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Adsorptive removal of Reactive Yellow 84 dye from aqueous solutions onto animal bone meal

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Abstract

The adsorption of a reactive dye, Reactive Yellow 84, from aqueous solution onto animal bone meal was investigated. The experiments were carried out to investigate the factors that influence the dye uptake by the adsorbent, such as the contact time under agitation, adsorbent amount, initial dye concentration, temperature and pH of dye solution. The experimental results show that the amount of dye adsorbed increases with an increase in the amount of animal bone meal. The maximum adsorption occurred at the pH value of 6.6. The equilibrium uptake was increased with an increase in the initial dye concentration in solution. The experimental isotherm data were analyzed using Langmuir isotherm model. The maximum monolayer adsorption capacity was 57.15 mg/g. The adsorption has a low temperature dependency and was endothermic in nature with an enthalpy of adsorption of 2.52 kJ/mol.

Keywords: Animal Bone Meal, Reactive Yellow 84, Adsorption, Isotherm Langmuir

Introduction

The world wide high level of production and use of dyes generates colours wastewaters, which give cause of environmental concern. Textile companies, dye manufacturing industries, paper and pulp mills, tanneries, electroplating factories, distilleries, food companies and a host of other industries discharge colour wastewater [1]. As a matter of fact, the discharge of such effluents in the environment is worrying for both toxicological and esthetical reasons.

The pollution is characterized by biochemical oxygen demand, chemical oxygen demand, suspended solids, bad smell, toxicity (high concentration of nutrients, presence of chlorinated phenolic compounds, sulphur and lignin derivatives, etc.) and especially colour [2,3]. Colour is the first contaminant to be recognized in wastewater and the presence of very small amounts of dyes in water is highly visible and undesirable [4,5].

Discharge of coloured wastewaters from various industries such as textile and dyeing, pulp and paper, leather tannery, plastic, cosmetics and food processing industries presents a major environmental problem for developing countries. Reactive dyes have been used to dye cellulose for over 100 years. Because of the ease of their application and the wide gamut of products available at a modest cost, reactive dyes are still a popular dye class [6]. The discharge of coloured wastes into streams not only affects their esthetical nature but also interferes with the transmission of sunlight into streams and therefore reduces photosynthetic action. Further, coloured wastes may contain chemicals which exhibit toxic effects toward microbial populations and can be toxic and/or carcinogenic to mammals [7,8]. In general, dyes are poorly biodegradable. Accordingly conventional biological treatment process is not very effective in dye removal. The decolourization of dyes containing wastewater can be accomplished in two ways: chemical and physical methods [9,10]. Various electrochemical techniques [11-13] and adsorption with activated carbon [14,15] were investigated.

Among the above mentioned methods, adsorption is considered relatively superior to other methods because of simplicity of design, availability, and ability to treat dyes in more concentrated form and provides sludge-free cleaning operations [16,17]. Activated carbon has long been used in industry as a standard adsorbent for removing colour. However, although it is the most widely used adsorbent for the removal of colour and the treatment of textile effluents, its use is limited mainly because of its high cost [18,19]. Therefore, the development of low cost alternative adsorbents has been focused.

A wide variety of low cost adsorbents have been reported in literature such as sugarcane bagasse [20], soy meal hull [21], orange peel [22], saw dust [23], palm ash [24], rice husk [25], bagasse fly ash [26], rice husk ash [27,28], Trichoderma harzianum mycelial waste [29], flay ash [30], rice straw [31], and waste wood-shaving bottom ash [32]. However, new economical, easily available and highly effective adsorbents are still needed.

This work aims to study a convenient and economic method for Reactive Yellow 84 removal from aqueous solutions by adsorption onto animal bone meal as an abundantly available and a low cost adsorbent.

2. Materials and methods

Animal bones were collected from nearby butcher shops. All of he attached meat and fat were removed and cleaned from the ones. The bones were then washed several times with tap water and left in open air for several days to get rid of odours. Later, they were transferred to the oven at 80°C for drying. The dried bones were crushed and milled into different particle sizes in the range 45-200 µm then calcined for 2 h at 800°C. The residue was washed with water and was used after drying for 24 h at 80°C. The residue was washed with water and was dried overnight at 100°C in a conventional drying oven, and then calcined at a heating rate of 2°C/min to 400°C and kept at this temperature for 4 h. The resulting material was denominated ABM. 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 $S_p = 85\ m^2/g$.

Adsorption experiments were carried out by varying the initial concentration dye from 10 to 40 mg/L, the amount of ABM from 0.4 to 1.6 g/L, the temperature from 20°C to 50°C and the pH from 2.1 to 10. The pH was adjusted to a given value by the addition of HCl (1 mol/L) or NaOH (1 mol/L) and was measured using a pH-Metre Basic 20+ model pH-meter.

The zero point charge 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 adsorbent were added to each flask, which was securely capped immediately. The suspensions were shaken in a shaker at 298°K and allowed to equilibrate for two days. 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 ΔpH ($pH_f - pH_i$) versus pH_i crosses the line equal to zero.

The ABM is identified by X-ray diffraction (Philips X'Pert PRO), IR spectroscopy (spectrometer Bruker-Tensor 27) and chemical analysis. ABM was characterized by X-ray diffraction analysis which the spectrum is given in Figure 1 and with Infrared-spectra as shown in Figure 2. X-ray diffraction analysis confirms the presence of hydroxyapatite. The characteristic phosphate and calcium bands are observed in Infra Red spectra analysis.

Figure 1 depicts the XRD spectrum of ABM adsorbent. The diffractogram of calcined ABM show only the characteristic pattern of hydroxyapatite. These results confirm that the amorphous organic component was removed after calcinations. For 2θ between 25° and 45°, the main lattice reflections originate peaks at 25, 28.1, 32.8, 33.7, 34.5 and 39.7° being respectively assigned to the (0 0 2), (1 0 2), (2 1 0), (2 1 1), (1 1 2) and (3 0 0) Miller plans of hydroxyapatite.

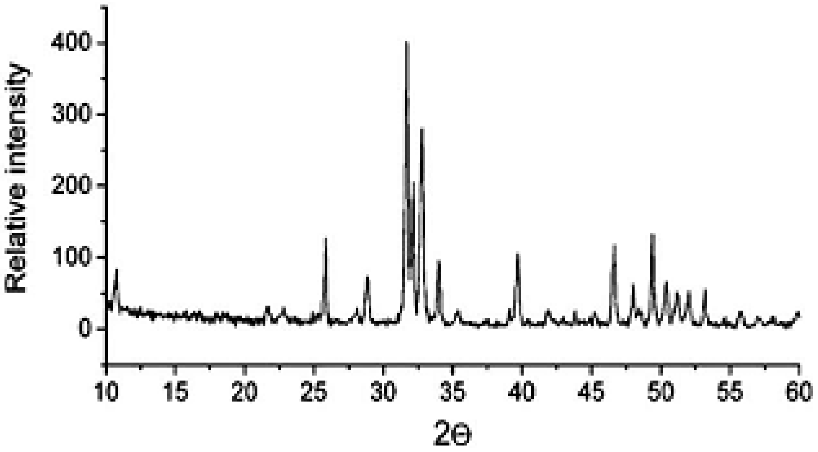

Figure 1: X-ray diffraction of ABM

Figure 2 shows the FTIR spectra of ABM adsorbent. FTIR spectra were carried out by encapsulation 0.5 mg of finely powder with 400 mg of KBr to get translucent disk. Carbonate is the most abundant substitution in bone mineral and according to its crystal position, carbonate apatite is designated as type A (OH^-) or type B (PO_4^{3-}), the latter being the most frequent bone. It is recognized that hydroxyapatite derived from natural bone. FTIR spectrum of ABM given in Figure 2 shows the characteristic bands of hydroxyapatite (571, 603, 962 (shoulder), 1047 and 1091 (shoulder) cm^{-1} due to phosphate vibrations and collagen (C=O stretching vibration at 1635 cm^{-1}, N-H in plane bending at 1458 cm^{-1}, C-H and N-H stretching modes in 3000 – 3571 cm^{-1} region). Additionally, the typical bands of carbonate substituting for phosphate site (type B) in the apatite lattice are also observed: band at 874 cm^{-1} and double bands 1385/1445 cm^{-1}.

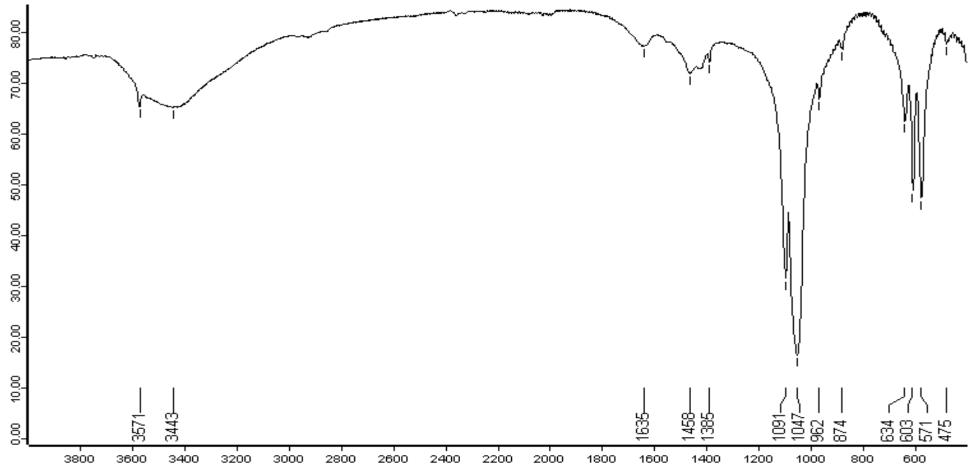

Figure 2: IR spectra of ABM

Elemental analysis shows a high yield of Ca (49.62%) and P (42.36%) compared to 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%).

The Reactive Yellow 84 was obtained from a textile firm as a commercial available dye formulation designed as Suncion Yellow H-E4R. The chemical structure of the dye is shown in Figure 3. Solutions were prepared by dissolving requisite quantity of the dye in distilled water. The volume of colour solution was 500 mL.

The dye solutions were filtered by Millipore membrane type 0.45 µm HA, and the concentrations of dyes were determined from its UV-Vis absorbance characteristic with the calibration method. A BioMate 6, England UV/Visible spectrophotometer was used. For this measurement, the wavelength of maximum absorption, λ_{max}, was 226 nm. The quantity adsorbed was calculated by measuring the concentration of the solution before and after adsorption using the following equation:

$$q = \frac{C_0 - C}{R} \tag{1}$$

Where q (mg/g) is the quantity of dye adsorbed per unit mass of adsorbent, C_0 (mg/L) is the initial dye concentration, C (mg/L) is the dye concentration at any time and R (g/L) is the mass of adsorbent per litre of aqueous solution.

The dye removal percentage can be calculated as follows:

$$\% \quad of \quad dye \quad removal = \frac{C_0 - C_e}{C_0} x100 \tag{2}$$

Where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of dye in solution.

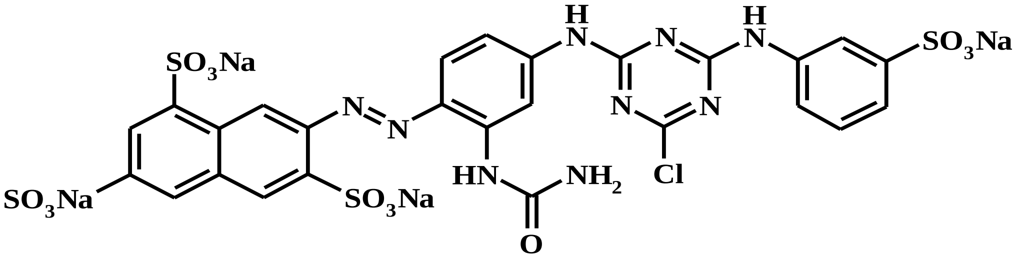

Figure 3: Chemical structure of Reactive Yellow 84

3. Results and discussion

3.1. Effect of ABM quantities on the kinetics of adsorption

Kinetics of retention describes speeds of reactions that permit to determine the contact time under agitation put to reach the adsorption equilibrium. The adsorption kinetics of Reactive Yellow 84 onto ABM was studied by changing the quantity of adsorbent from 0.4 – 1.6 g/L in the test solution and keeping unchangeable the initial dye concentration at 25 mg/L, temperature and pH.

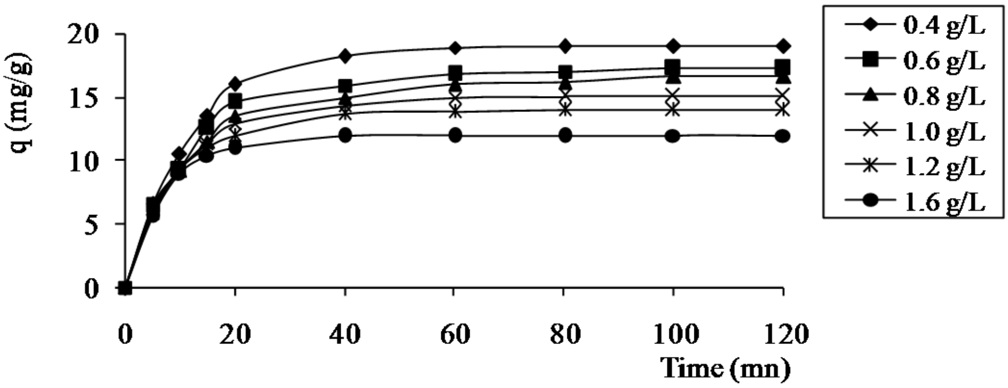

Figure 4: Kinetics of adsorption of Reactive Yellow 84 on ABM at different amounts

Figure 4 shows change of adsorbed quantity per gram of adsorbent, the adsorption was found to be rapid at the initial period of contact time and then to be slower with the increase in contact time. In another case, as adsorbent amount increases, the quantity of dye adsorbed per mass of adsorbent and the equilibrium time decrease consequently.

Additionally, the percentage of decolouration increases from 72% to 92% by increasing the amount of ABM from 0.4 – 1.6 g/L, this is due to the surface area available by more adsorbent ABM particles.

3.2. Effect of initial dye concentration on the kinetics of adsorption

The kinetics of adsorption of Reactive Yellow 84 at different initial concentrations was achieved. Figure 5 shows the extent of dye adsorption as function of reaction time. It was found that, as the initial concentration increases, the equilibrium time and the amount of dye adsorbed per gram amount of adsorbent increase. It is further noted that the amount of Reactive Yellow 84 increases from 15.24 to 37.52 mg/g by increasing the initial concentration from 10 to 40 mg/L. The kinetics adsorption curves are smooth and continuous leading to saturation of ABM by Reactive Yellow 84. This result suggests the possibility of monolayer coverage adsorption of Reactive Yellow 84 on ABM.

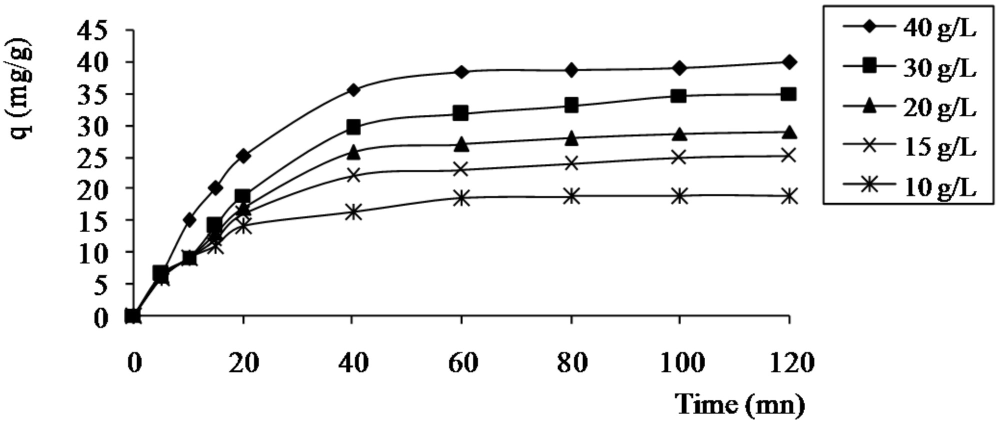

Figure 5: Kinetics of adsorption of Reactive Yellow 84 at different initial concentrations

From the kinetics curves, the amounts of dye adsorbed after 120 min of contact time are illustrated in Figure 6. This isotherm belongs to type L of the Giles et *al*. Classification[33], which indicates that, as more sites in the substrate are filled, it becomes increasingly difficult for the solute molecules to find an available vacant site. This could be either because the adsorbed molecules are more likely to be adsorbed on monolayer on a surface containing a finite number of identical sites and there is no strong competition from the solvent.

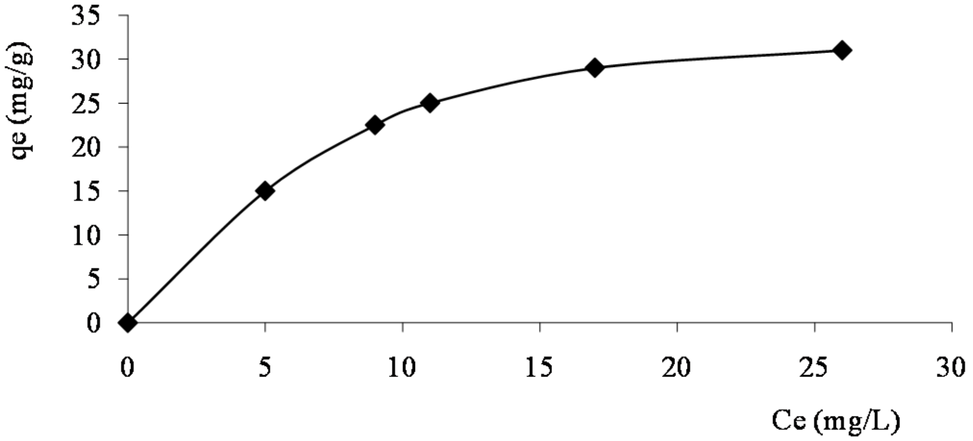

Figure 6: Adsorption isotherm of Reactive Yellow 84 on ABM. Langmuir isotherm model

The description of adsorption isotherm has been achieved by applying the linear form of Langmuir equation proposed by Stumm and Morgan [34]:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{Kq_m}\frac{1}{C_e} \qquad (3)$$

Where q_m (mg/g) is the monolayer coverage of the adsorbent particle in terms of mg dye/g of adsorbent, q_e (mg/g) is the amount of dye adsorbed at equilibrium, K (L/mg) is the Langmuir equilibrium constant and C_e (mg/L) is equilibrium concentration.

A plot of $1/q_e$ versus $1/C_e$ yields q_m and K. From the data obtained, the maximum adsorption capacity q_m and the constant K estimated are respectively 57.15 mg/g and 0.091 L/mg.

Although the affinity of ABM for the removal of dyes from aqueous solution was less than that of activated carbon cited in previous works [35,36], it can take a good place between low cost adsorbents investigated in the removal of dyes.

3.3. Effect of temperature on the kinetics of adsorption

The temperature has two major effects on the adsorption process. Increasing the temperature is known to increase the rate of diffusion of the adsorbed molecules across the external boundary layer and the internal pores of the adsorbent particles, owing to the decrease in the viscosity of the solution. In addition, changing temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [37]. Figure 7 shows the results of experiments carried out at different solution temperatures.

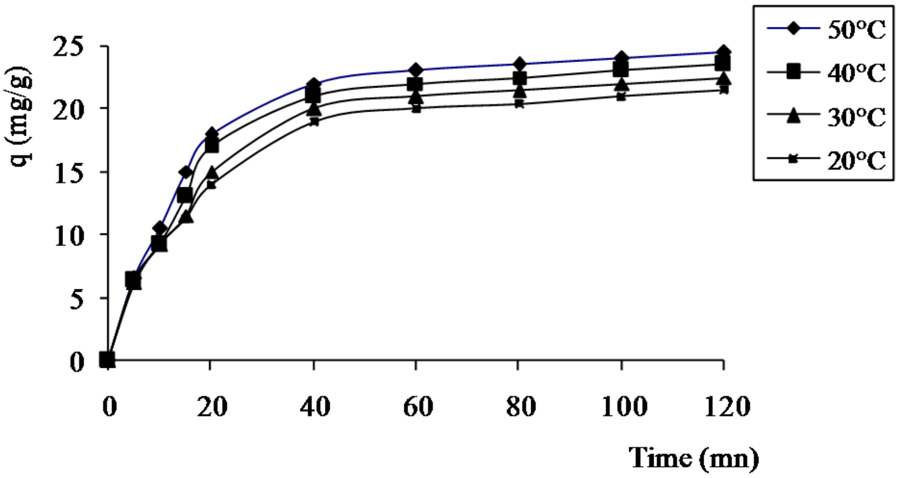

Figure 7: Effect of temperature on the kinetics of adsorption of Reactive Yellow 84 on ABM

The removal of Reactive Yellow 84 increases from 22.31 to 24.23 mg/g by increasing the temperature of the solution from 20°C to 50 °C, indicating that the process to be endothermic. This kind of temperature dependence of the amount of the dye adsorbed may be due to the fact that a possible mechanism of interaction is the reaction between the sulfonyl groups of Reactive Yellow 84 and the cationic sites of ABM such a reaction could be favoured at higher temperatures. The enthalpy of adsorption, ΔH, has been calculated using the following equation:

$$q_e = q_0 \exp\left[-\frac{\Delta H}{RT}\right] \qquad (4)$$

Where q_e (mg/g) is the amount of dye adsorbed at equilibrium, q_0 is the temperature independent factor (mg/g), ΔH is the enthalpy of adsorption (J/mol) and R is the gas constant (8.31 J/K.mol). The linear transformation of this equation expressed by Ln q_e as function of 1/T gives a straight line whose slope is equal to - ΔH/R. The results are shown in Figure 8.

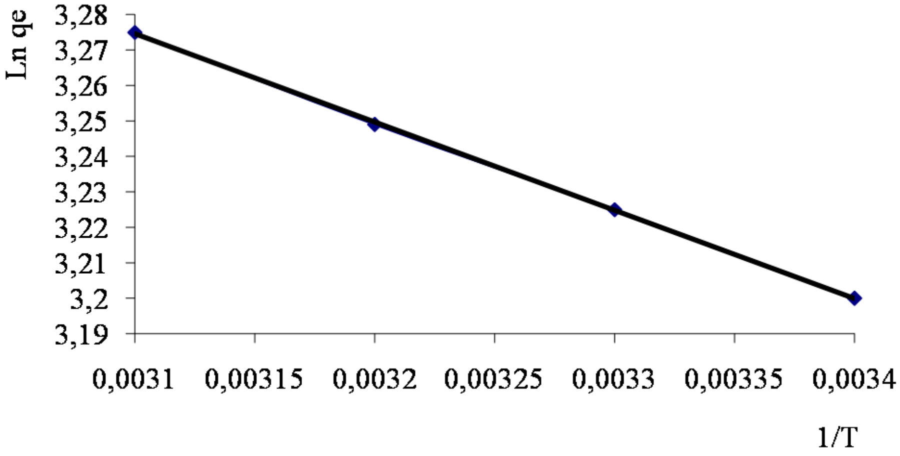

Figure 8: Plot of Ln q_e *versus* 1/T

The slope of the linear curve was - 279.45, which correspond to an enthalpy of adsorption of 2.52 kJ/mol. The enthalpy of adsorption was very lower and positive indicating that the process is endothermic, and hence it can be concluded that the process is governed by interactions of physical nature [38].

3.4. Effect of pH on adsorption

The pH is one of the most important factors controlling the adsorption of dyes onto suspended particles, because both adsorbed molecules and adsorbent particles may have functional groups which are affected by the concentration of hydrogen ions H^+ in the solution and which are involved in the molecular adsorption process at the active sites of adsorbent. Figure 9 shows the amount of Reactive Yellow 84 adsorbed for different pH_s.

It was found that above pH 7 and below pH 3 the adsorption of the dye decreases. The pH of the zero charge of the ABM is determined and to be 8.4, for pH values higher than 8.4. The surface of the ABM becomes negatively charged and this is the opposite for pH < 8.4. Moreover, the dye is a weak acid, it dissociate less towards an acid pH and is found consequently in neutral electrical form.

From the Figure 9, it can be seen that the amount of dye adsorbed on the ABM is high for pH between 3 and 8.4, which indicates that the positive form of ABM is responsible for adsorption in this range. For basic pH, the decrease of the amount of adsorbed dye molecules is prevented by the repulsive electrostatic forces existing between the negative charged surface of ABM and $Ph\text{-}SO_3^-$ groups of the dye predominant in this range of pH.

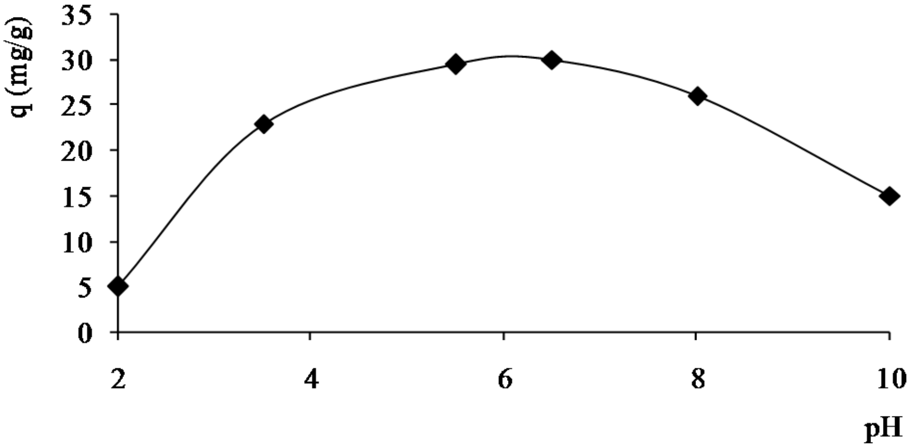

Figure 9: Effect of pH on the adsorption of Reactive Yellow 84 onto ABM

The decrease of the amount of adsorption below pH 3 can be due to the ionization of the amine and amide groups of the dye with H^+, which leads the molecules of the dye to be positively charged. The repulsive electrostatic forces of dye molecules positively charged with the positively charged surface of the adsorbent increase. Consequently, we show the decreasing adsorption.

Conclusion

ABM is efficiently utilized as an adsorbent for the removal of Reactive Yellow 84 dye from aqueous solutions. It has been found that, the adsorbed quantity of dye increases with an increase in the amount of ABM. The amount of dye adsorbed was high with high initial dye concentration according to Langmuir model. The Langmuir adsorption capacity was 57.15 mg/g. The adsorption has a low temperature dependency and was endothermic with an enthalpy of adsorption of 2.52 kJ/mol. The pH of solution affects both the surface of ABM and dye molecule charge. It was found that adsorption was disfavoured in acidic and basic ranges. The interactions between Reactive Yellow 84 molecules and ABM particles are essentially of physical nature. Finally, the use of ABM shows a greater potential for the removal of reactive textile dyes, as no costly equipment is required.

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