Removal of Brilliant Green Dye from Aqueous Medium by Untreated Acid treated and Magnetite Impregnated Bentonite Adsorbents

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Summary: The untreated bentonite (UB), acid treated bentonite (ATB) and magnetite impregnated bentonite (MIB) has been examined as adsorbents for the removal of Brilliant green (BG) dye from aqueous medium. The batch adsorption experiments were conducted at different pH, contact time, adsorbent dosage, dye concentration and temperature. The adsorption of BG was dependent on pH of the solutions and the optimized pH value for their adsorption is 8. The adsorption data were fitted to Freundlich and Langmuir adsorption models, which were best fitted to Langmuir isotherm model. The monolayer adsorption capacity of UB, ATB and MIB was 689.6, 785, 877 mg/g, respectively. The kinetic study was analyzed by pseudo first, second and intraparticle diffusion models. It was found that adsorption of BG onto all three adsorbents followed pseudo second order kinetic model. The prepared adsorbents were also characterized by scanning electron microscopy (SEM), energy dispersive X-rays (EDX) and XRD.

Keywords: Bentonite, Brilliant green, Adsorption, Kinetics

Introduction

Dyes are complex organic compounds, which is use as colorants in various industrial sectors like leather, textile, food, printing, pharmaceutical etc. Waste water discharged from these industries into an aquatic system contains up to 10% of used dyes [1]. The annual production of dyes is about 800,000 tons all over the world and 10-15% of its portion is being discharged continuously to the aquatic system [2,3]. The presence of dyes in water is not only aesthetically unpleasant, but also prevents light penetration, which may disturb the photosynthesis process and as a result the life cycle of aquatic organisms are drastically affect by these pollutnats. Beside these, dyes also contain very injurious organic compounds, which can cause both chronic and acute effect on the living organism depending upon the concentration of dye in water and exposure time of aquatic life [4,5]. The dyes present in water not only affect the aquatic life, but also affect drastically the health of terrestrial animals, human beings and birds living on dye contaminated water [6]. Some dyes are so toxic that they not only affect human's health, but can also pass to their next generations through birth defect, genetic disorder and inherited diseases [7,8]. In order to overcome these problems, it is necessary to the remove such pollutants from industrial effluents before discharging it into the hydrosphere. Various chemical and physical methods such as flocculation, coagulation osmosis, oxidation-reduction and adsorption processes are proposed for the removal of dyes from industrial effluents. Among these methods, adsorption process is the most attractive technique for the treatment of dye and pigments contaminated effluents, especially in the case when low cost and easily available adsorbent are used [9-11].

The bentonite is clay rock, which is using an efficient adsorbent for the removal of various types of pollutnats from aqueous solution due to its considerable ion exchange capacity, and cost-effective adsorbent [12]. Various research groups use Bentonite is an adsorbent for the removal of different types of pollutants. For example, Berez et al [13] used bentonite clay as an adsorbent for the removal of azo dyes from aqueous solutions, which significantly removed the dye. Sadeghalvad et al [14] removed copper from aqueous solution using Iranian bentonite as adsorbent. They were found that adsorption data were best fitted to Langmuir model as compared to Freundlich, Dubinin-Radushkevich (D-R), Redlich-Peterson, Khan, and Toth models. Ferhat et al [15] et al adsorbed heavy metals and zinc cations onto bentonite clay adsorbent. They reported that adsorption data follows the pseudo-second order model with high removal rates of 61.8 and 67.2 for zinc and copper, respectively. Freitas et al [16] used Verde-lodo bentonite as an adsorbent for the removal of silver and copper from waste water.

Keeping in view the above hazards, our present study is based on the removal of more toxic and carcinogenic basic dyes namely, BG from waste water. This basic dye belongs to the class of cationic

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dyes, which possess positive charge in their structure. Among different classes of the available dyes, cationic dyes were found to be the brightest and readily water soluble dyes. The toxic effects on the human health due to BG dye are: irritation of respiratory tract, irritation of skin and eye, irritation of gastrointestinal tract, neurological and reproductive disorder etc [17,18]. On heating BG also produces hazardous products such as nitrogen oxides, carbon oxides and sulfur oxides, which are the major perpetrators of air pollution [19]. In our present work, untreated bentonite, acid treated bentonite and magnetite impregnated bentonite was used as adsorbents for the removal of BG from aqueous solution.

Experimental

Materials

BG dye and nitric acid was purchased from Merck Company and Sigma Aldrich, respectively. While the Bentonite was obtained from soil sciences laboratory, Pakistan Council of Industrial Research (PCSIR). The bentonite was grinded and then sieved through a screener having mesh size of 120 µm. The bentonite was washed several times with distilled water for the removal of impurities. The washed bentonite was dried and stored for further use.

Acid Treatment of Bentonite

25 g bentonite was refluxed in 150 mL HNO_3 (0.1 M) solutions at about 70 °C for three hours. The bentonite was separated from HNO_3 solution by filtration and then several times washed with distilled water until free from acid. The bentonite was dried in oven and stored for further use.

Impregnation of Bentonite by Magnetite

$FeCl_2{\cdot}4H_2O$ and $FeCl_3{\cdot}6H_2O$ (ration of 1:2) were mixed in 80 mL of double distilled water and then shacked for 30 min at 85 °C. After 30 min, 20 mL of 30 % ammonium solution was added to the mixture solutions, which changed the orange color of solution into black. Then 8 g of pretreated bentonite was added to it and shaked at 85 °C for two hours. The magnetite impregnated bentonite was filtered and washed repeatedly with distilled water in order to removed extra chloride ions and were then dried in oven and stored for further use.

Batch Adsorption

Adsorption of BG onto UB, ATB and MIB were carried out at different experimental parameters such as different pH, shaking time, adsorbent amount, temperature, and at different dye concentration. For each experimental setup, known dye concentration, volume, pH of the dye and known mass of the adsorbent were taken in flask, and were shaked for the respective adsorption time.

After the specific adsorption time (5-60 min), the adsorbents were separated from BG solution through centrifugation. The concentration of dye in solution was determined by UV –Visible spectrophotometer. The dye adsorbed per unit mass of the adsorbent (mg/g), and the percentage adsorption was calculated using the following equations:

$$qe = \frac{(C_i - C_e)V}{W} \qquad (01)$$

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100 \qquad (02)$$

where q_e is the adsorption capacity in mg/g, C_i (mg/L) is the initial concentration of BG in aqueous solutions, C_e is the equilibrium concentration of BG in aqueous solutions, V is the volume of solutions in litter and W is the mass of adsorbent in gram

Results and Discussion

Surface Morphological Study of the Prepared Adsorbents

The morphological study of the prepared adsorbents was carried out with SEM. Generally the adsorbents with porous and rough morphology have high adsorption capacity [20, 21]. Fig. 1a-c shows the SEM images of UB, ATB and MIB. The SEM micrograph (Fig 1b) showed that the acid treatment has increased the porosity of the bentonite, which has positive effect on adsorption capacity. It means that the adsorbent porosity might facilitate the diffusion of dye from solutions to adsorbent surface. Fig. 1c showed the morphology of MIB, which has not only porous surface but also seems to be very rough, and as a result its adsorption capacity might be higher than UB and ATB. The surface roughness of MIB is due to the presence of magnetite particles, which are present in agglomerated form on the MIB surface.

EDX Analysis of the Prepared Adsorbents

The EDX technique is use for the determination of elemental compositions of the adsorbent [22]. Figs 2a-c shows the EDX spectra of UB, ATB and MIB, respectively. The EDX spectra of UB and ATB show highest percentage of oxygen, silicon and aluminum, while other elements like iron, sodium, calcium, sulfur, chlorine, potassium, and calcium are present in minute quantities. The EDX spectra of MIB show the highest percentage of oxygen, silicon, aluminum and iron (higher percentage of iron than UB and ATB) along with minute quantities of calcium, potassium and magnesium, which showed that the bentonite was successfully impregnated by magnetite nanoparticles.

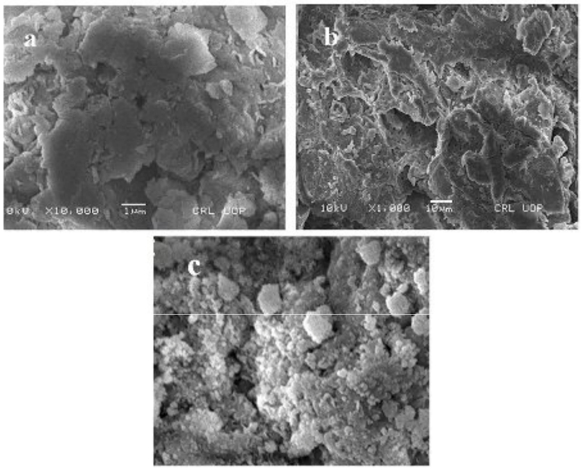

Fig. 1: SEM images of (a) UB (b) ATB (c) MIB.

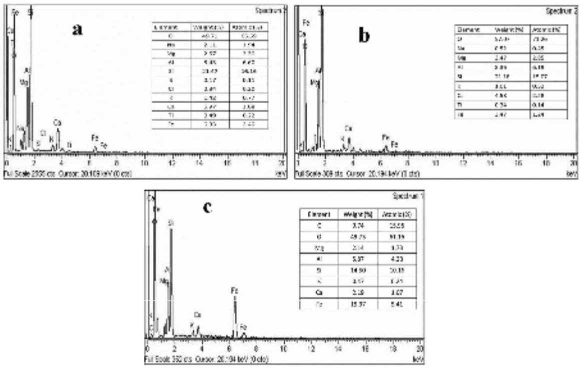

Fig. 2: EDX spectra of (a) UB, (b) ATB and (c) EDX spectra of MIB.

Effect of pH

pH of solutions is one of the most important parameters in the adsorption study, because at certain pH, the dye become more unstable, and become easy to remove it from aqueous solution through selective adsorbent. Fig. 3 shows the adsorption of BG onto all three form of bentonite at different pH (ranged from 2 to 12), and other experimental conditions such as contact time (60 min), initial dye concentration (100 mg/L of 30 mL), adsorbent dosage (0.01g) and temperature (25°C) were kept constant. The results showed that the maximum adsorption of BG onto UB, ATB and MIB was occurred at pH 8, and then level off after pH 8. It can be concluded that at low pH (acidic medium) the BG is more stable, and its stability decreases with increasing pH value of the solutions and become completely unstable at pH 8. The instability of BG at high pH value is might be contribute to the structural changes occurred in the molecules of BG, and thus become easy to remove it from aqueous solutions. Fig. 3 also presented that the MIB adsorbed higher quantity of BG as compared to ATB and UB.

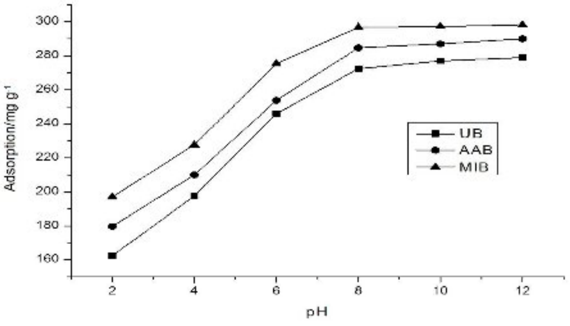

Fig. 3: The effect of pH on the BG adsorption onto UB, ATB and MIB.

Effect of Contact Time

Fig. 4 shows the adsorption of BG onto UB, ATB and MIB, which was carried out at different contact time (5-55 min) at constant initial dye concentration (100 mg/L), pH 8, adsorbent dose (0.01g) and temperature (25 °C). The result illustrates that the rapid uptake of BG onto all form of bentonite is increased up to 30 min and then level off after 30 min. At 30 min adsorption time, adsorption capacity of BG onto UB, ATB and MIB was 270.6, 285 and 323.73 mg/g, respectively. For further adsorption study 30 min was selected as an equilibrium time.

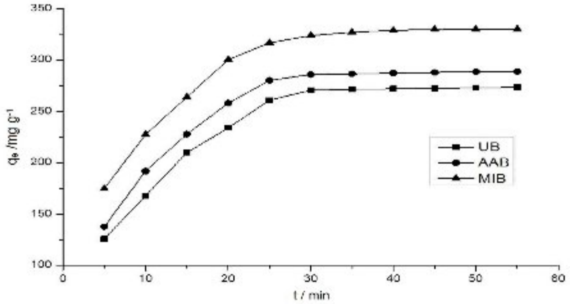

Fig. 4: Effect of contact time on the adsorption of BG onto UB, ATB and MIB.

To determine a suitable mechanism for the adsorption of BG onto UB, ATB and MIB, the equilibrium adsorption data were tested through different adsorption kinetic model, i.e. pseudo first order, pseudo second order and intraparticle diffusion models.

Lagergren proposed pseudo first order kinetic model is given as [23]:

$$Log\ (qe - qt) = Logqe - K_{1t}/2.303 \quad (3)$$

where q_e and q_t is the amount of dye adsorbed in mg/g at equilibrium and at respective time, and K_1 is the rate constant of pseudo first order kinetic model which can be calculated from the linear plot of Log (q_e –q_t) versus time.

The pseudo second order kinetic model is given as [24]:

$$\frac{t}{qt} = \frac{1}{K_2 q^2} + \frac{1}{qe} t \quad (4)$$

By plotting t/q_t versus t give a straight line from which K_2 (mg/L) and q_e (mg/g) can be calculated.

The intraparticle diffusion model is given as [25]:

$$q_t = K_{id}\ t^{1/2} + C \quad (5)$$

The plots obtained for Pseudo first, Pseudo second and intraparticle diffusion models are given in Figs. 5-7 and the parameters are given in Table-1. Table1 showed that the adsorption equilibrium data of all three adsorbents were best fitted to pseudo second order kinetic model, because regression coefficient (R^2) values of pseudo second order kinetic model were very close to 1 and also the calculated q_e values from the plot of pseudo second order kinetic model were very close to experimental q_e values. It was also found that the plot of intraparticle diffusion model (Fig. 7) of all type of adsorbents consist of two different linear plots. The first linear plot represents the rapid adsorption of BG molecules on the adsorbent surface through boundary layer diffusion process, in which molecules of dye move from solutions to the surface of the adsorbent with very fast rate and tend to cover the pores of the adsorbent surface. The second straight line represents the establishment of the equilibrium stage. Moreover, the deviation of plot from the origin in intraparticle diffusion model indicated that the adsorption was not controlling by pore diffusion process. Table-1 also showed that in intraparticle diffusion model, intercept value (C) is very large for all type of adsorbents. The larger C values indicate that the adsorbent provide larger surface for the adsorption of BG, and the larger surface thus enhanced the boundary layer effect [26].

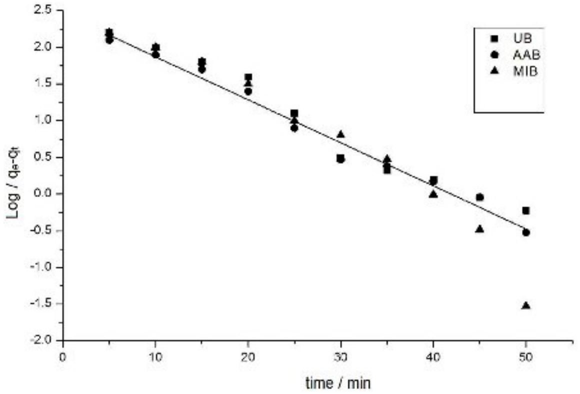

Fig. 5: Pseudo first order for the adsorption of BG onto UB, ATB and MIB.

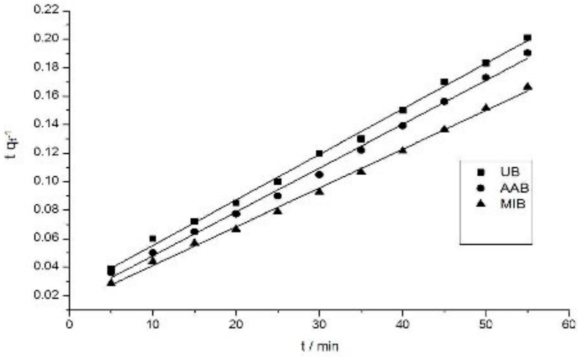

Fig. 6: Pseudo second order kinetic model of the BG adsorption onto UB, ATB and MIB.

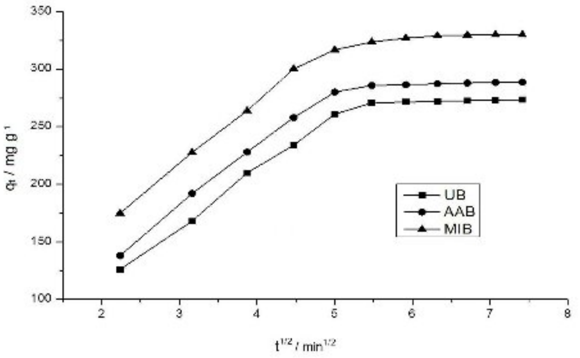

Fig. 7: Intraparticle diffusion model of the BG adsorption onto UB, ATB and MIB.

Table-1: Parameters of pseudo first, second and intraparticle diffusion models.

	Pseudo first order			**Pseudo second order**			**Intraparticle diffusion model**	
Adsorbents	**qe (mg/g)**	**K_1(min)$^{-2}$**	**R^2**	**qe (mg/g)**	**K2(g/mg min)**	**R^2**	**K_{id}(mg/g min)$^{1/2}$**	**C(mg/g)**
BG on UB	**316**	**0.135**	**0.971**	**277.7**	**7.2×10^{-4}**	**0.9965**	**27.98**	**92.663**
BG on ATB	**251**	**0.177**	**0.9836**	**294.4**	**6.2×10^{-4}**	**0.9939**	**27.29**	**113.46**
BG on MIB	**630**	**1.2**	**0.9511**	**333**	**6.2×10^{-4}**	**0.9975**	**28.43**	**146.71**

Effect of Adsorbent Dose on the Adsorption of BG

The adsorption of BG on to all form of bentonite was carried out at different adsorbent ranged from 0.01 to 0.05g while other experimental conditions like pH (8), contact time (30 min), dye concentration (100 mg/g) and temperature (25 °C) were kept constant. Fig. 8 shows the percent adsorption of BG, which is presented that the adsorption of BG onto all form of BC was increases with increasing the adsorbent dose. The increase in percentage adsorption with increasing adsorbent dose was because of the availability of larger amount of active sites of the adsorbent to the fixed concentration of dye [27]. While decrease in mg/g adsorption of BG with increasing the adsorbent dose is due to the remaining of unsaturated sites of the adsorbent [28].

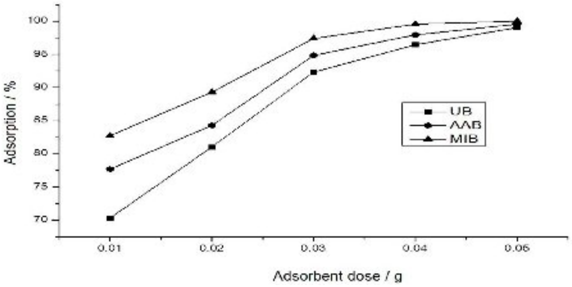

Fig. 8: Effect of adsorbent dose on the BG adsorption onto UB, ATB and MIB.

Effect of Initial Dye Concentration on the Adsorption of BG

The adsorption of BG onto the adsorbents was carried at different initial dye concentration ranged from 100-700 mg/L with constant experimental conditions. The adsorption of BG (mg/g) is shown in Fig. 9. It can be seen that the adsorption of BG per unit mass of the adsorbent increases with increasing the initial dye concentration. This increase in adsorption per unit mass of the adsorbent with increasing the dye concentration is might be due to small resistance for the adsorbent to uptake the dye molecules from aqueous solutions at higher dye concentration [29]. The percentage adsorption of BG decreases with increasing the initial dye concentration. The decrease in percentage adsorption with increasing the initial dye concentration is might be due to the saturation of the available active sites of the adsorbent.

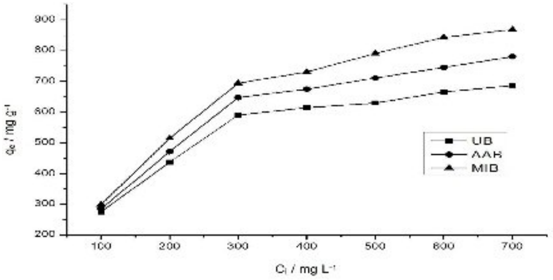

Fig. 9: The effect of initial dye concentration on the adsorption of BG on to UB, ATB and MIB.

Adsorption Isotherm

The interaction of adsorbate with the adsorbent and the adsorption capacity of the adsorbent for the adsorbate can be determined from the adsorption isotherm. In the present work, two commonly used adsorption isotherm namely Langmuir and Freundlich adsorption isotherm were applied to equilibrium adsorption data.

The Freundlich adsorption isotherm is given as [30]:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{06}$$

The linear form of Freundlich adsorption isotherm is:

$$Inq_e = InK_F + \frac{1}{n} InC_e \tag{7}$$

Where q_e (mg/g) is the amount of dye adsorbed at equilibrium, C_e (mg/L) is the remaining concentration in solution, K_F (mg/g)(L/mg) and n is constant which can be calculated from the slope and intercepts of linear plot of Inq_e Versus In C_e.

The Langmuir adsorption isotherm is given as [31]:

$$q_e = K \times q_{max} \frac{C_e}{1+K\times C_e} \tag{08}$$

In equation 12, q_e (mg/g) is the amount of dye adsorbed at equilibrium, q_{max} (mg/g) is the adsorption capacity, K is the Langmuir constant and C_e is the equilibrium concentration in solutions.

The linear form of Langmuir isotherm is:

$$\frac{C_e}{q_e} = \frac{1}{Kq_{max}} + \frac{C_e}{q_{max}} \qquad (09)$$

The plot of Freundlich and Langmuir adsorption isotherm are given in Figs. 10 and 11, while their parameters are listed in Table-2. The correlation coefficient values are much closed to the experimental data.

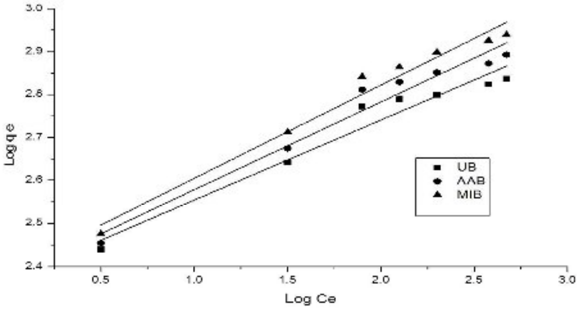

Fig. 10: Freundlich isotherm for the adsorption of BG onto UB, ATB and MIB.

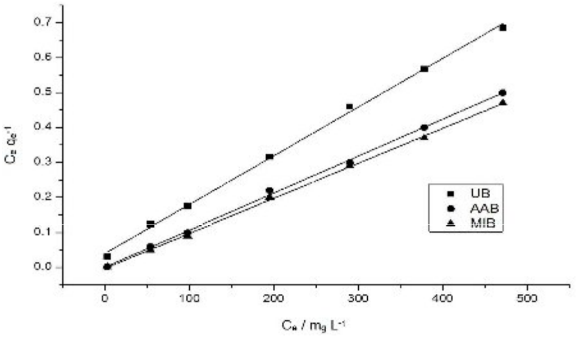

Fig. 11: Langmuir plot for the BG adsorption onto UB, ATB and MIB.

Table-2: Parameters of Freundlich and Langmuir adsorption isotherms.

	Freundlich isotherm			Langmuir isotherm		
Adsorbents	**K_F(L/mg)**	**n**	**R^2**	**q_{max}(mg/g)**	**K_L(L/mg)**	**R^2**
BG on UB	**177.9**	**4.3**	**0.9548**	**689.6**	**5.9×10^{-5}**	**0.9973**
BG on ATB	**205.8**	**4.42**	**0.9648**	**785**	**2.4×10^{-4}**	**0.9964**
BG on MIB	**337.2**	**6.4**	**0.9836**	**877**	**6.6×10^{-5}**	**0.9949**

Effect of Temperature on the Adsorption of BG

The adsorption of BG onto adsorbents was studied at different condition of temperature ranged from 30-60 °C while the other experimental conditions were kept constant. The adsorption of BG (mg/g) onto all form of bentonite adsorbents at different temperature condition is shown in Fig. 12. It was found that the adsorption of BG onto all form of bentonite was increased as increased the adsorption temperature, which showed that the higher temperature is favorable for adsorption.

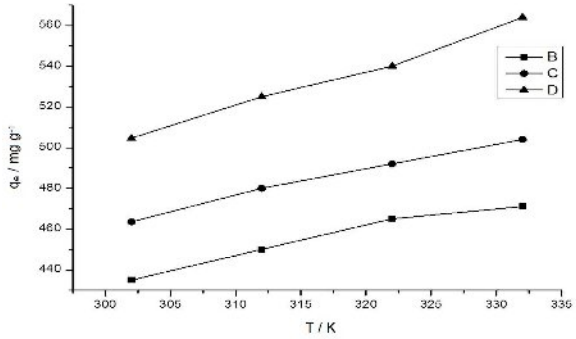

Fig. 12: Effect of temperature on the BG adsorption on to UB, ATB and MIB.

Thermodynamic Study

The effects of temperature on the adsorption of BG were further explained in term of different thermodynamic parameters like: Gibbs free energy (ΔG), Entropy (ΔS) and Enthalpy (ΔH) by using equations [32]:

$$\Delta G^{\circ} = -RT\,InK_D \qquad (10)$$

$$InK_D = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \qquad (11)$$

$$InK_D = \frac{q_e}{C_e} \qquad (12)$$

where K_D is the distribution coefficient, R is the ideal gas constant (8.314 J $mol^{-1}K^{-1}$) and T is the absolute temperature in Kelvin. Using equation 15 lnK_D were plotted versus 1/T as given in Fig. 13. From the slop and intercept of linear plot of lnK_D vs 1/T, ΔH and ΔS were calculated, while the values of ΔG at different temperature were calculated by using Equation 10. The value of ΔG, ΔH and ΔS are listed in Table-3. The values of ΔG are negative which indicated that the adsorption of BG on to all form of bentonite adsorbents was spontaneous and thermodynamically feasible. The values of ΔS and ΔH for all type of adsorbents is positive, the positive value of ΔS indicated that the adsorption of BG onto all form of Bentonite adsorbents was randomly, while the positive values of ΔH indicated that the adsorption of BG was favorable at higher temperature.

Table-3: Thermodynamic parameters for the adsorption of BG onto UB, ATB and MIB.

	ΔH° (KJ/mole)	ΔS° (KJ/mole K)	$-\Delta G^{\circ}$ (KJ/mole)			
Adsorbents			**303K**	**313K**	**323 K**	**333 K**
BG on UB	**9.14**	**46.6**	**5.3**	**5.71**	**6.3**	**6.63**
BG on ATB	**13.4**	**63.4**	**5.8**	**6.5**	**7**	**7.73**
BG on MIB	**29.9**	**121.4**	**7.1**	**7.8**	**8.8**	**10.8**

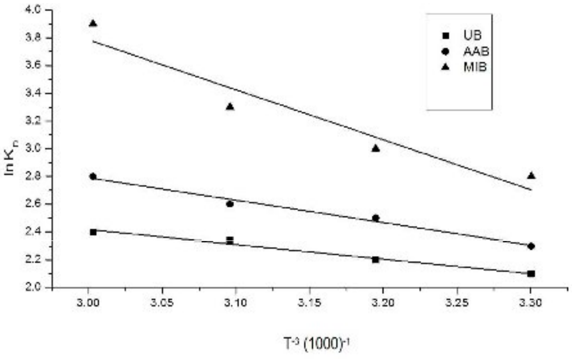

Fig. 13: The Van't Hoff plots for the adsorption of BG onto UB, ATB and MIB.

Conclusion

It was concluded that the MIB was found to be more effective adsorbent than UB and MIB for the removal of BG from aqueous solution. The high adsorption capacity of MIB was because of its porous and rough surface as well as better interaction of magnetite with dye molecules. The adsorption of BG on to all three types of adsorbents was highly dependent on pH and its maximum adsorption was found at pH 8. The kinetic studies were interpreted by pseudo first, pseudo second and intraparticle diffusion models, which were best, correlated to pseudo second order kinetic model. The equilibrium isotherm data was analyzed by Langmuir and Freundlich adsorption isotherm models, which were best fitted to Langmuir adsorption isotherm model.

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