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Adsorptive Removal of Basic Dye Rhodamine B from Aquoeus Media onto Animal Bone Meal as New Low Cost Adsorbent

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Abstract

Adsorptive removal of a cationic dye â?? Rhodamine B â?? from aquoeus solutions was achieved by the use of Animal Bone Meal as a new low cost adsorbent. Adsorption of Rhodamine B was occured by studing the effects of contact time, adsorbent amount, dye concentration and temperature. Dye adsorption equilibrium was rapidly attained after 60 minutes of contact time. The isotherms of adsorption data were analyzed by Langmuir and Freundlich adsorption isotherm models. The adsorption capacity (Qm) obtained from the Langmuir isotherm plots were 62.11, 63.69, 64.13 and 64.95 mg/g respectively at 303, 313, 323 and 333°K. Thermodynamic parameters such as Î?"H0, Î?"S0 and Î?"G0 were calculated, which indicated that the adsorption was spontanoeus and endothermic nature. The characteristic results and dimensionless separation factors RL showed that animal bone meal can be employed as an alternative to commercial adsorbents in the removal of Rhodamine B from aquoeus solution and wastewater.

Index terms— Animal Bone Meal, Rhodamine B, Removal, Kinetics, Thermodynamic studies.

1 Introduction

yes are widely used in various industries, such as textiles, paper, plastics, cosmetics and leather for coloring their final product. The release of colored wastewater from these industries may present an ecotoxic hazard and introduce the potential danger of bioaccumulation, which may eventually affect man throught the food chain. Wastewater containing even a small amount of dyes can severely affect the aquatic life due to the reduction of light penetration and their toxicity [1,2]. Due to the good solubility of dyes, they are common water polluants and they may frequently be found in trace quantities in industrial wastewaters. An indication of the scale of the problem is given by the fact that 2% of dyes produced annually are discharged in effluent from manufacturing operations, while 10% was discharged from textile and associated industries [3].

Many treatment methods have been investigated to remove dyes from wastewater. These methods can be divided into physical, chemical and biological methods. Adsorption has been observed to be an effective process for color removal from dye wastewater. Use of activated carbon has been found to be effective, but it is too expensive. Many studies have been under taken to investigate the use of low cost adsorbents [4][5][6].

The aim of the present study was to investigate the effect of the adsorbent amount, contact time, dye concentration and temperature on the adsorption of Rhodamine B dye onto animal bone meal. Both Langmuir and Freundlich isotherm models were used to describe the adsorption process. Kinetic and thermodynamic studies were achieved to determine the adsorption rate constants and thermodynamic parameters Î?"G0, Î?"H0 and Î?"S0.

2 Materials & Methods

Rhodamine B (Rd-B) is the cationic dye used in this study, which was supplied from Fluka and was used without purification. The chemical structure of Rd-B is shown in Figure **??**. Colored solutions were prepared by dissolving

requisite quantity of Rd-B in distilled water. The final volume prepared was 500 mL. Adsorption studies for the evaluation of Animal Bone Meal (ABM) adsorbent for the removal of Rd-B dye from aquoeus solutions were carried out in triplicate time using a batch contact adsorption method. Preliminary experiments demonstrated that the equilibrium was established at 55 min. A 50 mg sample of ABM was mixed with 50 mL dye solution of appropriate concentration. Samples of 10 mL of mixture were withdrawn from the batch at predetermined time intervals and the supernatant was centrifuged for 15 min at 3600 rpm. All dye solutions prepared were filtered by Millipore membrane type 0.45 µm HA, and the concentrations of dyes were determined from its UV/Visible absorbance characteristic with the calibration method. A BioMate 6, England UV/Visible spectrophotometer was used. A linear correlation was established between the dye concentration and the absorbance at ? max = 554 nm, in the dye concentration

3 II.

range (0 -100 mg/L) with a good correlation coefficient R 2 = 0.999.

In order to characterise ABM, elemntal analysis, IR and X-Ray diffraction spectrums were studied. Elemental analysis of ABM shows a high yield of Ca (49.62%) and P (42.36%) with a (Ca/P) ratio equal to 1.17. Small amounts of Si (3.88%), Mg (1.32%), Na (0.77%), Al (0.35%), Fe (0.24%), Cl (0.24%), S (0.11%), K (0.07%), Sr (0.03%), Cu (0,03%) and Zn (0.02%) are found. The IR absorption spectrum of ABM depicted in Figure 2 shows bands characteristics of hydroxyapatite and more particularly a carbonated fluorapatite type B. We note the bands located between 1455 and 1430 cm-1, these waves numbers are comparable with those of carbonated fluorapatites Type B prepared according to the procedure used by Bonel [7]. Moreover, the IR shows independently of the bands of phosphates, bands located between 780 and 800 cm-1 which could appear from the vibration of silicates groups. X-ray diffraction analysis confirms the presence of hydroxyapatite as shown in Figure 3. The specific surface area of ABM was determined by BET method from adsorption -desorption isotherm of nitrogen at its liquid temperature 77°K and was found to be Sp = 85 m 2 /g. The amount of adsorption at time t, Qt (mg/g) was calculated using the following formula :

(1) Where C t (mg/L) is the liquid concentration of dye at any time, C 0 (mg/L) is the initial concentration of the dye in solution. V is the volume of the solution (L) and W is the mass of dye adsorbent (g).

The amount of equilibrium adsorption Q e (mg/g) was calculated using the formula:

(2)

Where C 0 and C e (mg/L) are the liquid concentrations of dye initially and at equilibrium.

The dye removal percentage can be calculated as follows:

(3)

Where C 0 and C e (mg/L) are the initial and equilibrium concentrations of dye in solution.

To understand the adsorption mechanism, it was necessary to determine the zero point charge pH (pH ZPC) of the adsorbent. The pH ZPC of ABM was measured using the pH drift method [8]. In this fact, the pH ZPC of the adsorbent was determined by adding 20 mL of 5.10 -2 mol/L NaCl to several 50 mL cylindrical high-density polystyrene flasks (height 117 mm and diameter 30 mm). A range of initial pH (pH i) values of the NaCl solutions were adjusted from 2 to 12 by adding 10 -1 mol/L of HCl and NaOH. The total volume of the solution in each flask was brought to exactly 30 mL by further addition of 5.10 -2 mol/L NaCL solution. The pH i values of the solutions were then accurately noted and 50 mg of each adosrbent were added to each falsk, which was securely capped immediately. The suspensions were shaken in a shaker at 298°K and allowed to equilibrate for 48 hours. The suspensions were then centrifuged at 3600 rpm for 15 min and the final pH (pH f) values of the supernatant liquid were recorded. The value of pH ZPC is the point where the curve of ?pH (pH f -pH i) versus pH i crosses the line equal to zero. In this study, the determination of pH ZPC of ABM was depicted in Figure 4 and was found to be 8.4 .

4 Results and Discussion

5 a) Effect of contact time and initial dye concentration onto the removal dye

In order to achieve accurate effect of contact time and Rd-B concentration, we have used initially a concentration dye of 60 mg/L, 50 mg of ABM quantity and 50 mL as solution volume. The results are expressed with percentage removal of Rd-B versus differents contact time in the range 10 -90 minutes and are depicted in Figure 5. Percentage removal of Rd-B increases when increasing contact time and occurs that the adsorption equilibrium of Rd-B was rapidly attained after 60 minutes of contact time. Figure 5 reveals that the curve is single, smooth and continoeus leading to saturation, that suggesting the possible monolayer coverage of Rd-B onto ABM. In the second hand, we have achieved the effects of concentrations Rd-B (20, 40, 60, 80 and 100 mg/L) and temperature (303, 313, 323 and 333°K) on the percentage of removal dye. Table **??** depicts the different liquid concentrations of dye at equilibrium C e (mg/L), amount of equilibrium adsorption Q e (mg/g) and percentage of removal dye versus concentration Rd-B and temperature. At constant temperature, increasing concentration Rd-B causes an increasing of concentrations dye at equilibrium and amount of equilibrium adsorption. It means that the adsorption is hightly dependent on initial concentration of dye. The best percentage of removal Rd-B

was observed at lower concentration dye. It is because of the fact at lower concentration, the ratio of the initial number of dye molecules to the availlable surface area is low subsequently the fractional adsorption becomes independent of initial concentration. However, at high concentration the availlable sites of adsorption becomes fewer and hence the percentage removal of dye dependents upon concentration. At constant concentration dye, the increasing of temperature decreases the concentration of dye at equilibrium and To evaluate the effect of adsorbent dose on the adsorption of Rd-B, we have used 60 mg/L as initial concentration Rd-B and 50 mL of solution volume. Figure **??** depicts the variation of percentage of removal Rd-B versus adsorbent dose from the range of (10 -90 mg). The percentage of removal Rd-B increases with increasing adsorbent dose. The decolorization of aquoeus solutions by Rd-B varied from 37% to 84% when the adsorbent dose increases from 10 to 90 mg. This was attributed to increased ABM surface area and availlability of more adsorption sites. Hence, the following experiments were carried out with the adsorbent dose of 50 mg using 50 mL of solution volume.Year V W C C Q t t ? = 0 V W C C Q e e ? =

6 c) Adsorption isotherm

The adsorption isotherm is the most important information which indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves. The experimental data were analyzed according to linear form of the Langmuir and Freundlich isotherms [9,10]. The linear form of Langmuir isotherm is expressed as: (4) Where C e is the equilibrium concentration of dye in solution (mg/L), Q e is the amount of dye adsorbed per unit weight of adsorbent at equilibrium (mg/g), Q m is the monolayer adsorption capacity (mg/g) and b is related with the energie of the adsorption (L/mg). Plots of C e /Q e versus C e yield a straight line with slope 1/Q m and intercept 1/Q m b suggest the applicability of the Langmuir isotherm at different temperatures (Figure **??**). Table 2 Lists the maximum adsorption capacity Q m values for Rd-B adsorption onto ABM at different temperatures. From the results, it is clear that the value of adsorption efficiency Q m and adsorption energy b of the ABM increases when increasing the temperature. From the values it is concluded that the maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on adsorbent surface with constant energy and no transmission of adsorbate in the plane of the adsorbent surface. The observed b value shows that the adsorbent prefers to bind acidic ions and that speciation predominates on sorbent characteristics, when ion exchange as the predominant mechanism takes place in the adsorption of Rd-B, it confirms the endothermic nature process involved in the system. The essential characteristics of the Langmuir isotherm can be expressed in terms of dimmensioless constant separation factor R L given by [11,12]: (5) Where L is the Langmuir constant and C 0 is the highest initial dye concentration (mg/L). R L values indicate the type of Langmuir isotherm and to be [11,12]: Irreversible: R L = 0 Favorable: $0 < R L < 1$ Linear: R L = 1 Unfavorable: $R L > 1$

According to the values of R L calculated at 303, 313, 323 and 333°K are in range between 0 and 1 and are given in Table 3, which indicates that the adsorption process is favorable at operation conditions studied.

The Freundlich isotherm is an empirical equation based upon a heterogeneous surface [13]. A linear form of the Freundlich expression can be presented as below: (6)

7 d) Determination of thermodynamic parameters

The adsorption capacity of ABM increased with increase in the temperature of the system from 303 -333°K. Thermodynamic parameters such as change in free energy Î?”G 0 (kj/mol), enthalpy Î?”H 0 (kj/mol) and entropy Î?”S 0 (kj/°K.mol) were determined using the following equations:(7) (8) (9)

Where K 0 is the equilibrium constant, C solid is the solid phase concentration at equilibrium (mg/L), C liquid is(D D D D) b © 2012 Global Journals Inc. (US) 2012 Year b Q Q C Q C m m e e e 1 + = 0 1 1 bC R L + = e f e C n K Q log 1 log log + = liquid solid C C K = 0 0 0 ln K RT G ? = ? RT H R S K 303 . 2 303 . 2 log 0 0 0 ? ? ? =

A plot of log Q e versus log C e enables to determine the constant K f and n. K f represents the quantity of dye adsorbed onto adsorbent for an equilibrium concentration. The slope n ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero. These values together with the correlation coefficients are summarized in Table 2.

the liquid phase concentration at equilibrium (mg/L), T is the temperature expressed in ° Kelvin and R is the gas constant. The Î?”H 0 and Î?”S 0 values obtained from the slope and intercept of Van't Hoff plots are presented in Table 4. The values of Î?”H 0 are within the range of 1 -93 kj/mol indicating the physisorption. From these results it is clear that physisorption is much more favourable for the adsorption of Rd-B. The positive values of Î?”H 0 show the endothermic nature of adsorption and it governs the possibility of physical adsorption [14][15][16]. Since in case of physical adsorption, while increasing the temperature of the system, the extent of Rd-B adsorption increases, this rules out the possibility of chemiosorption [17,18]. The low value of Î?”H 0 suggests that the Rd-B is physisorbed onto ABM adsorbent.

The negative values of Î?”G 0 (Table 4) shows that the adsorption is highly favourable and spontaneous. The positive values of Î?”S 0 (Table 4) shows the increased disorder and randomness at the solid solution interface of Rd-B with ABM adsorbent that bring about some structural changes in the Rd-B and the ABM. The enhancement

of adsorption capacity of the ABM at higher temperatures was attribuated to the enlargement of pore size and activation of the adsorbent surface [19,20].

8 e) Study of kinetics adsorption

In present study, the kinetics studies of dye removal was carried out to understand the behaviour of the low cost ABM adsorbent. The adsorption of dye from aquoeus media by the adsorbent follows reversible first order kinetics, when a single species is considered on a heterogeneous surface. The heterogeneous equilibrium between the Rd-B solutions and the ABM is expressed as:

Where k 1 is the forward rate constant and k 2 is the backward rate constant. (Rd-B) Liq represents dye remaining in the aquoeus solution and (Rd-B) Sol represents dye adsorbed on the surface of ABM. The equilibrium constant K 0 is the ratio of adsorbate concentration in adsorbent and in aquoeus solution:K 0 = k 1 /k 2

In order to achieve the kinetics of the adsorption process, we have used the following kinetic equation [21,22]: (11) Where C 0 and C t are the concentration of the dye (mg/L) at time zero and at time t, respectively. The rate constant (k ad) for the adsorption processes have been calculated from the slope of the linear plots of log C 0 /C t versus t for different concentrations and temperatures. The determination of rate constants as described in literature is given as: (12) Table 5 depicts the overall rate constants kad for the adsorption of Rd-B at different temperatures are found from the slope of the plots of equation (11). From these values shown in Table 5, the rate constant kad increases with increase in temperature suggesting that the adsorption process is endothermic nature. Further, kad values decrease with increasing initial concentration of the Rd-B. In cases of strict surface adsorption a variation of rate should be proportional to the first power of concentration. However, when pore diffusion limits the adsorption process, the relationship between initial dye concentration and rate of reaction will not be linear. Thus, in the present study pore diffusion limits the overall rate of Rd-B adsorption. The overall rate of adsorption is separated into the rate of forward and reverse reactions using the above equation. The rate constants of forward and reverse processes are also collected in Table 5. It indicates that at all initial concentrations and temperatures, the forward rate constant is much higher than the reverse rate constant suggesting that the rate of adsorption is clearly dominant.

9 Conclusion

The results indicated that ABM is a promising new low cost adsorbent for removal of Rhodamine B from aquoeus solutions. The equilibrium data have been analyzed. The results showed that the Rhodamine B flollowed Langmuir isotherm model. Thermodynamic studies indicated that the dye adsorption onto ABM was a spontaneous, endothermic and physical reaction. Table **??** : Equilibrium parameters for the adsorption of dye onto ABM adsorbent. Year (10) (Rd-B) Liq (Rd-B) Sol k 1 k 2 t k C C ads t 303 . 2 log 0 = ? ? ? ? ? ? ? ? ? + = + = + = 0 1 0 1 1 2 1 1 1 K k K k k k k k [1] [2] [3]

Figure 1:

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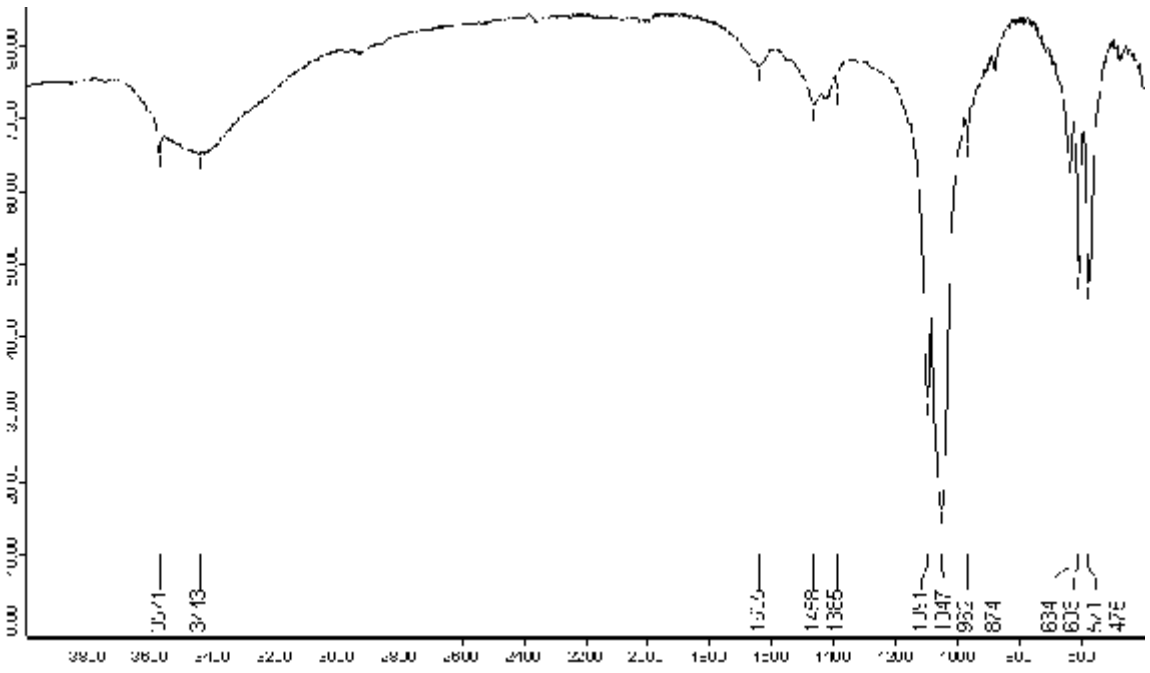

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Figure 2: Figure 2 :

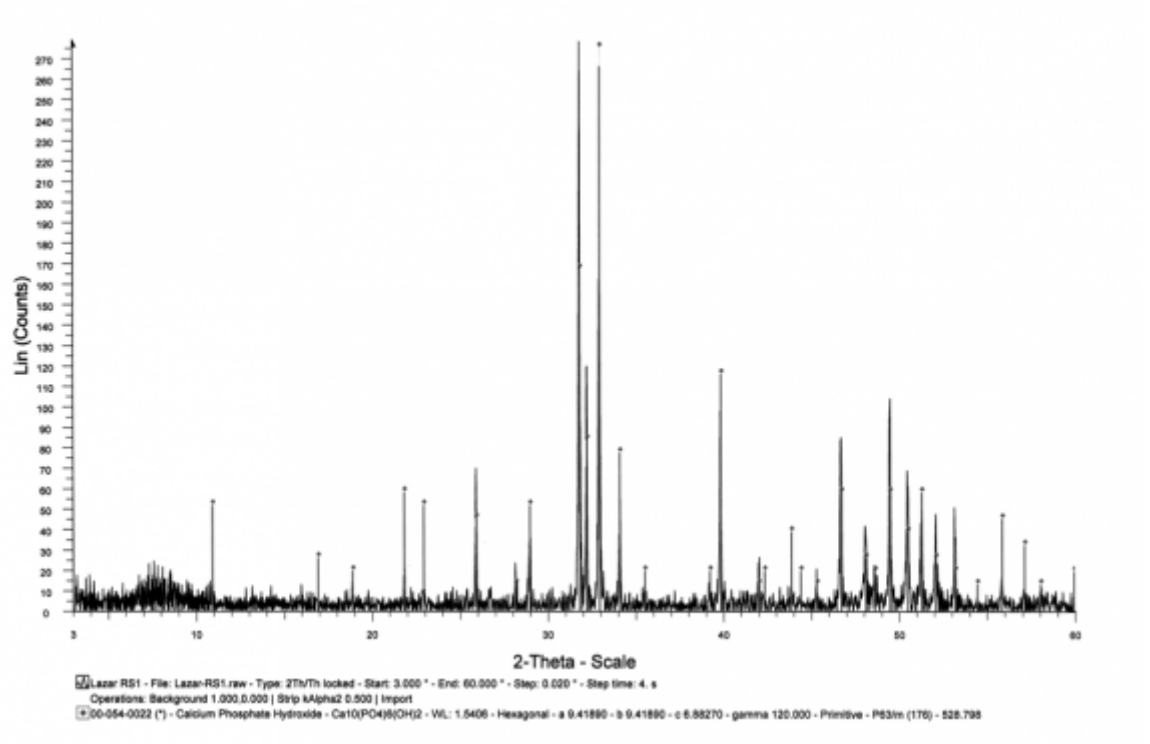

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Figure 3: Figure 3 :

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Figure 4: Table 2 :

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Figure 5: Table 3 :

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Figure 6: Table 4 :

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Figure 7: Table 5 :

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[Figure 1 : Chemical structure of Rhodamine B] *Figure 1 : Chemical structure of Rhodamine B*,

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