average of three trials). The mean weight of this known volume of beads was evaluated (11.31 g) removing only the excess of water by filter paper, after their collection by filtration. From these data, 1 cm^3 of beads had wet weight of 1.03 g. Successively, these were introduced in an oven at 50 °C for 24 h. The dry weight of beads was estimated to be 0.226 g. The same was repeated for other sizes of the beads. The moisture content of the alginate beads was estimated to be 98%. All values expressed in this study are on the dry weight basis. Excess water on the surface of the beads was removed by filter paper, immediately before using for the experiments.

Preparation of simulated dye solution

The dye solution was prepared by dissolving the above-mentioned three dyes separately, in deionized water to produce a stock solution of 1000 mg dm^{-3} (pH=6.45). This stock solution was diluted in accurate proportions to produce solutions of different initial concentrations.

Fig. 1(a).

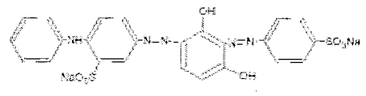

Fig. 1(b).

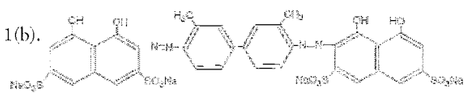

Fig. 1(c).

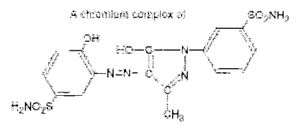

Figure 1. - Chemical structure of the commercial dyes used in the experiments. (a) Acid brown, (b) Direct blue, (c) Acid orange.

Dynamic batch studies for dye removal

Batch adsorption equilibrium and kinetic experiments were undertaken by contacting varying amount of adsorbent with 50 cm^3 of 500 mg dm^{-3} dye solutions. The bottles were placed in a temperature controlled mechanical shaker at room temperature (33 ± 2 °C) and samples were withdrawn at known time intervals to study the kinetics of the adsorption process. The initial and final concentrations of the dyes were measured using Lambda 35 UV-visible spectrophotometer at 443, 617 and 481 nm for acid, direct and metal complex dyes, respectively. The dye uptake by calcium alginate beads (q) was calculated from the difference between the initial and final dye concentration as follows:

$$q = [(C_o - C_f)V]/M \quad (1)$$

where q is the dye uptake (mg g^{-1}), C_O is the initial dye concentration, C_f is the final dye concentration (mg dm^{-3}), M is the adsorbent dosage (g) and V is the solution volume (dm^3). Each experimental result was obtained by averaging the data from two parallel experiments.

The effect of initial dye concentration on dye removal was studied by varying the concentration from 100 to 500 mg dm^{-3}. The amount of adsorbent was maintained constant as 0.2 g and the adsorption was followed till equilibrium was reached.

Adsorbent dosage

Effect of adsorbent dosage was determined by agitating 0.1, 0.2, 0.3, 0.4 and 0.5 g (dry weight basis) of calcium alginate beads with 50 cm^3 of 500 mg dm^{-3} dye solution for a contact time of 15, 30, 45, 60, 90, 120 150 and 180 min for all three dyes. After agitation the contents of the flasks were decanted and absorbance was determined at their respective absorption maxima.

Effect of pH and temperature

Experiments were carried out to find out the effect of pH and temperature on the dye (acid, direct and metal complex dyes) uptake by the alginate beads. The pH was varied from 4.0 to 8.0 (4.0, 5.0, 6.0, 7.0 and 8.0) using 0.1 N KOH and 0.1 N HCl. The temperature was varied from 35 to 75 °C (35, 45, 55, 65, 75 °C) at a constant pH of 6.0 for temperature studies. For both the experiments, 0.2 g of beads per 50 cm^3 of 100 mg dm^{-3} dye solution was employed. After agitation for a period of 180 min, the contents of the flasks were decanted and absorbance was determined at their respective adsorption maxima.

Effect of particle size of the absorbent

The effect of the particle size of the beads on the uptake of dyes was determined by agitating 0.2 g of alginate beads of 3 different sizes (0.5, 1.5, 2.5 (±0.1) mm diameter) separately with 50 cm^3 of 300 mg dm^{-3} dye solution for a contact time of 120 min for all three dyes. After 2 h, the contents of the flasks were decanted and absorbance was determined at their respective absorption maxima.

Desorption experiments

Dye loaded alginate beads were treated with 20 cm^3 of 0.5 N KOH in batches for a period of 2 h in a mechanical agitator. The absorbance at the lmax of the dyes was measured after each batch to study the % removal of dyes.

Experiments with commercial tannery effluent containing dye

Effluent from a commercial tannery in India employing the same dyes used in this study was obtained. The optimized parameters were used to treat the commercial effluent. One litre of commercial effluent was treated with alginate beads in several stages till there was considerable reduction in the dye concentration in the final effluent. Optimised quantity of alginate beads were used at every stage and the liquor was in contact with the alginate beads for a period of 2 h in rotary mechanical shaker. The absorbance was measured at respective wavelengths after each stage.

RESULTS AND DISCUSSION

Sorption process involves a solid phase (sorbent) and a liquid phase (solvent) containing a dissolved species to be sorbed (sorbate). Due to the higher affinity of the sorbent for the sorbate species, the latter is attracted onto the solid and bound there by different mechanisms. The degree of the sorbate's affinity towards the sorbent determines its distribution between the solid and liquid phase.

TABLE I
First Order, Second Order and Intraparticle Diffusion Kinetic Parameters for the Three Dyes

Alginate quantity (g)	$q_{e,exp}$ (mg g^{-1})	First order rate constants			Second order rate constants			Intraparticle diffusion rate constant	
		k_1 (min^{-1})	$q_{e,cal}$ (mg g^{-1})	R_2	k_2, (g mg^{-1} min^{-1})	$q_{e,cal}$	R_2 (mg g^{-1})	k_i, (mg/(g $min^{1/2}$)	R_2
Acid dye									
0.1	53	0.0177	33.27	0.833	0.0007	59.0319	0.991	2.932	0.852
0.2	48	0.0136	8.59	0.649	0.0042	48.4262	0.998	0.826	0.807
0.3	33.3	0.0058	4.11	0.164	0.0127	31.5060	0.984	0.355	0.1921
0.4	24.38	0.0150	9.06	0.541	0.0060	24.9352	0.997	0.495	0.876
0.5	21.5	0.0124	4.89	0.909	0.0070	21.9068	0.998	0.471	0.838
Direct dye									
0.1	27.5	0.0177	13.48	0.894	0.0017	30.3610	0.99	1.423	0.708
0.2	32	0.0177	23.49	0.825	0.0009	36.4431	0.98	1.852	0.942
0.3	30	0.0157	12.36	0.978	0.0025	31.3913	0.997	1.033	0.947
0.4	26	0.0279	28.44	0.84	0.0015	29.0588	0.988	1.27	0.961
0.5	24.6	0.0246	13.96	0.89	0.0025	26.8557	0.997	1.087	0.853
Metal complex dye									
0.1	23	0.0101	5.69	0.561	0.0044	23.0494	0.977	0.287	0.284
0.2	32.6	0.0209	10.50	0.854	0.0044	33.6157	0.999	0.728	0.89
0.3	27.83	0.0155	9.71	0.858	0.0037	28.4892	0.993	0.626	0.921
0.4	25.88	0.0102	9.44	0.781	0.0033	25.7255	0.988	0.694	0.857
0.5	21.8	0.0206	6.95	0.768	0.0056	22.6721	0.997	0.463	0.933

TABLE II
Percentage Removal of Dyes After Desorption

Dye	Stages of treatment	Dye in beads before desorption (mg g^{-1})	Dye in beads after desorption (mg g^{-1})	% desorption
Acid	I	9.75	5.75	41
	II	5.75	4.25	56
Direct	I	9.5	4.25	55
	II	4.25	1.75	81
Metal complex	I	7	2	71
	II	2	0.5	92

TABLE II
% Removal of Dyes From Commercial Tannery Dye Effluent

Stage no.	Conc. of acid dye (ppm)	% reduction	Conc. of direct dye (ppm)	% reduction	Conc. of metal complex dye (ppm)	% reduction
Initial concentration	500	-	85	-	970	-
I	405	19	65	24	750	23
II	356	29	45	47	580	40
III	310	38	40	53	440	55
IV	275	45	36	58	355	63
V	250	50	20	76	270	72
VI	200	60	10	88	190	80

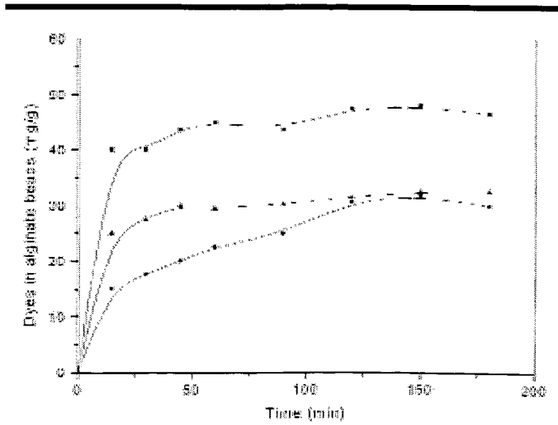

Figure 2. - Kinetics of different dyes uptake by alginate beads. -■- acid dye, -▲- direct dye, -●- metal complex dye, Co 500 mg dm-3, Alginate dose 0.2 g.

Kinetics of adsorption process

The kinetics of the dye uptake by calcium alginate beads was followed by contacting the dye of initial concentration 500 mg dm^{-3} with different quantity of alginate beads (on dry weight basis) for different time intervals. Fig. 2 shows the dye uptake for 0.2 g of alginate beads at various time intervals for the three dyes. As can be seen from the figure, adsorption capacity of the beads during the initial time of contact is very high. After which there is only marginal increase in the dye removal. Equilibrium for all three dyes is almost reached in about 90 min. The sorption kinetics describes the solute uptake rate, which in turn governs the residence time of a sorption reaction. It is one of the important characteristics in defining the efficiency of a sorption process. In order to understand the behavior of the adsorbent, kinetic studies were carried out. Several kinetic models are available to examine the controlling mechanism of the adsorption process and to test the experimental data. In order to understand the dye adsorption kinetics of calcium alginate beads, various kinetics models were used to test the experimental data. The Langergren equation or pseudo-first order equation describes the kinetics of adsorption process as follows;

$$\mathrm{Log}(q_e - q_o) = \mathrm{Log}q_e - \left(\frac{k_1}{2.303}\right)t \qquad (2)$$

where, q_t is amount of dye adsorbed (mg g^{-1}) at any time, k_1 is the rate constant. The first order rate constant (k_1) and q_e were determined from the slopes and intercepts of plots of log (q_e-q) vs. t at different alginate dosages.

The pseudo second order equation describes the kinetics of adsorption as follows and the linearized form of this model is:[22]

$$t/q_t = 1/k_2 q_e^{\,2} + 1/q_e t \qquad (3)$$

The second-order rate constant (k_2) and q_e were determined from the slope and intercepts of the plot obtained by plotting

t/q_t vs. t. The value of q experimentally determined ($q_{e(exp)}$), q_e calculated ($q_{e(cal)}$), correlation coefficient together with the kinetic adsorption rates k_1 and k_2 are shown in Table I.

The correlation coefficients for the first order kinetic model obtained at various concentrations are generally lower than in the case of second order equation for all three dyes. Also the calculated values of q_e found from the first order kinetic model gave less reasonable values for all quantities of alginate beads for all three dyes than those from the second order kinetic model. For these dyes, the $q_{e(cal)}$ obtained agreed very well with the experimental values, $q_{e(exp)}$, in the case of second order equation. The kinetics of the adsorption fitted best to a pseudo-second order model with regression coefficients, $R^2 > 0.985$. The Fig. 3a-c shows the pseudo-second order fit of the adsorption kinetics for acid, metal complex and direct dye, respectively. The linearity of the plot shows the applicability of the pseudo-second order kinetic model obtained by plotting t/q_t versus t for all the three dyes. This indicates that the dye sorption system is not first order reaction and that the pseudo second order model provides a better correlation of data.

The data were further processed for testing the role of diffusion (as a rate controlling step) in the adsorption process. According to the Morris and Weber[25] model uptake is proportional to the square root of contact time during the course of adsorption. Accordingly,

$$q_t = k_d\sqrt{t} \qquad (4)$$

k_d is the rate constant of intraparticle transport (mg/g per $min^{1/2}$)

Plot of uptake q_t vs $\sqrt{t}$ should be linear if intraparticle diffusion is involved in the adsorption process and if the lines pass through the origin then intraparticle diffusion is the rate controlling step. But in the present adsorption process, intraparticle diffusion is involved (figure not shown) but is not the only rate limiting mechanism, as the lines do not pass through the origin.

Effect of initial concentration of dye

Adsorption of dyes onto alginate beads at given contact times for five different initial concentrations (C_o) of dyes at an adsorbent dose of 0.2 g per 50 cm^3 was studied. The effect of initial dye concentration on the rate of adsorption by calcium alginate beads is shown in Fig. 4. As obvious from the figure, the amount of dye adsorbed per gram of adsorbent increases with the increasing concentration of dye. The dye uptake values (q) for acid dye are higher than those of direct dye and metal complex dye for all concentrations. This shows the effect of initial dye concentration on the dye uptake by calcium alginate beads.

Effect of adsorbent dosage

In order to study the effect of adsorbent dosage on dye removal, various amounts of alginate beads were contacted with a fixed initial dye concentration of 500 mg dm^{-3}. The dye adsorbed per gram of adsorbent after agitation for various time intervals for

Fig. 3(a).

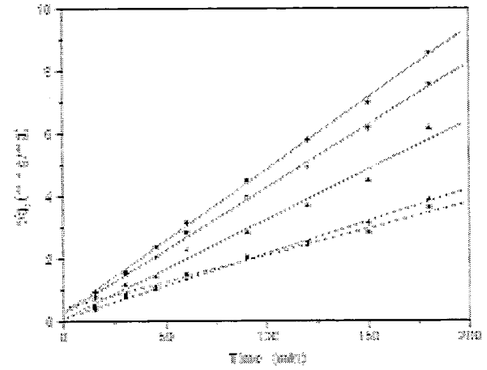

Fig. 3(b).

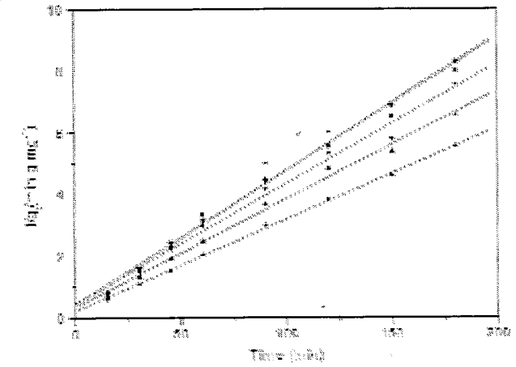

Fig. 3(c).

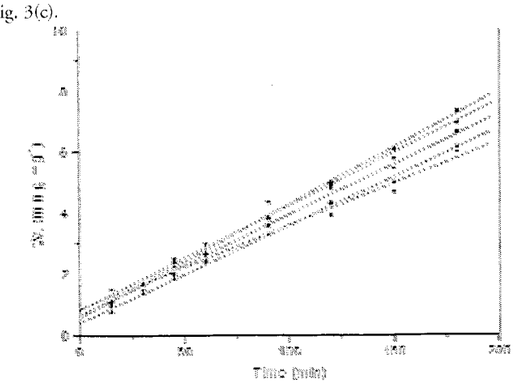

Figure 3. - Dyes uptake by alginate beads according to pseudo-second order model. (a) acid dye (b) metal complex dye (c) direct dye. -■- 0.1 g, -◆- 0.2 g, -▼- 0.3 g, -▲- 0.4 g, -●- 0.5 g.

acid, metal complex and direct dye versus the time of contact are shown in Fig. 5a-c, respectively. These results with various time of contact of different dosages of dyes with beads also indicate the adsorption capacity of the beads during the initial period of contact. It could be seen from Fig. 5(a), that 0.2 g of alginate beads has more dye uptake (q) showing that it removes more acid dye per gram of alginate beads than

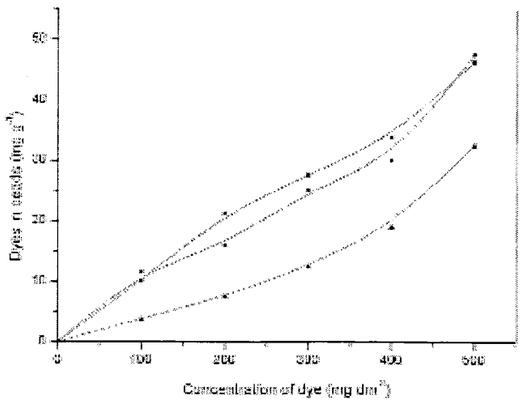

Figure 4. - Effect of initial concentration of dyes (Co) on removal of dye at alginate dose of 0.2 g. -● - acid dye, -■ - metal complex, -▲ - direct dye.

other weights. The same is observed for direct dye and metal complex dye, where 0.2 g of dye shows more dye uptake (Fig. 5(b) and 5(c)). The q values for acid dye are higher when compared to direct and metal complex dye for the same alginate dose of 0.2 g.

Effect of temperature and pH on sorption

In order to study the effect of temperature and pH on adsorption of dyes by alginate beads experiments with varying temperatures and pHs were carried out and the results of the same are given in Fig. 7 and 8, respectively. It can be seen from Fig. 6 that there is an increase in uptake value for metal complex dyes as the temperature is increased from 35 to 75 ^{o}C. Whereas, in the case of acid and direct dyes, there is an increase in uptake values up to 55 ^{o}C and then a decrease is observed. It can be seen from Fig. 7 that there is no significant influence of pH on the uptake values for all three dyes. Also, spectra run after adjusting the pH of the dye solution to respective pH did not show any change, which confirmed that there is neither structural modification in the species of dye nor a new product is formed. Thus, it can be envisaged that adsorption plays a vital role in the removal of dye from the effluent.

Effect of particle size of the adsorbent

Fig. 8 shows the adsorption of the three dyes on the alginate beads for three different bead sizes (pH 6.0) with an initial concentration of 300 mg dm^{-3}. It is seen that the adsorption of the dyes by the smaller sized beads is higher than that of the medium and large sized beads. Fig. 8 indicates that the dye uptake decreases with increasing diameter of the alginate beads for a given initial concentration. This can be attributed to the fact that for the same dosage of the adsorbents (0.2 g) the maximum surface area of contact would be available for smaller sized beads.

Desorption studies

In order to asses the reuse potential of dye loaded alginate beads, desorption studies were carried out using KOH as the beads are soluble in NaOH. The percentage removal of dyes

Fig. 5(a).

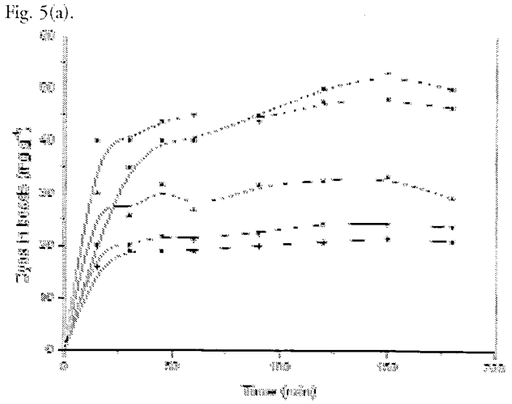

Fig. 5(b).

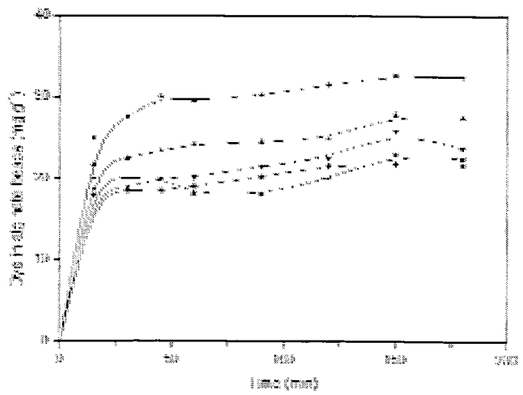

Fig. 5(c).

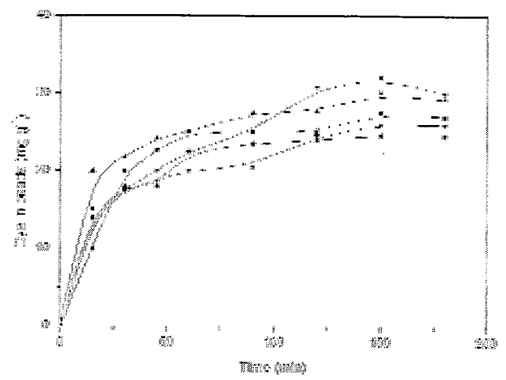

Figure 5. - Effect of dose of alginate beads on dyes removal (mg g-1) at initial concentration of dye (Co) 500 mg dm-3. (a) acid dye (b) metal complex dye (c) direct dye. -● - 0.1 g, -▲ - 0.2 g, -▼ - 0.3 g, - ◆ - 0.4 g, - ■ - 0.5 g.

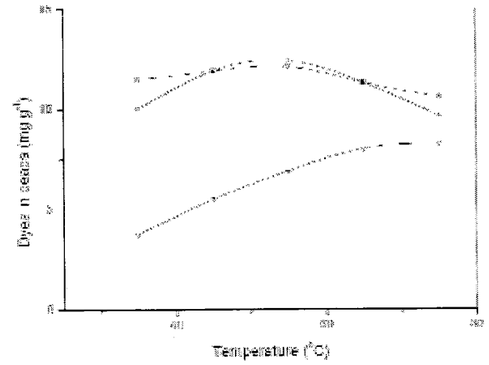

Figure 6. - Effect of temperature on the uptake of -⊠ - acid dye,-⊕ - direct dye,-▽- metal complex dye, Co 100 mg dm-3, Alginate dose 0.2 g.

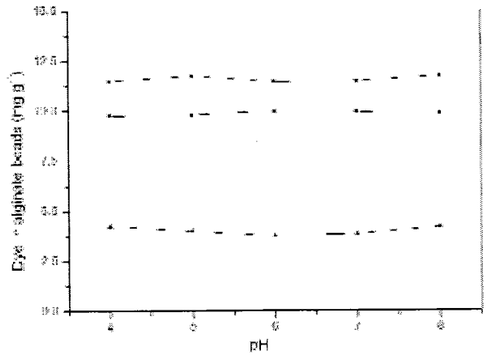

Figure 7. - Effect of pH on the uptake of -●- acid dye, -■- direct dye, -▲- metal complex dye, Co 100 mg dm-3, Alginate dose 0.2 g.

from the dye loaded alginate beads is shown in Table II. The % removal of acid dye, direct dye and metal complex dye is 56, 81 and 92% respectively. This shows that the alginate beads can be reused after desorption. Also, dye loaded alginate beads can be used as gelling agents and thickeners in dye industry.

Studies on dye removal from commercial tannery dye effluent

Experiments were carried out for dye removal from commercial tannery dye effluent using the same three dyes in order to assess the ability of alginate beads to remove dyes in the presence of other chemicals used in leather processing. Generally, the dyeing operation during leather processing is carried out in the same float along with other operations like retanning and fatliquoring. Variety of chemicals is added during these processes to get the desired end properties on the final leather. The removal of dyes was carried out in 6 stages as indicated in the schematic diagram (Fig. 9). The standardized parameters such as time of treatment with alginate beads and amount of alginate beads standardized in the batch experiments using synthetic dye effluent have been used for the removal of dyes from the commercial tannery dye effluent. The % removal of

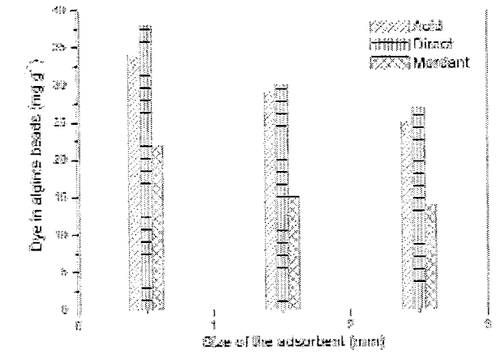

Figure 8. - Effect of size of alginate beads on the uptake of dyes; acid dye, metal complex dye, direct dye.

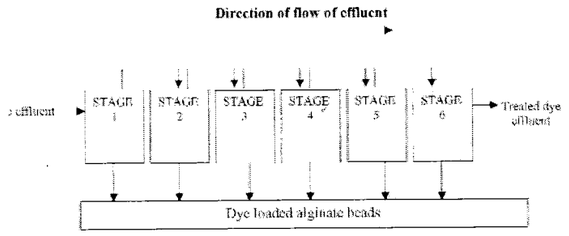

Figure 9. - Schematic diagram representing the six-stage removal of dye from commercial tannery dye effluent.

the three dyes from the commercial dye effluent is shown in Table III. The increase in the % reduction after every stage of treatment indicates that complete removal of dyes can be achieved on several stages of treatment. A reduction of 60, 88 and 80% has been achieved for acid dye, direct dye and metal complex dye, respectively using calcium alginate beads for commercial tannery dye effluent. It could be seen that the % reduction for acid dye is less when compared to direct and metal complex dye, which could be due to the lowering of affinity of acid dye in liquid phase in the presence of other chemicals.

Conclusions

The present study explores the potential of calcium alginate beads to remove dyes present in the effluent from leather industry. Various parameters that affect the removal of dyes have been standardized. Kinetic data of adsorption were well fitted to pseudo-second order kinetic model. Desorption studies indicate the reuse potential of the dye loaded alginate beads. Studies using commercial tannery dye effluent were carried out and the adsorption potential of alginate beads in the presence of other chemicals was determined. This study indicates the potential of calcium alginate beads to act as an effective adsorbent for removal of dyes from tannery effluents.

ACKNOWLEDGEMENTS

The authors wish to thank Dr. T Ramasami, Director, Central Leather Research Institute, for helpful discussions and encouragement at all stages of the work. One of the authors (R.A.) is grateful to Council of Scientific and Industrial Research, Govt. of India, New Delhi for granting Senior Research Fellowship (SRF) for his Ph.D program.

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