Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Online publication date: 07 June 2002

To cite this Article Namasivayam, C. , Yamuna, R. T. and Arasi, D. J. S. E.(2002) 'Removal of procion orange from wastewater by adsorption on waste red mud', Separation Science and Technology, 37: 10, 2421 — 2431
To link to this Article: DOI: 10.1081/SS-120003521
URL: http://dx.doi.org/10.1081/SS-120003521

SEPARATION SCIENCE AND TECHNOLOGY, 37(10), 2421–2431 (2002)

REMOVAL OF PROCION ORANGE FROM WASTEWATER BY ADSORPTION ON WASTE RED MUD

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ABSTRACT

The ability of waste red mud, an industrial by-product produced during the processing of bauxite ore, to remove procion orange was investigated at different initial dye concentrations, agitation time, adsorbent dosage, and pH. Adsorption followed the Freundlich isotherm model. A maximum removal of 82% of the dye was observed at pH 2.0. Desorption studies showed that maximum desorption occurred at a pH of 11.

INTRODUCTION

Color is one of the characteristics of an effluent which is easily detected and readily traced back to its source. Most dyes are stable to biological degradation. Colored waters are objectionable on aesthetic grounds for drinking and other agricultural purposes. Color affects the nature of the water, inhibits sunlight penetration into the stream, and reduces the photosynthetic action. Some of the

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dyes are carcinogenic and mutagenic (1). Procion orange is one of the dyes used in textile industries in India. The discharge of dyes—containing industrial wastewaters into streams and river constitutes one of the major sources of water pollution. Hence, there is a need to prevent dyes from dyeing wastewaters before it reaches the water bodies. The treatment of dyes in industrial wastewaters poses several problems as the dyes are generally stable to light and oxidation (2), and hence cannot be treated by conventional biological methods. The adsorption process provides an attractive alternative if the adsorbent is inexpensive and readily available. Activated carbon, being expensive, is the most powerful and popular adsorbent and has been used with great success (3). High costs in the procurement of activated carbon restrict its use in developing countries like India. Recently, a number of nonconventional adsorbents, such as coconut husk (2), saw dust (4), clay minerals (5), chitosan (6), and hardwood (7) have been used for color removal from wastewater by several investigators. Wollastonite was used for the removal of congo red (8). Basic dyes have been shown to be adsorbed onto silica gel (9–11). Biogas residual slurry (12), waste banana pith (13), orange peel (14), and Fe(III)/Cr(III) hydroxide (15) have been used as nonconventional adsorbents for the removal of dyes in our laboratory. Recently, activated sludge (16) and activated carbon fiber (17) have been used for dye removal. Photocatalytic degradation of dyes has also been investigated (18,19).

The utilization of one industrial solid waste, for the treatment of wastewaters from another industry, could be helpful not only for the economy of the treatment to some extent, but also for solving the solid waste disposal problem of industries. Red mud has been used for the treatment of dairy wastewaters (20). Removal of toxic metals using red mud has been reported (21,22). This study aims to evaluate the adsorption capacity of red mud in the treatment of dye-containing wastewaters with procion orange as a typical case.

EXPERIMENTAL

Materials

Waste red mud obtained from Mettur Aluminium Factory, Mettur, Tamil Nadu, was used as an adsorbent. It was washed thoroughly with distilled water and dried at 60°C for 5 hr to maintain surface characteristics. The red mud comprises of Al_2O_3—16.94%, Fe_2O_3—39.34%, CaO—13.2%, SiO_2—6.95%, and TiO_2—4.79%. The powder was then used for adsorption studies. Procion orange M2R was obtained from Atul, Bombay.

Methods

Batch adsorption studies were carried out by agitating 250 mg of adsorbent with 50 mL of aqueous solution of procion orange at a desired pH, at a desired initial dye concentration, for a predetermined time interval at 140 rpm using a shaker machine at 30 $\pm$ 2°C. The dye solution was separated from the adsorbent by centrifugation at 15,000 rpm. The dye removal was estimated spectrophotometrically by monitoring the absorbance changes at the wavelength of maximum absorption (490.8 nm) using Hitachi spectrophotometer (Model U-3210 Tokyo, Japan).

For studies on pH effect, the initial pH of the dye solution was varied from 2 to 11. The effect of adsorbent dosage was studied by varying the adsorbent weight from 0.05 to 0.95 g at the dye concentration of 10 mg/L at pH 2.0. Langmuir and Freundlich isotherms were employed to evaluate the equilibrium data.

Batch desorption studies were carried out by agitating 50 mL of dye solution of 10 mg/L and 250 mg of adsorbent for an agitation time greater than the equilibrium time i.e., 90 min, and the supernatant dye solution was discarded. The dye-loaded adsorbent was washed gently to remove any unadsorbed dye. Several samples were prepared. Then, the spent adsorbent was agitated with 50 mL of water at different pH values for 90 min. The desorbed dye was separated from the adsorbent by centrifugation and estimated as before.

RESULTS AND DISCUSSION

Effect of Agitation Time and Initial Dye Concentration

Figure 1 shows the effect of agitation time and initial dye concentration on the adsorption of procion orange by red mud. The removal of dye was rapid in the initial stages of contact time and gradually decreased with lapse of time until equilibrium. The equilibrium time was 60 min for all the dye concentrations used. The equilibrium uptake of the dye decreased from 80 to 73% with an increase in dye concentration from 10 to 40 mg/L.

Effect of Adsorbent Dose

Figure 2 (Curve A) shows that the removal of procion orange increased to 89% (0.45 mg), with an increase in adsorbent dose up to 7.0 g/L. With a further increase in adsorbent dose, the percent removal decreased to zero. The decrease

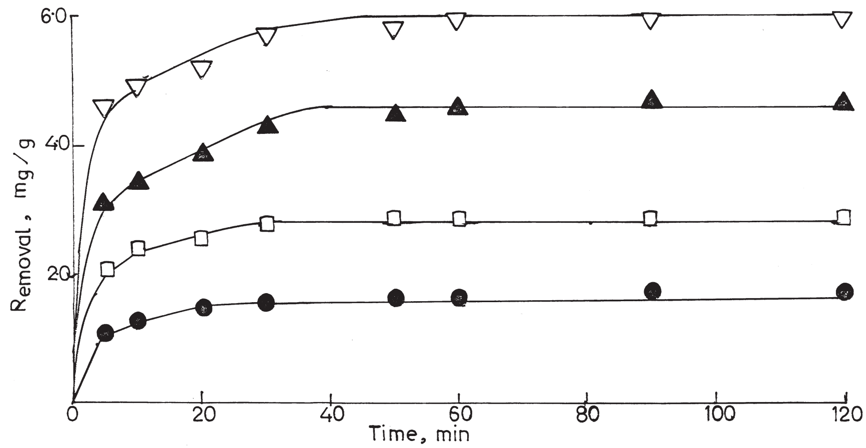

Figure 1. Effect of agitation time on the adsorption of the dye Procion orange. Dye concentration = (●) 10 mg/L, (□) 20 mg/L, (▲) 30 mg/L, (▽) 40 mg/L; Adsorbent dose = 250 mg/50 mL; Initial pH = 2.0.

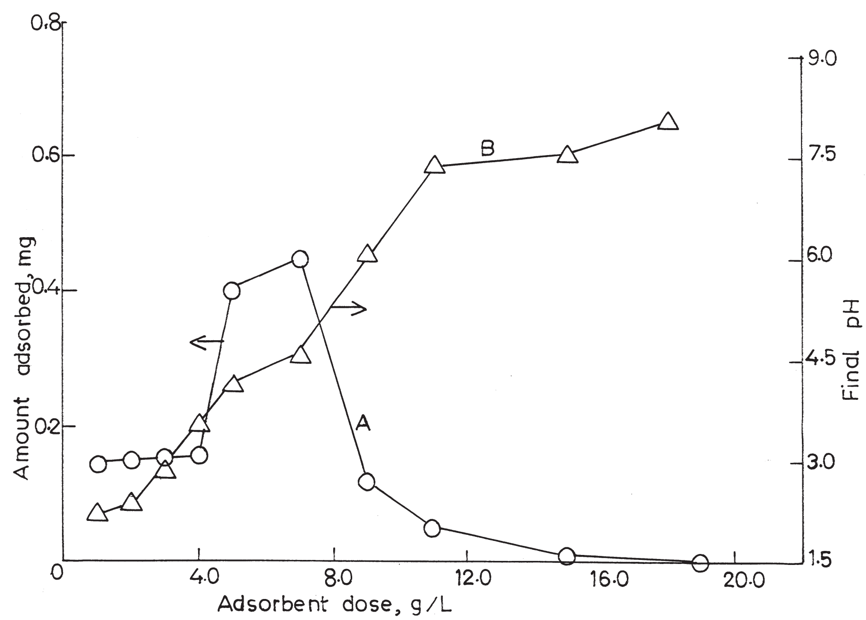

Figure 2. Effect of absorbent dosage on the adsorption of Procion orange. Dye concentration = 10 mg/L; Initial pH = 2.0; Curve A: Amount adsorbed vs. adsorbent dose; Curve B: Final pH vs. adsorbent dose.

in the percent removal is due to the alkalinity contributed by red mud (Fig. 2, Curve B) (21).

Adsorption Rate

The rate constant for the adsorption of procion orange by red mud was studied using Lagergren rate equation (13).

$$\log(q_e - q) = \log q_e - k_{ad}t/2.303 \tag{1}$$

where q_e and q are amounts of dye adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_{ad} the rate constant of adsorption. Linear plots of log $(q_e - q)$ vs. t were obtained for different dye concentrations, which indicate first order rate expression (Fig. 3). The k_{ad} values are presented in Table 1. The adsorption rate constant for procion orange (20 mg/L) on biogas waste slurry (12) was reported to be 1.5×10^{-2} l/min compared to 2.2 l/min for red mud. The higher k_{ad} value for red mud may be due to the presence of metal oxides.

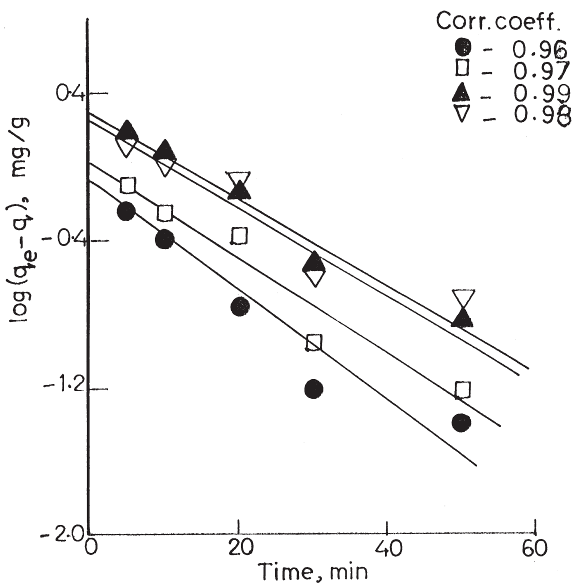

Figure 3. Lagergren plot for the adsorption of Procion orange on waste red mud. Dye concentration = (●) 10 mg/L, (□) 20 mg/L, (▲) 30 mg/L, (▽) 40 mg/; Adsorbent dose = 250 mg/50 mL; Initial pH = 2.0.

Table 1. Adsorption Rate Constants for Procion Orange

Concentration (mg/L)	Adsorption Rate Constant, k_{ad} (1/min)
10	2.20
20	2.23
30	2.27
40	2.26

Adsorption Isotherms

Freundlich equation was also applied for the adsorption of procion orange on red mud (13).

$$\log(x/m) = \log k_f + (1/n) \log C_e \tag{2}$$

where x is the amount of dye adsorbed (mg), m the weight of the adsorbent used (g), C_e the equilibrium dye concentration in solution (mg/L), and k_f and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity. Linear plot of log (x/m) vs. log (C_e) shows that the adsorption also follows Freundlich isotherm (Fig. 4). Values of k_f and n were calculated from the intercept and slope of the plot, and were found to be $0.86\,(\text{mg/g})(\text{L/mg})^{1/n}$ and 1.30, respectively. In general, as the k_f value increases, the adsorption capacity of the adsorbent for the given dye increases. The values for k_f and n for adsorption of procion orange on biogas waste slurry (12) was reported to be 0.01 and 0.84, respectively. The higher values of k_f and n for red mud may be due to the presence of metal oxides in red mud.

Effect of pH

In the pH range 2.5–11.0, there was no change in adsorption with pH. When the initial pH of the solution was increased from 2 to 11.0, the percent removal decreased from 82 to 0 (Fig. 5, Curve A). The final pH after adsorption was higher than the initial pH from 2.5 onwards. This is due to the contribution of alkalinity of red mud (Fig. 5, Curve B) (21,22). Hence, the final pH is important to explain the percent removal. The decrease in adsorption with an increase in pH may be explained on the basis of aqua complex formation and subsequent acid–base dissociation at solid/solution interface.

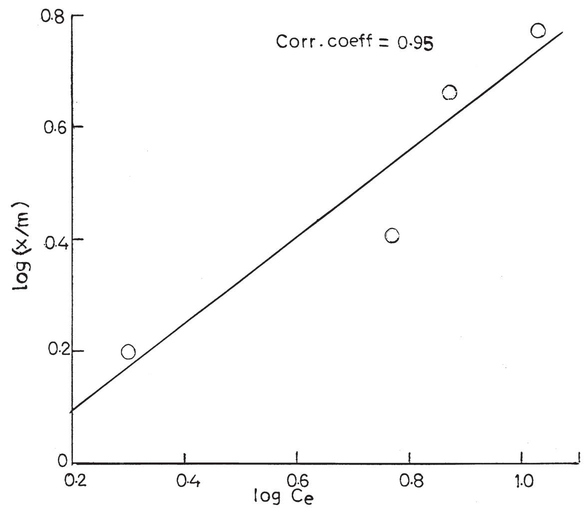

Figure 4. Freundlich plot for the adsorption of procion orange on waste red mud. Dye concentration = 10 mg/L; initial pH = 2.0.

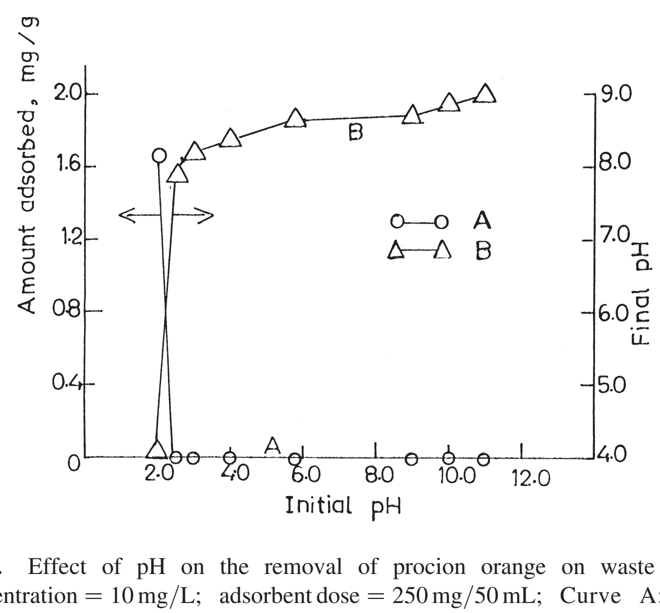

Figure 5. Effect of pH on the removal of procion orange on waste red mud. Dye concentration = 10 mg/L; adsorbent dose = 250 mg/50 mL; Curve A: Amount adsorbed vs. initial pH; Curve B: Final pH vs. initial pH.

In acid medium, positive charge develops on the surface of oxides of the adsorbent, and may be written as:

$$\begin{array}{lll} O & & O \\ \ \backslash & H^+ & \ \backslash \\ M - O + H - OH & \text{------------>} & M - OH_2^+ + OH^- \quad \ldots\ldots\ldots\ldots \\ \ / & & \ / \\ O & & O \end{array} \qquad (3)$$

where M stands for Al, Fe, or Si present in the red mud. Since the solution is acidified by hydrochloric acid, the outer surface of positively charged interface will be associated with Cl^- ions. The chloride ions are exchanged with dye anions.

$$\begin{array}{l} O \\ \ \backslash \\ M - OH_2^+ / Cl^- + Dye^- \text{------>} M - OH_2^+ /Dye^- + Cl^- \ldots\ldots\ldots \\ \ / \\ O \end{array} \qquad (4)$$

With an increase in pH, the positive charge on the oxide/solution interface decreases. At pH values above the pH_{ZPC} of the adsorbent, i.e., 7–9, the adsorbent surface becomes negatively charged and will be associated with positively charged ions of the solution in the following manner.

$$\begin{array}{l} O \\ \ \backslash \\ M - O^- / Na^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \\ \ / \\ O \end{array} \qquad (5)$$

Thus, there are no exchangeable anions on the outer surface of the adsorbent at higher pH values and consequently the adsorption decreases. A similar trend was observed in the adsorption of procion orange on biogas waste slurry (12).

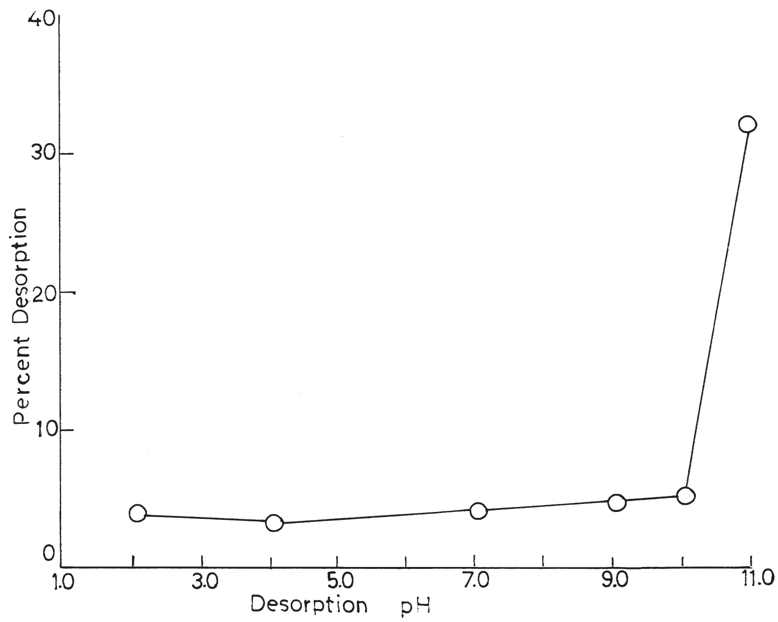

Figure 6. Desorption of procion orange. Dye concentration = 10 mg/L; adsorption dose = 250 mg/50 mL; initial pH before adsorption = 2.0.

Desorption Studies

Desorption studies help to elucidate the mechanism of adsorption and also help in the recovery of dye and adsorbent, which makes the treatment process more economical. The percent desorption increases with an increase in the pH of the aqueous solution (Fig. 6). A maximum desorption of 32% occurred at pH 11.

CONCLUSIONS

The red mud, a waste byproduct from bauxite processing industry, can be effectively used as an adsorbent for the removal of procion orange from wastewaters. The adsorption followed Freundlich isotherm. Maximum dye removal occurred at pH 2.

ACKNOWLEDGMENTS

Authors are thankful to the Bharathiar University authorities for providing Central Instrumentation Lab facilities. One of the authors (RTY) is grateful to the Council of Scientific and Industrial Research (CSIR), Government of India for the award of Research Associate Fellowship.

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Received March 2001
Revised October 2001