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Adsorption of Reactive Dye by Eggshell and Its Membrane

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ABSTRACT

The use of eggshell and its membrane as adsorbents for the removal of reactive dye from aqueous solutions was investigated. The adsorption characteristics of C.I. Reactive Yellow 205 by various components of eggshells were investigated by fitting the experimental data to Freundlich and Langmuir isotherms. Eggshell membranes had a much larger (10 to 27 - fold) capacity to adsorb the dye than did the other components. The initial pH of dye solutions in the range 4-9 did not influence significantly the adsorption of dye by eggshell with membrane and the highest value of adsorption capacity was observed at 35°C. The extent of adsorption of the dye was related directly to the surface area of the adsorbent. The results presented demonstrate clearly that eggshell with its membrane attached is a potentially useful material to be used for the removal of reactive dyes from industrial wastewater.
Key words: eggshell, eggshell membrane, reactive dye, adsorption, Freundlich isotherm

INTRODUCTION

Large quantities of reactive dyes are utilised by the textile industry. Mainly due to their extensive application in the dyeing of cotton, about 20-30% of all of the dyestuffs used worldwide are reactive dyes. Biodegradation of this group of compounds is significantly slower than that of acid and direct dyes (Zollinger, 2003). The persistent nature of reactive dyes complicates wastewater treatment within the textile industry. Removal of dyestuffs from wastewater occurs by either biological methods or physicochemical methods (e.g., adsorption, oxidation-reduction, chemical coagulation, ozone treatment, and membrane filtration). Removal of reactive dyes by adsorption is one of the many methods widely used. Various adsorbent materials (e.g., activated carbon, chitosan, agricultural waste, and natural waste) have been studied (McKay, 1996; Batzias and Sidiras, 2004; El Zawahry and Kamel, 2004; Papic *et al.*, 2004; Valix *et al.*, 2004; Zheng *et al.*, 2005; Orfao *et al.*, 2006).

Hens' eggs are used in enormous numbers by food manufacturers and restaurants and the shells are discarded as waste. Many investigations have been conducted to explore useful applications for eggshells. Such research has shown that eggshells may be used as a fertiliser and a feed additive for livestock and it appears to be able to effectively adsorb certain heavy metals and organic compounds (Kuh and Kim, 2000; Koumanova *et al.*, 2002; Chojnacka, 2005; Vijayaraghavan *et al.*, 2005).

The porous nature of eggshell makes it an attractive material to employ as an adsorbent. Each eggshell has been estimated to contain between 7000-17000 pores (William and Owen,

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1995). The principal component of the shell is calcium carbonate which comprises more than 90% of the material (William and Owen, 1995; Kuh and Kim, 2000; Stadelman, 2000). The eggshell membrane, which is located between the egg white and the shell, is composed of a network of fibrous proteins that has a large surface area (Tsai *et al.*, 2006). Eggshell membrane has found applications as an adsorbent and as a supporting medium for immobilisation of enzymes. However, the application of discarded eggshells in the removal of reactive dyes by adsorption has received very little attention. This work has been designed to examine the possibility of using eggshell and its membrane as adsorbents for this type of compound. The effects of temperature, pH, and particle size of the adsorbents on the adsorption of a reactive dye were investigated.

MATERIALS AND METHODS

Reactive Dye

C.I. Reactive Yellow 205, a sulphonated reactive azo dye, was obtained from Ciba Specialty Chemicals Inc.

Preparation of adsorbents

Discarded eggshells were collected from local restaurants. To prevent decomposition, eggshells were first washed in tap water, then boiled in distilled water, and finally dried at 105°C in a hot air oven for 2 h. The membranes were separated from dried eggshells by hand. The dried eggshells and membranes were ground separately using a blender. The powdered materials were sieved to obtain particles of various size ranges. The sieved materials were tested for their adsorbent qualities without further chemical or physical treatment.

Adsorption of Reactive Dye by Adsorbents

The 50 ml volumes of solutions (pH adjusted to 5.7 with 1M hydrochloric acid) containing various concentrations of dye were mixed with 2 g of membrane-free eggshell, 2 g of eggshell with membrane, or 0.5 g of eggshell membrane. The size range of the particulate solids was 0.250-0.425 mm. The mixtures were agitated at 35°C using a shaking incubator set at 300 revolutions per minute.

Effect of pH on Adsorption of Reactive Dye

The pH of 50 ml volumes of solutions containing various concentrations of the dye were adjusted with 1M hydrochloric acid or 1M sodium hydroxide to various values of pH and mixed with 2 g of powdered eggshell with membrane (particle size, 0.250-0.425 mm). The mixtures were incubated at 35°C.

Effect of Temperature on Adsorption of Reactive Dye

The 50 ml volumes of solutions containing various concentrations of the dye were mixed with 2 g of eggshell with membrane (particle size, 0.250-0.425 mm). The mixtures were agitated at 28, 35, and 40 °C.

Effect of Particle Size on Adsorption of Reactive Dye

The 50 ml volumes of solutions containing various concentrations of the dye were mixed with 2 g of eggshell with membrane of various size ranges. The mixtures were agitated at 35°C.

Determination of Reactive Dye

The concentrations of reactive dye in aqueous solutions were determined by measuring the absorbance of the solution at 419 nm using a Shimadzu model UV-1201 spectrophotometer. Aqueous solutions of the dye within the concentration range 0-60 mg/L were used for calibration. Plots of absorbance against concentration were linear. The concentrations of the dye remaining in the aqueous phase of the mixtures were determined periodically until adsorption attained equilibrium. The remaining solids were separated from the liquid phases by centrifugation at 10,000 rpm for 2 min. The experiments were carried out in triplicate.

RESULTS AND DISCUSSION

Adsorption of Reactive Dye by Adsorbents

The various components of eggshell investigated under batch conditions were powdered eggshell devoid of membrane, powdered eggshell with membrane attached, and powdered membrane. Within the range of initial concentrations (20-100 mg/L) of dye investigated, approximately 72% to over 99% of the compound was adsorbed by the various components at equilibrium. The values of q_e (amount of dye adsorbed per unit weight of component at equilibrium) are shown in Figure 1. The value of q_e for eggshell membrane was much higher than those for the other two fractions.

The data were assessed more closely by considering them in relation to the isotherms of Langmuir (Eqn 1) and Freundlich (Eqn 2), where C, q_0 and q_e represent the residual (unadsorbed) concentration of dye (mg/L), the maximum amount of dye that can be adsorbed onto the solid matrix (mg/g), and the amount of dye that is adsorbed (mg/g) at equilibrium, respectively.

$$1/q_e = K/q_0C + 1/q_0 \qquad \text{(Eqn 1)}$$

$$q_e = K_fC^{1/n} \qquad \text{(Eqn 2)}$$

The term K/q_0 gives an estimate of the monolayer adsorbent capacity, q_0 being known also as the solute adsorptivity. K_f and n (the Freundlich constants) are indicators of adsorption capacity and adsorption affinity, respectively. When the data were assessed using Freundlich's isotherm, the logarithmic form of Eqn 2 was employed and log q_e was plotted against log C. When the Langmuir's Eqn was used, $1/q_e$ was plotted against 1/C.

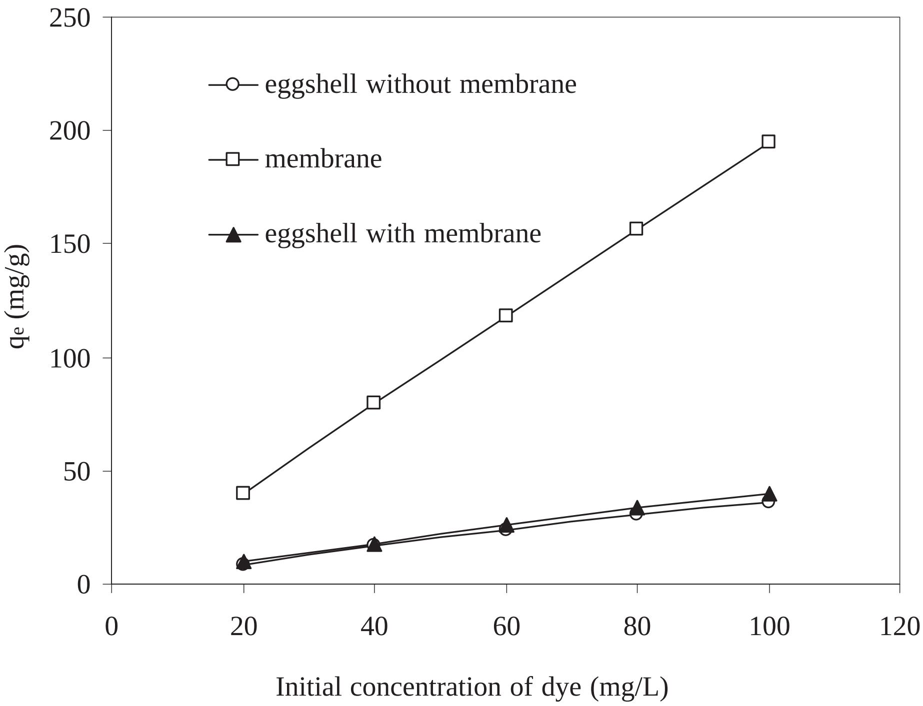

Figure 1 Adsorption of dye by eggshell components at 35°C

All of the plots were linear and the estimates of the various parameters were extracted from the values of their slopes and intercepts. However, better fits to the data were observed much more frequently in the Freundlich plots (Table 1). The values of K_f (adsorption capacity) extracted demonstrated conclusively that eggshell membrane adsorbed the reactive dye much more extensively (10 to 27 – fold) than did the other two fractions (Table 1). Values of n (adsorption affinity) indicated that the membrane had a greater affinity for the dye than did the shell.

Tsai *et al*. (2006) have reported that the properties of the pores of eggshells and the associated membrane are similar and the porosity of the shell is larger than that of the membrane. The results shown in Table 1 and Figure 1 reveal that the eggshell membrane has a much greater adsorption capacity (K_f) and, possibly, adsorption affinity (n) for the reactive dye than the shell. It is concluded, therefore, that adsorption of the dye is not related to the properties of the pores present in these structures. However, the results obtained here indicate that the charged nature of the adsorbing surfaces is the primary mechanism by which the dye is adsorbed. The reactive dye used contains several sulphonic acid groupings and is negatively charged at the pH of the mixtures employed (pH 7.9–9.2, see Table 2). The eggshell membrane is constructed of a network of fibrous proteins with a surface that bares positively charged sites produced by the basic side chains of the amino acids arginine and lysine. Accordingly, it is not unreasonable to attribute adsorption of the dye involves electrostatic attraction of these oppositely charged species. This idea is supported by the finding that the basic dye methylene blue is very poorly adsorbed by both eggshells and their membranes (Tsai *et al.*, 2006).

Effect of pH on Adsorption of Reactive Dye

Despite the membranes of eggshells having a substantially greater capacity to adsorb the dye, the procedure for separating this eggshell component is labour intensive and time consuming. Therefore, eggshells with membrane attached were selected for all further investigations.

Solutions of dye in water were initially adjusted to pH 4, 7, or 9. Immediately after adding

Table 1 Adsorption of dye onto components of powdered eggshell at 35ºC: parameters extracted from Freundlich and Langmuir plots.

	Freundlich isotherm			Langmuir isotherm		
	n	K_f	r^2	K/q_0	q_0	r^2
Eggshell	1.63	4.89	0.9964	0.2569	48.78	0.9974
Membrane	2.74	131.80	0.9937	0.0007	144.93	0.9516
Eggshell with membrane	2.76	13.09	0.9980	0.0366	30.96	0.9206

Table 2 Adsorption of dye from solutions of various initial pH onto powdered eggshell with membrane: parameters extracted from Freundlich plots.

pH of dye solution before addition of powdered eggshell with membrane	Freundlich isotherm			pH of Mixtures	
	n	K_f	r^2	Initially	At equilibrium
4	2.11	8.81	0.9992	8.7	8.0
7	2.04	8.41	0.9995	8.6	7.9
9	2.22	9.07	0.9991	9.2	8.0

eggshells with membrane, the pH of the mixtures observed were 8.7, 8.6, and 9.2 respectively (Table 2) and, at equilibrium, all of the mixtures had very similar values of pH (7.9-8.0, see Table 2). Consequently, all of the Freundlich plots and adsorption parameters generated from the data of these experiments were essentially identical (Table 2).

The principal component of the shell is $CaCO_3$ in the form of the mineral calcite. In aqueous solution the carbonate species derived from calcite are H_2CO_3, HCO_3^-, and CO_3^{2-}, the proportions of which are determined by the pH of the resulting solution. The pH of mixtures of eggshell with membrane and solutions of the dye of different initial pH all eventually attained a pH of near 8.0 (Table 2). From this finding it is concluded that sufficient amounts of carbonates are solubilised from the shells to buffer the mixtures to a faintly alkaline pH.

Effect of Temperature on Adsorption of Reactive Dye

The adsorptions of reactive dye at temperatures of 28, 35 and 40°C were investigated and the relevant values of the Freundlich parameters are displayed in Table 3. There was no obvious relationship between temperature and the adsorption parameters. However, the highest value of adsorption capacity (K_f) was noted at 35°C and temperature appeared to have little effect on adsorption affinity (n).

Effect of Particle Size on Adsorption of Reactive Dye

Three different size ranges of particles of adsorbent were examined. The results shown in Table 4, as might be expected, demonstrated clearly that the capacity of the matrix to adsorb the reactive dye is indirectly proportional to its particle size, and, hence, directly related to the surface area of the matrix exposed to the molecules of solute. However, particle surface area did not appear to affect adsorption affinity (n).

The results recorded in this study indicate conclusively that the adsorptions of C.I. Reactive Yellow 205 by the components of eggshells take place according to the classical model of adsorption described by Langmuir and Freundlich. However, better fits to the experimental data usually were observed using the logarithmic form of Freundlich's equation. This observation is not unexpected. It can be explained by considering the nature of the errors associated with the experimental values of q_e (the dependent variable). Any small error in q_e will become reduced within the term log q_e (see Eqn 2) and will become magnified in the value of its reciprocal (see Eqn 1).

CONCLUSIONS

Powdered membrane has a substantially larger capacity to remove the reactive dye by adsorption than all of the other eggshell

Table 3 Adsorption of dye onto powdered eggshell with membrane at various temperatures: parameters extracted from Freundlich plots.

Temperature (°C)	Freundlich isotherm		
	n	K_f	r^2
28	2.00	7.44	0.9991
35	2.71	13.09	0.9980
40	2.24	9.85	0.9983

Table 4 Adsorption of dye onto powdered eggshell with membrane for three particle sizes : parameters extracted from Freundlich plots.

Particle size range (mm)	Freundlich isotherm		
	n	K_f	r^2
0.175 – 0.250	2.23	15.57	0.9951
0.250 – 0.425	2.71	13.09	0.9980
0.425 – 0.850	2.27	10.41	0.9951

components. The temperature at which the adsorption occurred and the surface area of the adsorbent influenced markedly the adsorption capacity of eggshells with membrane without having any major effect on its adsorption affinity. Even eggshell devoid of membrane had a significant capacity to adsorb the dye. These results show that eggshell with membrane is a potentially useful material for the removal of reactive dyes from industrial wastewater. It is suggested that work designed to increase the scale of its application to cope with the removal of these compounds under industrial conditions should be initiated.

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