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Studies on the removal of Neutral Red on sand from aqueous solution and its kinetic behavior

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Abstract

Neutral Red (NR) dye in aqueous solution present as a pollutant material in textile waste water was removed by adsorption on sand at 298 K. Local sand sample which was used as an adsorbent in this work was initially characterized for its textural properties including surface area, mean pore radius and total pore volume. These properties were examined from the low-temperature adsorption of nitrogen on sand samples at 77 K. Later on the conditions of maximum adsorption of the dye on characterized sand sample were optimized. It was seen that under optimized conditions, up to 85% dye could be removed from solution onto the sand surface. The adsorption data were fitted to Freundlich and Lagergen equation for the calculation of various adsorption parameters. The Freundlich constants n and A were determined to be 0.997 and 0.2001 mol/g, respectively. The rate constant for adsorption of Neutral Red on sand sample as calculated by using the Lagergen equation was estimated to be 3.85 min^{-1}. The application of Boyd's equation revealed that particle diffusion was not operative in this case and thus does not control the kinetics of dye adsorption on sand. The adsorption behavior of the dye was also investigated in terms of added cations and anions. It was found that the dye adsorption decreased in the presence of chloride, sodium and copper ions.

Keywords: Neutral Red; Adsorption; Sand; Freundlich isotherm; Lagergen equation

1. Introduction

The use of synthetic chemical dyes in various industrial processes has increased considerably over the last few years. Some areas where these chemicals are frequently used are paper and pulp manufacturing, plastics, dyeing of cloth, leather treatment and printing etc. Industrial waste water containing such dyes is generally discarded as effluents. Since some of these dyes are toxic in nature, their removal from the industrial effluents is a major environmental problem [1–4]. The waste water which is highly colored in the presence of various dyes can block the penetration of sunlight and oxygen which are both essential for various aquatic forms of life. Moreover, the dye solution can also undergo anaerobic degradation to form potentially carcinogenic compounds, which can end up in food chain [5].

Literature citation has revealed the importance of this subject and many different approaches have been suggested to handle such wastes. These methods include biodegradation, photocatalytic, photolytic and advanced oxidative degradation of various dye solutions [6–10]. Literature findings have shown a considerable amount of interest regarding the adsorption of some dyes from solutions on various adsorbent surfaces such as clays, flyash, polymers and activated carbon; however, no such study is available on sand surfaces [11–16].

The present study focuses attention on the adsorption of Neutral Red (NR) on a naturally occurring cheaper source of adsorbent, namely sand, which is certainly available in most of the places. The study was carried out in the absence and presence of various ions. Conditions of maximum adsorption were evaluated in this study, besides fitting the adsorption data to various equations to obtain certain constants related to the adsorption phenomena.

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2. Experimental

Neutral Red (NR) with a labeled purity of more than 98% was obtained from Fluka and was used as such. Deionized water was used to make the dye solutions of desired concentration. Initial experiments on the dye solution were carried out to ascertain the working concentration in the Lambert–Beer range. The dye solution shows an intense absorption peak in the visible region at 540 nm. In an adsorption process, a change in the intensity of absorption peak of the dye solution can be used to characterize the removal of dye from the solution.

In the present study, sand was used as an adsorbent because of its enormous availability in the local environment. Sand sample was procured from the local dunes in the vicinity of Al-Ain city located in the south eastern region of UAE. The sand sample used in this study was not treated in any other way except sieving it to obtain different portions.

Sieving analysis carried out on the sand sample gave the following composition: coarse sand, 0.02%; 350 μm, 0.41%; 250 μm, 65.75%; 180 μm, 21%; 125 μm, 7.5%; 88 μm, 3.6% and the remaining fraction below 88 μm. In the present study, 250 μm fraction was used. The BET surface area of this sand fraction was found to be 5.2176 m^2/g by using the nitrogen adsorption method. Average pore diameter was determined to be 37.2498 Å and the pore volume was estimated to be 1.198 cm^3/g. The adsorption of dye on sand surface was calculated by monitoring the changes in absorption value of the solution on a CARRY 50 UV/VIS spectrophotometer, using a 1 cm quartz cell.

Generally speaking, Neutral Red (NR) stock solution of 1×10^{-3} M was prepared in 100 mL of deionized water in a flask followed by necessary dilutions of this stock solution. A given amount of sand sample (usually 0.05–0.1 g) was then added to 5 mL of this diluted solution. The contents of the dye solution were then shaken for a given amount of time using a magnetic stirrer operated at a constant speed. The contents were then centrifuged and the supernatant solution was pipetted out and monitored instantaneously on a spectrophotometer for absorption values. The absorbance value of the dye solution obtained in each case was then used to calculate the percentage adsorption of the dye on sand.

$$\%\ \text{adsorption} = \left[\left(A_i - A_f\right)/A_i\right] \times 100 \qquad (1)$$

where, A_i and A_f are the initial and the final absorbance values of the dye solution, respectively.

Table 1
Effect of various ions on the percent adsorption of Neutral Red on sand (sand = 0.06 g, [Dye] = 1.8×10^{-5} M, shaking time = 8 min)

Anions	% Adsorption	Cations	% Adsorption
Chloride	69.5	Potassium	76
Bromide	73.5	Sodium	69.5
Iodide	81.5	Copper	65.5

Anions were added as sodium salts, whereas cations were added as nitrates (concentration of each ion in solution = 1×10^{-3} M).

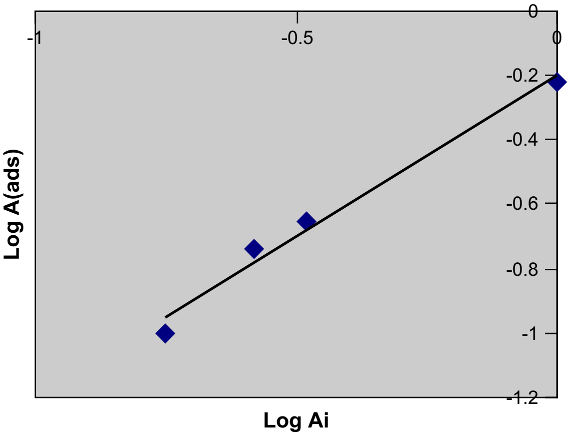

Fig. 1. Application of Freundlich equation to the adsorption of Neutral Red on sand.

The pH of the neat dye solution was found to be 5.5. This was changed by adding incremental amounts of either dilute HCl or NaOH to the solution. Adsorption measurements were then carried out for these cases in a similar way as stated before.

3. Results and discussion

Conditions for maximum adsorption were initially optimized for the dye solution on sand sample. In this regard, amount of sand, the concentration of the dye solution and the shaking time were varied over a wide range. From such studies it was found that maximum adsorption (85%) took place when the solution pH was 5.5, dye concentration was 1.8×10^{-4} M, the sand sample was 0.06 g and the shaking time was 8 min. These optimized conditions were then fixed for subsequent studies.

Industrial effluents are always contaminated with various additives such as inorganic salts. It is therefore important to study the effect of these ions on the adsorption property of dye solution. The adsorption of dye in the presence of anions (added as sodium salts) and cations (added in the nitrate form) was therefore carried out. The concentrations of all these ions in solution were kept at 1×10^{-3} M in each case. The results are tabulated in Table 1. It can be seen that adsorption of the dye decreased more in the presence of chloride, sodium and

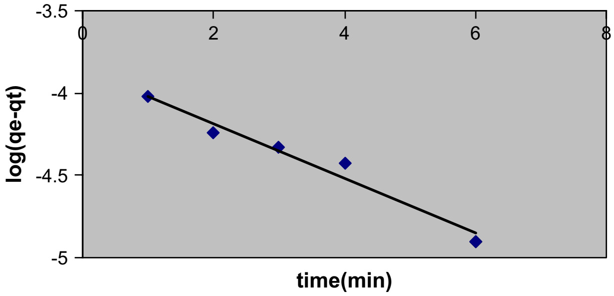

Fig. 2. Application of Lagergen equation to the adsorption of Neutral Red on sand.

copper ions. Thus these ions should be removed from the dye solution prior to its adsorption on sand.

The data for NR adsorption on sand were subjected to various equations. In this regard the data were firstly fitted to Freundlich equation which has the following form [17].

$$\log A_{\mathrm{ads}} = \log A + n \log A_{\mathrm{i}} \tag{2}$$

where A_{i} and A_{ads} are the concentration of the dye in solution and on the sand surface at equilibrium, respectively, and A and n are constants for a particular system. A plot of $\log A_{\mathrm{ads}}$ versus $\log A_{\mathrm{i}}$ gave a straight line ($R^2 = 0.9829$), as shown in Fig. 1. From the slope and the intercept of this graph, the values of n and A were found to be 0.997 and 0.2001 mol/g, respectively. The slope value of nearly 1 indicates the monolayer sorption of dye solution on sand.

The adsorption data were also analyzed by using the Lagergen equation which is given by [17].

$$\log(q_{\mathrm{e}} - q_{\mathrm{t}}) = \log q_{\mathrm{e}} - Kt \tag{3}$$

where q_{e} and q_t are the amounts adsorbed at equilibrium and at time t, respectively. The slope of the plot of $\log(q_{\mathrm{e}} - q_t)$ versus time gives the overall rate constant K. The plot ($R^2 = 0.9679$) is shown in Fig. 2. Value of K from the plot was found to be 3.85 min^{-1}.

In order to determine the actual rate controlling step involved in dye adsorption process, the adsorption data were further analyzed by using the kinetic expression given by Boyd et al. [18].

$$F = 1 - \left(6/\Pi^2\right)\mathrm{e}^{-B} \tag{4}$$

The values of B, which is a mathematical function of $q_t/q_{\mathrm{e}} = F$, can be calculated for each value of F (fraction of solute adsorbed at different times) as shown in the literature.

Taking ln value of both sides of the above equation simplifies it to

$$B = -0.4977 - \ln(1 - F) \tag{5}$$

A plot of B versus time in this case was found to be linear ($R^2 = 0.9239$), as shown in Fig. 3, and does not pass through the origin as observed in the other cases [19]. This indicates that particle diffusion mechanism is not operative and hence does not control the kinetics of Neutral Red adsorption on sand.

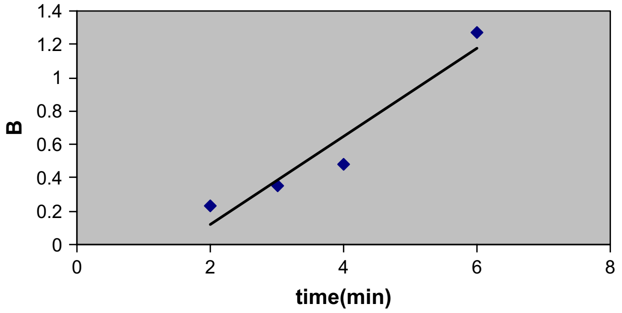

Fig. 3. Boyd plot for Neutral Red adsorption on sand.

4. Conclusion

Removal of Neutral Red (NR) dye from aqueous solution onto sand surface was carried out at room temperature. The conditions of maximum adsorption of the dye were optimized. It was seen that under optimized conditions, up to 85% dye can be removed from the solution onto the sand surface. The experimental data were fitted to Freundlich isotherm which showed that adsorption was monolayer in nature. The rate constant for adsorption of Neutral Red on sand sample was found to be 3.85 min^{-1} by using the Lagergen equation. Furthermore, the Boyd equation revealed that the adsorption process was physical in nature and that the dye does not actually diffuses in the sand. The adsorption of the dye decreased in the presence of all the added ions; the effect was more pronounced in the presence of chloride, sodium and copper ions.

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