Removal of Neutral Red Dye from Water Samples Using Adsorption on Bagasse and Sawdust

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Summary: The neutral red dye is used in textile and leather industries and in environmental research. Therefore, the removal of this dye from the factory wastewaters is environmentally significant. In this research, two very inexpensive, abundant and easily available adsorbents, i.e. sugarcane bagasse and sawdust, were employed to remove the neutral red from water. The effects of various conditions such as pH, electrolyte concentration, adsorbent dose, contact time and agitation rate were studied for the removal of the dye in a concentration of 100mg L^{-1}. The obtained conditions were applied for various concentrations of the dye (100 – 400 mg L^{-1}) and in all the cases, an efficiency of more than 96 % was attained. Adsorption isotherms were studied which were well in line with both Langmuir and Freundlich equations. The possibility of employing columns was studied and good results were achieved. The method was applied for the removal of dye from real samples of different waters.

Keywords: bagasse, sawdust, adsorption, dye removal, neutral red

Introduction

Adsorption on inorganic or organic matrices, sonolysis, photocatalysis, electrochemical, ozonation [1] and cloud point extraction [2] is among the techniques employed for the removal of dyes from wastewaters. From among these techniques, the process of adsorption is one of the most effective methods [3-5] because it enjoys a simple process and takes place through a physical procedure. Different adsorbents are used to remove dyes from industrial wastewaters, including: zeolite [6], rice husk [7], corn cob [8], and coir pith [9]. Sawdust is used as an adsorbent for the removal of Remazol [10] dyes and bagasse fly ash is used for the removal of Congo red [11] Methyl violet and orange-G dyes [12].

The neutral red dye is a toxic dye, which has generally been removed from water samples through the use of sand [13], nanoparticle Fe_3O_4 [14] and modified hectoric [15]. In this research, the neutral red dye was removed through the use of inexpensive adsorbents of sugarcane bagasse and sawdust, the advantage of which, in addition to their inexpensiveness, is their abundance. It is necessary to be mentioned that in this research no transformation was done in regard with these adsorbents. Both adsorbents are very appropriate and favorable, which makes the task very simple, easy and fast.

Results and Discussion

In order to obtain the best results, that is, the highest amount of dye removal, various factors were optimized. The approach for optimization in all cases was the "one at the time" approach (i.e. changing a single variable while all other variables are kept constant).

The equation number (1) was employed to calculate the amount of dye removal:

$$\mathrm{Removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100 \qquad (1)$$

In this equation, C_0 is the initial dye concentration (before being mixed with the adsorbent), and Ce is the equilibrium concentration (after being mixed with the adsorbent). The equilibrium concentration was obtained through a calibration curve for the neutral red dye.

Effect of pH

Considering the point that in various pHs, NR dye has different λ_{max} and absorbance (below pH=6.8 it is red and above pH=6.8 it is yellow [16]), some solutions with a concentration of 10mg L^{-1} in pHs of 3 to 6 were prepared and their absorbance were studied in λ_{max} =533; in this way, the effects of pH of absorbance changes of NR dye in different pHs could be studied. The results revealed that in such a pH range, the adsorption of the sample had no change. At the next stage, some solutions were prepared with a dye concentration of 100mg L^{-1} and different pHs and they were mixed with the adsorbent. After 30 minutes, the adsorption of the solution was studied and the percentage of removal of the dye was calculated. The results show (fig.1) that an increase in pH is accompanied with an increase of percentage of removal, and percentage of

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removal remains almost unchanged from a pH of 4 to 5.5; therefore, pH=5.0 was chosen as the optimum pH. The other researches on the removal of cationic dye through the use of cellulose-based adsorbent report that the percentage of removal [17] of cationic dye increases when there is an increase in pH. Therefore, it can be said that when pH of dye increases, the association of dye cations with negative charged site is facilitated and this results in an increase of removal.

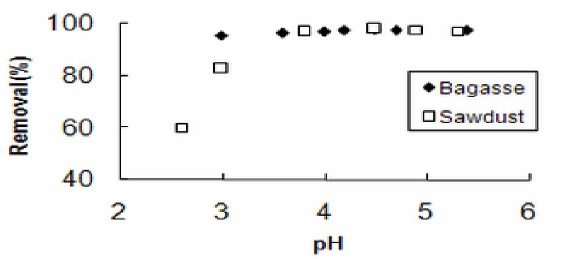

Fig. 1: Effect of pH on Neutral Red removal.

Effect of Absorbent Dose

In order to obtain the minimum amount of adsorbent for the removal of a maximum amount of NR dye, the adsorbent dose was optimized. The results showed (fig.2) that an adsorbent dose of 10g/L for a concentration of 100mg L^{-1} can remove more than 97 % of the dye. It is well to mention that an adsorbent dose of 2g/L can remove more than 91 % of dye for bagasse and more than 84% of dye for sawdust, which is better in comparison to sawdust with a dose of 25g/L for the removal of congo red up to 77% [18].

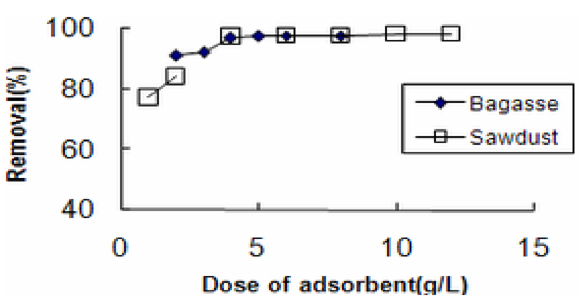

Fig. 2: Effect of adsorbent dose on Neutral Red removal

Effect of Electrolyte

KCl and $NaNO_3$ were used as electrolytes. The studies demonstrated that an increase of electrolyte concentration up to 0.2 mol L^{-1} does not have a considerable effect in the removal of neutral red (removal decreases of about 2 and 1 percent were observed for sawdust and bagasse, respectively), while, in many adsorption methods, the presence of electrolyte results in a severe decrease of removal [12,19].

Effect of Contact Time and Agitation Rate

In this study, some solutions of NR were prepared with a concentration of 100mg L^{-1} in the intended pH, and the necessary time interval was studied. The results showed that even in a short interval of 15 minutes, more than 90% of the dye is removed (fig.3). However, for a removal of about 98%, a time interval of 30 minutes (when the shaker shakes at 135rpm) is needed. This method needs less time [20-26] in comparison with many other methods and more time [2] in comparison with some others.

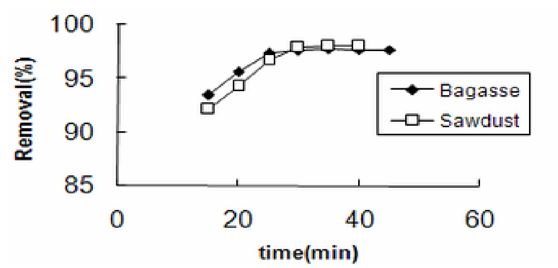

Fig. 3: Effect of contact time on Neutral Red removal.

Furthermore, the effect of agitation rate was studied. When samples of neutral red dye with a concentration of 100mg L^{-1} and intended pH are shaken for 30 minutes at 135 rpm, there is a dye removal of 98% with each of the adsorbents. Of course, there would be a removal of about 96% of dye at 80 rpm.

Effect of Initial Dye Concentration

In all the cases of optimization, the dye used had a concentration of 100mg L^{-1}. In order to study the possibility of dye removal in other concentrations with the same optimization condition, other concentrations were studied as well. The results showed that the optimization condition was applicable for high concentrations up to 400mg L^{-1} and in all cases; the dye removal will be more than 96%.

Isotherms of Adsorption

$$q_e = (C_o - C_e)\frac{V}{W} \qquad (2)$$

In this study, Langmuir and Freundlich isotherms were employed for the study of the adsorption of NR dye on sugarcane bagasse and sawdust. Such isotherms were achieved for an initial concentration of 100-400 mg L^{-1} in the previous optimization condition and a temperature of 25±2 ^{0}C; and qe was obtained achieved through equation (2):

In this equation, qe is the adsorption capacity in an equilibrium of (mg L^{-1}); C_0 is the initial concentration of dye (mg L^{-1}); C_e is the equilibrium concentration (mg L^{-1}); V is the volume of solution; and W is the weight of the adsorbent.

Langmuir Isotherm

In order to study the adsorption of dye according to Langmuir Isotherm the following equation (3) was used, in which Q_0 and b are the constants of Langmuir. C_e/q_e was plotted vs. C_e. The results presented in fig. 4and Table-1 show that R_L^2 achieved for both of the graphs are quite acceptable.

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \quad (3)$$

Table-1: Isotherm parameter removal of Neutral Red.

Isotherm	Parameters	Values for sawdust	Values for Bagasse
Langmuir	q_m(mg/g)	72.46	123.46
	K (L/mg	0.0902	0.076
	R^2	0.97	0.99
Freundlich	K_F	6.831	10.488
	n	1.42	1.42
	R^2	0.96	0.99

Freundlich Isotherm

This isotherm is obtained through equation (4), in which K_f is the constant of Freundlich and is dependent on the adsorption capacity by the adsorbent. For this isotherm, $\log q_e$ was plotted vs. $\log C_e$. The results are presented in fig 5 and Table-1. The amount of R_f^2 is well controlled in both cases. Both of the isotherms are well adapted with the adsorption of neutral red on bagasse and sawdust. In fact, this means that the adsorption of neutral red on bagasse and sawdust is both monolayer and reversible, and it also practically shows that adsorption develops appropriately.

$$\ln q_e = \ln K_f + \frac{1}{n}(\ln C_e) \quad (4)$$

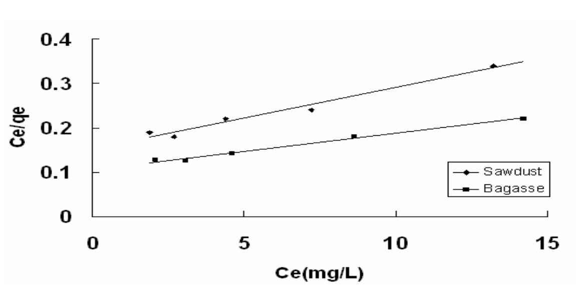

Fig. 4: Langmuir isotherms for Neutral Red adsorption at 25ºC

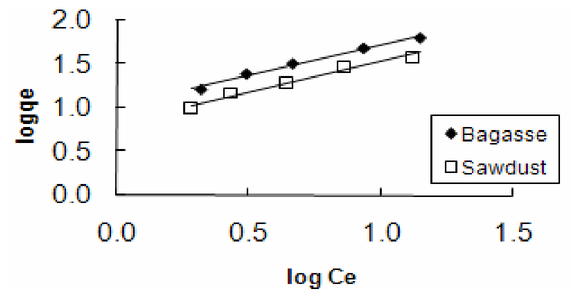

Fig. 5: Freundlich isotherms for Neutral Red adsorption at 25ºC

A Study on Real Samples

The researchers studied dye removal from real samples of the waters from Ahvaz city, Karoun River, and the industrial wastewaters. To do this, 25 mL of each real sample was examined and it was revealed that all the samples were void of NR; therefore, different amounts of NR were added to them and the removal process explained above was studied on them. Dye removal, in all the samples, was more than 95% which reveals the effectiveness of this method for all samples.

Experimental

Apparatus

In this research the following apparatus were employed:

A spectrophotometer uv –visable, manufactured by Perkin Elmer, model: Lambda 35; A pH meter, manufactured by HORIBA, model: pH METER F-11; A shaker, manufactured by KA-WERKER, Model: Hs501 digital.

Preparation of the Adsorbents and Solutions

To prepare the adsorbents, sugarcane bagasse and sawdust were first washed well with distilled water; next, they were kept in an oven with a temperature of 70°C for 24 hours; and then they were both sieved with mesh 0.50mm.

The neutral red dye used in the experiment had the chemical formula of $C_{15}H_{17}N_4Cl$, and a molecular weight of 288.8 and λmax =533 nm and it was produced by Merck Company. In all the cases, the materials were made by Merck Company, Germany.

Procedure of General Removal

In the experiment, NR dye with a concentration of 100mg L^{-1} and intended pH was prepared in a volumetric flask; and then it was added to a 250mL Erlenmeyer flask, containing 0.3 g of the adsorbents (sugarcane bagasse or sawdust). The Erlenmeyer flasks were placed on a shaker at 135rpm, for 30 minutes. Next, the solution mixed with sawdust or sugarcane bagasse was filtered with filter paper and the extent of the adsorption was λ estimated at$_{max}$ =533 nm. The resulted adsorption was obtained through a calibration curve for neutral red in concentration range of 0.05 to 20.00 mg L^{-1}. It was then changed to a concentration and the percentage of dye removal was calculated.

Conclusions

The study of the adsorption of NR dye on two very inexpensive adsorbents, or in other words industrial wastes, i.e. sugarcane bagasse and sawdust, shows that these adsorbents are highly suitable for the removal of the toxic NR dye in acidic mediums. The rather fast removal of the dye, the possibility of employing column system, possibility of application in different industrial environments (considering the point that no serious trouble was realized in this regard) and also the low amount of the adsorbents necessary for the removal of the dye with high concentration reveals the effectiveness of this method. Both of the adsorbents (sugarcane bagasse and sawdust) were used without operation changes on them. It is well to mention that the adsorbents, besides being economical, cause no environmental problems. The results of all cases are very close to each other for both of the adsorbents; however, the maximum adsorption capacity in sugarcane bagasse is higher than that in sawdust.

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