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Use of a Specific Type of Bentonite Clay for the Removal of Reactive Dyes

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ABSTRACT

In this study two reactive dyes (RR and RG) in single solution were adsorbed by bentonite clay in equilibrium and kinetic experiments. Batch Experiments of pH (4-9) and initial concentration (5-100) mg/l were carried out for single solution for each dye. Experiments of adsorbent dosage effect (0.2-1) g per 200 ml. models of Freundlich and Langmuir were used as Equilibrium isotherm models for single solution, the adsorption model were applied to implementation to fit the experimental data of the adsorption process. The results show that the Langmuir model was more suitable to represent the removal of reactive dyes (red, green) than the Freundlich model by bentonite clay.

Keywords : Bentonite Clay, Adsorption, Reactive Dye.

I. INTRODUCTION

In the last decade, increasing number of different toxic organic and inorganic compounds has been recognized at basic levels in waste water, surface and ground waters. Human activities are causing water contamination on this planet. This water contamination is the consequences of utilizing pesticides, fertilizers, herbicides, hazardous industrial chemicals, soaps, detergents, pathogens, organic solvents, heavy metals, textile dyes and phenol product that reach their way into the water supply.

Dye wastewater generally consists of a number of contaminants, including acids, dissolved solids, toxic compounds, bases, and colour. Colour is the most noticeable contaminant even at very low concentrations, and it needs to be taken away or decolorized before the wastewater can be ejected.

The reactive dyes are most used in the textile industry due to because of their simple dyeing procedures and their high level of stability during washing, these being the main type of dyes used to dye cellulose and cotton. Reactive dyes appeared an increasing market share, currently about 20–30% of the total market for dyes because they are used to dye cotton which makes up about half of the world's fiber consuming. A large fraction, typically around 30%, of the applied reactive dye, is wasted because of dye hydrolysis in the alkaline dye bathtub [1]. However, these dyes have a high solubility in the water and have a low level of fixing to fibres; most of their initial concentrations are disposed to the effluent. It's usually characterized by aromatic dyes groups that are a serious environmental concern because of their mutagenic, carcinogenic, and inert properties. The dyes have a complex aromatic structures result in thermal, physicochemical and optical stability and resistance to common waste water treatment. When the water bodies receive the dyes that have been discharged, they produce toxic amines through reductive cleavage of azo linkages, which causes several effects on human beings by damaging the vital organs such as the liver, brain, central nervous, kidney and reproductive systems. Moreover, the containment of synthetic dyes on aromatics, chlorides, metals, etc. This causes adversely impact on photosynthetic activity of some aquatic life. Hence their removal from aquatic environment is great importance and subject of many scientific researches. Mechanism of Adsorption can has been found to be an excellent way to treat industrial waste effluents, show significant advantages like low-cost, availability, profitability, easy operation and efficiency and adsorption by different adsorbents were much used. Adsorption is one of the most favourable decolonization techniques in dyeing

II. METHODS AND MATERIAL

A. Adsorbent:

The adsorbent used in this research is natural bentonite clay. The physicochemical properties are shown in tables 1 and 2.

Table 1. Chemical Analysis Of Bentonite Clay By XRF

Composition	Content (wt %)	Composition	Content (wt %)
SiO_2	50.459	MnO	0.021
Al_2O_3	33.235	SrO	0.018
CaO	8.043	ZnO	0.010
Fe_2O_3	5.581	ZrO_2	0.008
K_2O	1.535	CuO	0.005
TiO_2	0.501	NiO	0.003
SO_3	0.497	MoO_3	0.003
V_2O_5	0.040	Y_2O_3	0.001
Cr_2O_3	0.030	CO_2	0.010

TABLE 2. PROPERTIES OF BENTONITE CLAY

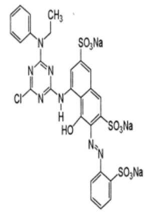
Characteristics	value
BET surface area	57.7362 m^2/g
Pore size Average pore width	7.1769 Å
Bulk density	1.2121 gm/cm^3
Real density	2.4092 gm/cm^3
Porosity %	0.49688

B. Adsorbates:

Two reactive dyes (RR, RG) characteristic are shows in Table 3 below

TABLE 3. CHEMICAL AND PHYSICAL CHARACTERISTIC OF REACTIVE DYES USED IN THE STUDY

items	Reactive red "RR"	Reactive green "RG"
Trade name	Drimarene Brilliant Red P-B	Drimarene Brilliant Green Z-3G
Origin	SWITZERLAND	SWITZERLAND
Phase	Solid/Powder	Solid/Powder
Molecular formula	$C_{27}H_{19}CLN_7Na_3O_{10}S_3$	$C_{60}H_{29}CL_3N_{16}NiO_{21}S_7$.6Na
Wave length (nm)	533	660
Molecular weight g/mol	802.1	1839.4499
pH	6.5	6.5
Solubility	95	99

g/L at 25^{o}C		
Chemical structure		Not disclosed by the manufacturer

C. Adsorption experiments

1) Stock Solutions

Simulated stock solutions of 1000 mg/L were prepare by dissolving one grams of both reactive dye (RR, RG) in one litter of distilled water then diluted to the desired solution concentration of the single dyes (RR, RG).

2) Calibration Curves

The calibration curves of two dyes (RR, RG) were prepared to find unknown concentrate value after treatment, in which standard solutions have different concentrations from 5 -100 ppm for two dyes was prepared using distilled water as a solvent and the absorbance for each sample solution was measured using a spectrophotometer thermo-Genesis 10 UV technique visible.

3) Batch Adsorption Study

In this experiment, a batch adsorption technique was used. To study the effects of various important parameters such as amount of adsorbent, pH values, the contact time between adsorbate and adsorbent. Weights of 0.2, 0.4, 0.6, 0.8 and 1g of bentonite clay were added each time to conical flasks containing 200 mg/L solution of RR, RG separately. The mixture was placed in a shaker orbital (Gemmy orbit shaker, Model: VRN-480, USA,) at 200 rpm Speed of mixing, while pH of the solution dye was varies 4, 7 and 9 by adding 0.1N HCL or 0.1N Na OH to get the desired pH by using pH-meter, Samples were withdrawn from the stirrer at different time intervals. Then the adsorbents were separated from the sample by using filter paper. The absorbance was measured for supernatant solution using UV-Spectrophotometer. Finally results where plotted the equilibrium concentration and the dyes removal (%) vs . all-inclusive sets of experiments were performed at different time intervals (30, 60, 90, 120 and 180 minutes). The amount of adsorption at equilibrium time, q_e (mg/g) was calculated using equation:

$$qe = C_0 - C_e V W \qquad (1)$$

Where,

C_0; it's the liquid-phase concentrations of adsorbent at initial (mg/L).

C_e; it's the liquid-phase concentrations of adsorbent at equilibrium (mg/L).

V; represents the volume of the solution, L.

W; mass of dry adsorbent used g.

III. RESULTS AND DISCUSSION

A. Initial concentration Effect

Study the initial dye concentration effect by varying from 5 to 100 mg/L. The maximum removal is 43.612, 86.5 for RR and RG, respectively which was found at initial concentration of 25 mg/L for RR and RG. According to The results show that in Fig. 1 and 2, the explanation for this is due to that in the case the higher initial concentrations, the greater the number of molecules competing on the sites available on the surface of the clay bentonite. If the concentrations were low for dyes (RR, RG) the adsorption sites available were higher and the higher adsorption yields were obtained. The adsorption removal ratio was found to increase somewhat and then decrease with the increase of the initial concentrations for dyes (RR, RG) due to the saturation of both surface area and active sites of adsorbents and is consistent with the study [2].

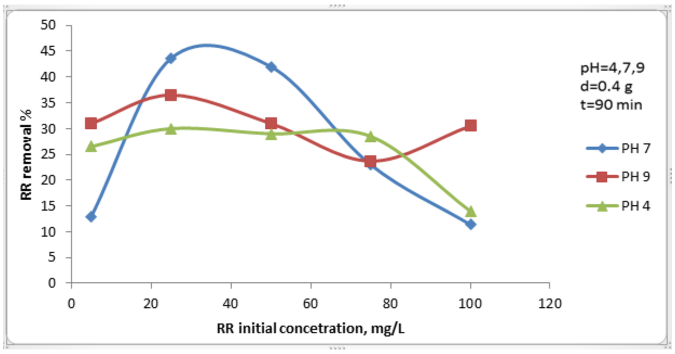


Figure 1. initial concentration effect on the removal efficiency of RR.

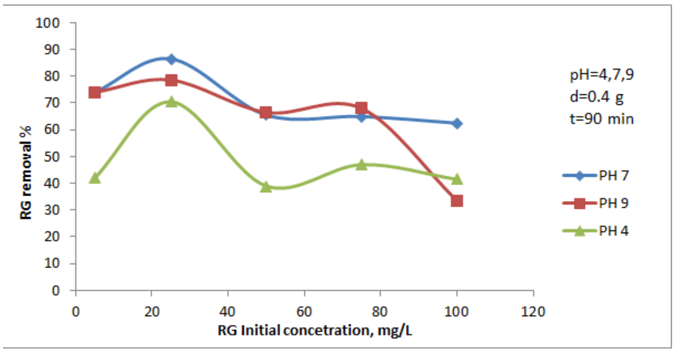


Figure 2. initial concentrations Effect on the removal efficiency of RG.

B. The Effect of pH

In this study the pH value was changed from (4-7 to 9) to cover pH range (basic, neutral and acidic) the adsorption removal efficiency of dyes was increasing in neutral at pH =7. The pH effects on the removal efficiency of reactive dyes is shown in fig. 3, The reason for the low efficiency of acidic or alkaline pH in the reactive dyes solutions is that the surface charge may be positive. This makes H+ ions compete effectively with positive reactive dyes due to the low electrical deterrent strength between positive dyes the adsorbed surface is positively charged. Which increases the pH by increasing hydrogen, which leads to competition with dyes anions of the adsorption sites, leading to a reduction in dyes the case of bentonite clay positively absorbent negative charge and this is consistent with [3]

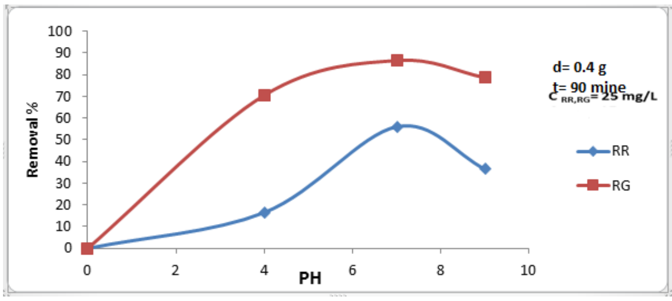


Figure 3. pH Effect on the Removal efficiency of RR, RG

C. Contact time effect

The optimum contact time for reactive dyes to be 120 min, with maximum removal efficiency is 57.59, 90.11 for RR and RG, respectively shown in fig. 4. The adsorption percentage increases by increasing of contact time; however, adsorption ratio reached to equilibrium after 120 min. With regarding to present study, the reactive dye (Red, Green) removal efficiency increased by increasing contact time which was due to more contact between pollutants and adsorbent.

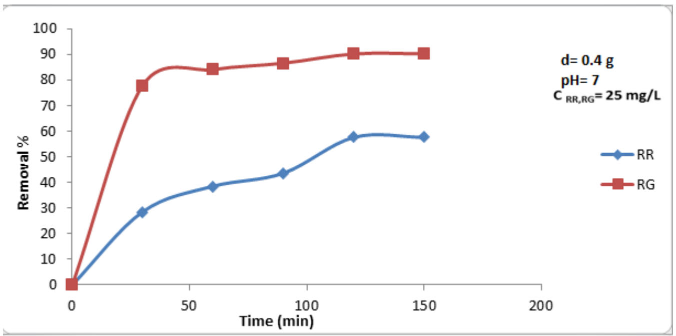


Figure 4. Contact Time Effect on the Removal efficiency of RR, RG

D. Effect of bentonite dosage

The optimum amount was found to be 1g for RR and 0.8 g for RG which was used for all subsequent adsorption studies. The removal efficiency at these doses is 65.6, 95.26 % for RR and RG respectively shown in fig. 5. The increase in adsorption capacity with the increase in the adsorption dose occurs as a result of the increase in the surface area, which leads to an increase in the total number of empty sites due to the increase of mass adsorbents. This corresponds to his study [4].

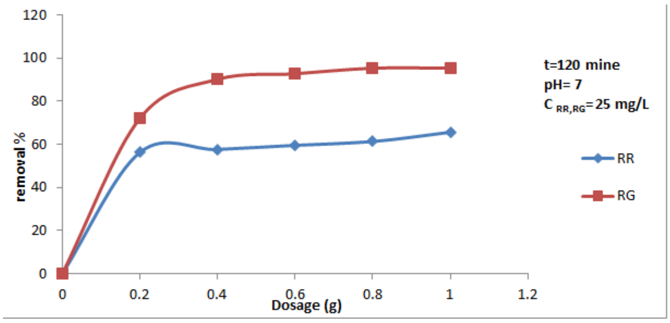


Figure 5. effect dosage the Removal efficiency of RR and RG.

E. Adsorption Isotherm:

In order to describe the equilibrium properties of adsorption in the current study two isothermal equations, namely Langmuir and Freundlich, The Langmuir and Freundlich isotherm is most frequently used to represent the data of adsorption from solution. The isotherm studied was carried out for optimum condition. The adsorption data were analysed according to the linear form of the Langmuir isotherm equation. In order to establish the maximum adsorption capacity, the Langmuir isotherm equation of the following linearized form was applied to the sorption equilibrium at different adsorbents doses. The isotherm is described by following equation.

$1/q_e = 1/q_m + 1/(k_1\ q_m)\ (1/c_e)$ (2)

Where C_e represents the equilibrium dye concentration in solution (mg/L), q_e is the adsorption capacities (amount of dye adsorbed per weight of adsorbent, mg/g) q_m and K_a are Langmuir constant that can be determined from above Langmuir linear equitation. A graph of $1/q_{evs}$ $1/C_e$ was plotted. The consant q_m and K_L can be evaluated from the intercept and slope of this linear plot. Figure.4 shows the Langmuir isotherm plot 1/qe versus $1/C_e$. The slope of this plot is equivalent to (1/qm KL) when it intercepts $1/q_m$.

Equation of the Freundlich;

$\text{Log}\ q_e = \log K_F + 1/n\ \log C_e$ (3)

Where

k_f and n: are constants of the Freundlich isotherm that signify adsorption capability and strength, respectively.

k_f and 1/n obtained from the interrupt and slope of the linear plot of log q_e versus log C_e.

The adsorption isotherms for two reactive dyes using adsorbents bentonite clay are shown in Figures by using models Langmuir and Fruendlich. The factors for both models were calculated from the experimental data, and then presented in Table 4. For reactive dyes (red, green), the value of R^2 was higher for the isotherm model of Langmuir shown in fig. 6 to fig. 9. The Langmuir equation represents a very good adsorption process for the reactive red and green dyes, its meaning that the adsorption take places as homogeneous sites, all sites are equivalent and there are no interactions between adsorbate molecule and adjacent sites.

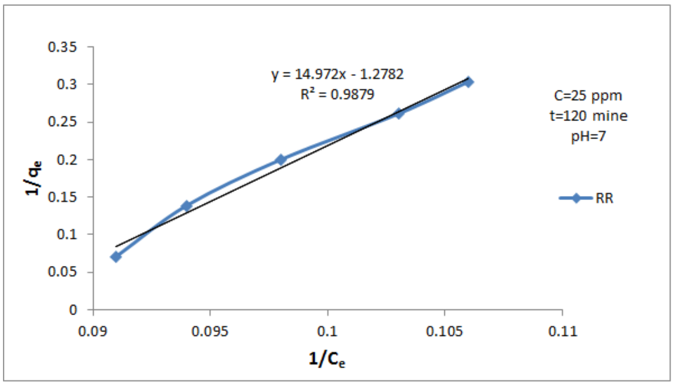


Figure 6. plot of Langmuir isotherm for RR removal from Water using bentonite clay.

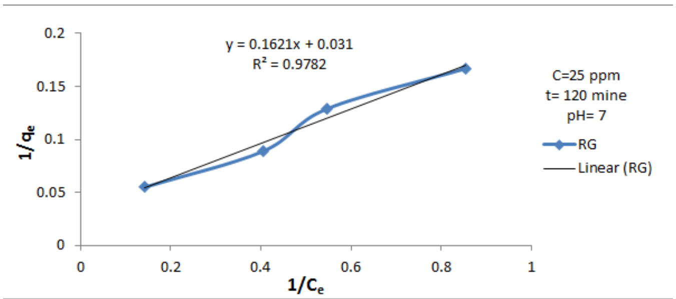


Figure 7. plot of Langmuir isotherm for RG removal from Water using bentonite clay.

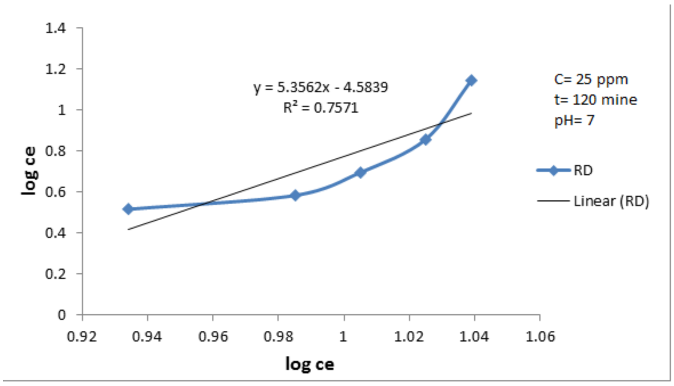


Figure 8. plot of Freundlich isotherm for RR removal from Water using bentonite clay.

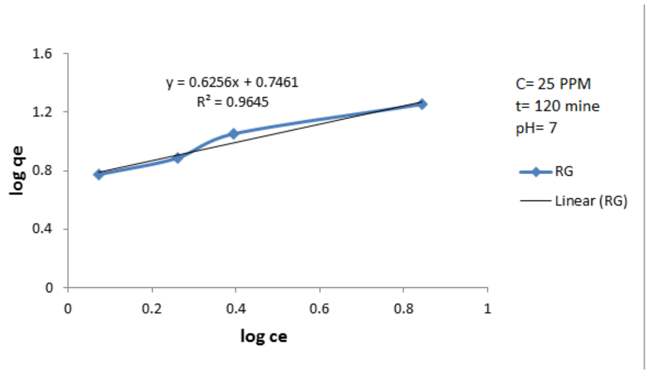


Figure 9. plot of Freundlich isotherm for RG removal from Water using bentonite clay.

TABLE 4. ADSORPTION ISOTHERM MODELS CONSTANTS

adsorbate Type	Isotherm of Langmuir $C_e/q_e=1/k_l q_e+1/q_o C_e$			Isotherm of Freundlich $\log q_e=\log k_f+1/n \log c_e$		
	K_l Mg/g	q^o l/mg	R^2	k l/g	n	R^2
Reactive red	-11.73	0.0667	0.9879	2.6×10^5	-0.187	0.757
Reactive green	5.228	6.17	0.9782	5.573	1.598	0.965

IV. CONCLUSION

From this study, it may be concluded that the removal of two reactive dyes by adsorption on bentonite clay has been found to be useful for controlling water pollution; the adsorption of dyes is influenced by pH values, amount of adsorbents and contact time. Also, the adsorption of dyes follows the Langmuir isotherm model. In the review the efficiency of bentonite clay as an adsorbent has been studied. For higher removal of dyes adsorbent dose of 1g was favourable. The uptake of the dye increased with increasing contact time and the optimum contact time was obtained at 120 min. Also, the adsorption was found to be higher for pH 7. From this research work it can be concluded that. With the experimental data obtained in this study, it is possible to design and optimize an economical treatment process for the dye removal from industrial effluents.

V. REFERENCES

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