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Adsorption-Desorption Of Herbicide Paraquat Dichloride By Mg-Bentonite Clay

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ABSTRACT

An investigation was conducted on the adsorption and desorption of herbicide Paraquat dichloride (1,1-dimethyl-4,4-bipyridyl dichloride) from aqueous solutions on Mg-bentonite clay by batch method has been studied . The effects of different experimental parameters such as shaking contact time, particle size, Mg-bentonite dosage, temperature and the initial concentration of the Paraquat dichloride(PQ) were studied. The results showed that the adsorption process could be satisfactorily described with the reaction model and were reasonably explained by assuming a competitive adsorption mechanism in the ion exchange process. Further, the fitted adsorption capacity at equilibrium decreased with increasing temperature, but desorption increased with increasing temperature, indicating that adsorption is an exothermic process while the desorption is endothermic. The adsorption equilibrium for Paraquat dichloride onto Mg -bentonite is reached in 30 min, the maximum adsorption capacity at pH 10 was found favorable for the removal of Paraquat dichloride. The thermodynamic parameters (ΔG, ΔH, and ΔS) were calculated from equilibrium constant and were explained in the mean of the chemical structure of the adsorbate.

Keywords: Paraquat, Mg-Bentonite, adsorption, desorption, isotherms.

INTRODUCTION

Organic pesticide residues have been reported in drinking water, agricultural water and groundwater [1]. These pesticides generally penetrate into surface water in runoff from land applications and from industrial wastewater discharges [2]. It is a known fact that herbicides give rise to serious health problems when not used properly [3]. Pesticide sorption affects other processes like transport, degradation, volatilization and bioaccumulation, which influence the final fate of these compounds in the soil[4]. The pesticide sorption process incorporates a wide range of different chemical mechanisms including ion exchange, cation-bridging, ion-dipole interactions, ligand exchange, charge transfer, hydrogen bonding and van der Waals' forces[5].

Paraquat dichloride (1,1^{-}-dimethyl-4,4^{-}bipyridylium chloride), which was extensively used as a non-selective herbicide, is one of the bipyridinium compounds [6]. However, it is well known that this compound is also one of the most acutely toxic compounds because it has caused many cases of human poisoning, with the lung being the primary target tissue [7]. Consequently it is important to study the adsorption behavior of cationic paraquat with clay minerals from the viewpoints of mobility in soil and/or methods of control in the adsorption process.

Bentonite is a rock formed of highly colloidal and plastic clays composed mainly of montmorillonite, and is produced by in situ devitrification of volcanic ash [8]. In addition to montmorillonite, bentonite may also contain feldspar, biotite, kaolinite, illite, cristobalite, pyroxene, zircon, and crystalline quartz [9]. The crystalline structure of the bentonite is composed of two building units, tetrahedral sheets linked together, and each tetrahedral sheet contains silicon atom in its crystalline center surrounded by four oxygen atoms of equidistance from each other, and a layer of octahedral aluminum composed of two hydroxyl sheets closely packed to each other, between the two sheets aluminum atoms arranged as octahedral[10,11]. Bentonite clay is widely used in many fields of technology including adsorption of dyes and surfactants [12], refining edible oils, and treatment of effluents from metal ions and organic pollutants. Moreover, the addition of surfactants to the suspension of bentonite was found to enhance the rheological properties of the latter [13]. The aim objective of this work was to be evaluated the adsorption – desorption behavior of the herbicide paraquat dichloride from aqueous solution. The adsorption equilibrium and the adsorption capacity were determined, thermodynamic parameters, adsorption isotherms and adsorption concentration were evaluated through this study.

MATERIALS AND METHODS

Materials: The bentonite clay used in this study was obtained from the geological scanning institute, have the general structure consisting mainly $Al_2O_2.4SiO_2.H_2O$[14], the chemical analysis of bentonite is listed in table 1.

Table 1. The chemical analysis of bentonite

Constituent	**Wt%**
SiO_2	**56.77**
Al_2O_3	**15.67**
CaO	**4.48**
Fe_2O_3	**5.12**
MgO	**3.42**
Na_2O	**1.11**
SO_3	**0.60**
Loss on ignition	**12.49**
Total	**99.66**

Paraquat dichloride($C_{12}H_{14}C_{l2}N_2$, formula weight = 257.2) obtained from Aldrich, (99.8% purity), bentonite sample has been treated before using in the experiments as follows -

It was suspended in(5% HCl) to remove carbonate of, it was washed by deionized water several times to remove soluble materials. Then it was dried in the oven at 105□ C overnight and was ground then sieved by 45 µm sieve. The particles under 45 µm are used in present work.

Digital balance, Sartoris ,BL 210S(Germany), U.V-Visible Spectrophotometer, Single Beam, Apel PD-303uv (Japan), Digital pH-Meter, knick (Germany), Shaker, Memmert Water Bath, WNB 22, Oven, Blue

M, Aunit of General Signal, Shaker, orbit VRN-480 (Taiwan), U.V- Visible Spectrophotometer, double Beam, Shimadzo uv-1650 PC (Japan) and Centrifuge machine, were used in this study.

Methods : Bentonite was sutured with 1N $MgCl_2.6H_2O$ solution, the excess $MgCl_2.6H_2O$ was removed by washing with deionized water several times until a negative chloride test (with $AgNO_3$) was obtained in the wash solution. Adsorption studies were carried out using (0.5 g) of Mg- bentonite in 100ml PQ solution of (40mg.L^{-1}) concentration in a tightly closed flask and the mixture was stirred on a rotary orbital shaker (150 rpm) for a priod time (5-120 min), until the adsorption of PQ solution on Mg-bentonite reaching equilibrium at certain pH and temperature. The sample was withdrawn from the shaker at the predetermined time intervals and absorbents were separated from the solution by centrifugation at 3000 rpm for 10 min. The absorbance of the supernatant solution was estimated to determine the residue of PQ concentration spectrophotometrically at λmax (256 nm) . The same procedure has been used to study the effect of initial concentration, pH, temperature, and particle size. The pH was adjusted either with 0.1M HCl or 0.1M NaOH . The amount of Paraquat adsorbed was determined by the following equation:

$$qe = \frac{[C]-[Ce].V}{m(g)} \qquad \textbf{(1)}$$

where, [C_0] and [C_e] are the initial and the equilibrium concentration of Paraquat solution in mg L^{-1}, respectively. V: is volume of the Paraquat solution in L, m :is mass of dry adsorbent used in gm.

Adsorption study: Batch adsorption experiments were performed at room temperature(20 °C) on a rotary shaker at 150 rpm using 100 mL PQ and 0.5 g of Mg-Bentonite clay adsorbents, the contact time was ranged from 5 min to 90 min. After agitation, the suspensions were centrifuged at 3000 rpm for 10 min and the supernatant was kept PQ analyses using UV-Visible spectrophotometer. Various conditions, including the contact time, the pH, the initial concentration and particle size of Mg-bentonite, were tested. All experiments were carried out in duplicates and the data obtained were used for analysis. Calculation of PQ adsorbed amount by Mg-Bentonite clay was described in the method [15].

Desorption study: For batch desorption study, the adsorbent utilized for the adsorption of an initial PQ concentration of 20-160 mg L^{-1} was separated from the PQ solution by centrifugation. The PQ-loaded adsorbent was washed gently with water to remove any unadsorbed PQ. Then the spent adsorbent was stirred using a magnetic stirrer with 100 mL of distilled water at different temperature for 30 min. The desorbed PQ was determined as mentioned before.

RESULTS AND DISCUSSION

Effect of contact time: The effect of contact time on the adsorption of paraquat dichloride (100 ppm) was investigation at different time intervals in the range of 5-120 min. After they were centrifuged the supernatant solutions were taken for PQ analysis using UV-Visible[16]. As shown in fig. 1, the equilibrium adsorption was established rapidly within 30 min indicating that the initial adsorption was very fast and maximum uptake was reached within 30 min for PQ thereafter, the amount of adsorption remained almost constant. This was due to the decrease of adsorption sites on the clays which gradually interacted with the PQ, but the adsorption rate depends on PQ which transported from the bulk liquid phase to the actual adsorption sites [17]. For example, in this study, 82.5% was adsorbed on the Mg-Bentonite clay when the equilibrium was reached at 30 min. On the basis of these results, it can be observed that Mg-Bentonite clay can be used to remove these pesticide.

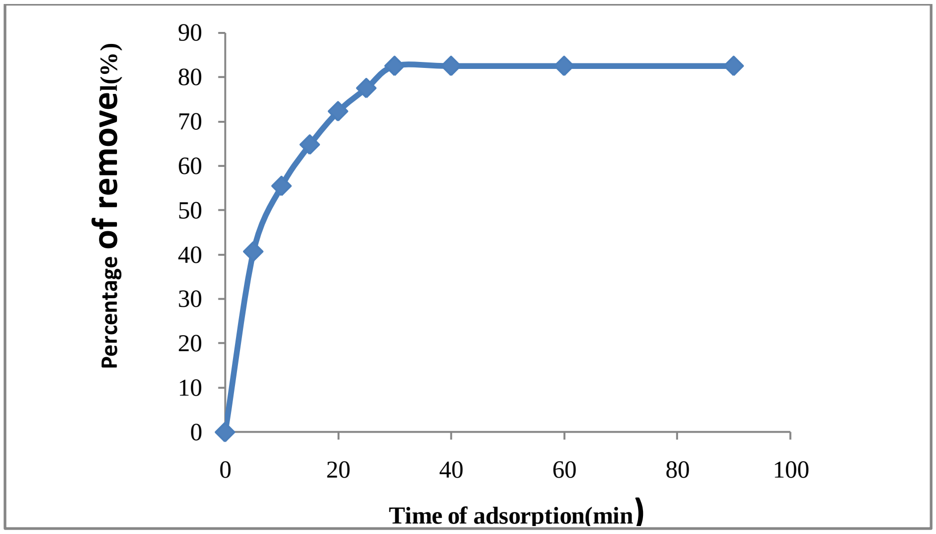

Fig 1: Effect of contact time on removel of PQ by the adsorbent at initial concentration 100 mg L^{-1}, dose of adsorbent 0.5g, 300 mesh, temperature of solution 20 °C and pH=6.

Effect of Initial Concentration: The removal of PQ by adsorption on Mg-Bentonite has been shown in fig.2 to occur rapidly for all initial concentration. The adsorption percent decreases with the increase in the initial PQ concentrations, while the actual amount of PQ adsorbed per unit mass of bentonite increased with the increase in PQ concentration. This gives an indication that the adsorption is highly dependent on the initial concentration of PQ. Because at lower concentration, the ratio of the initial number of PQ molecules to the available surface area is low, the fractional adsorption become in dependent on the initial concentration. However, at high concentration the available sites of adsorption become independent on the initial concentration [18,19].

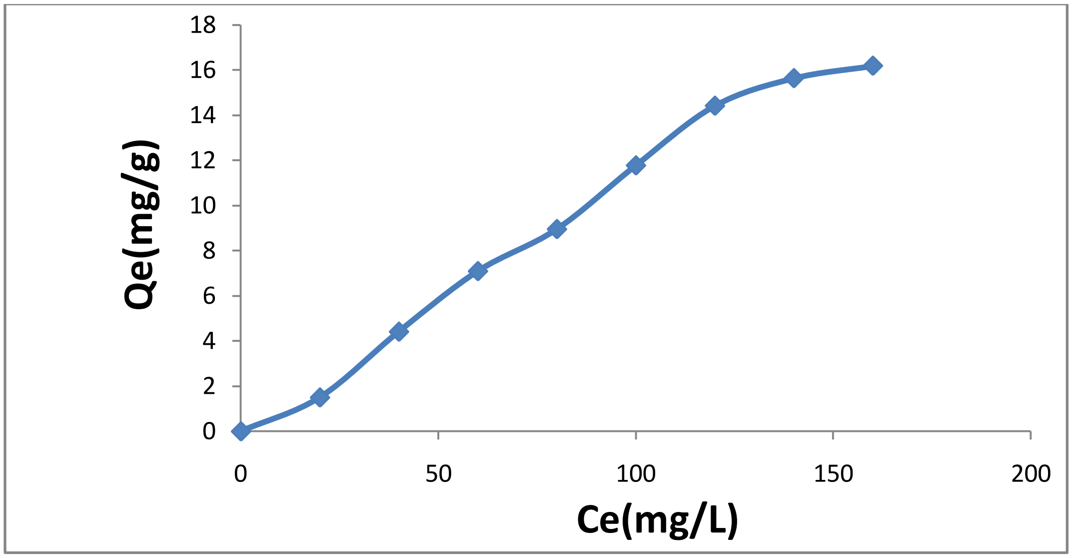

Fig 2: Effect of initial concentration on adsorption capacity of PQ by the adsorbent, dose of adsorbent 0.5g, 300 mesh, temperature of solution 20 °C, pH=6 and contact time 30min.

Effect of pH: pH of the solution is one of the most important variable in adsorption processes. For PQ adsorption on Mg-Bentonite studies were conducted at pH of the solutions 3.0, 6.0, 8.0, 10.0 . Figure 3 shows the typical plot between Qe (mg g^{-1}) versus Ce(mg L^{-1}), the equilibrium sorption increased with the rise in pH . It can be infer that in basic ranges of pH the anions increased on the surface of adsorbents due loss of H^+ ions and promotes the cationic Paraquat molecules to get closure to the adsorbents surface due to electrostatic force of attraction [20].

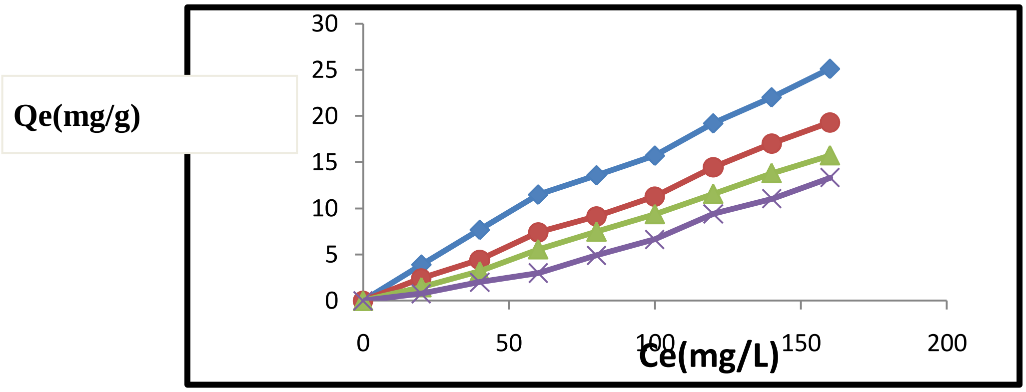

Fig 3: Effect of pH on adsorption capacity of PQ by the adsorbent, dose of adsorbent 0.5g, 300 mesh, temperature of solution 20 °C, and contact time 30min.

Effect of temperature: Temperature effect on the sorption capacity of Mg-Bentonite was observed for Paraquat solutes, temperatures selected for the studies were, 283.15, 293.15, 303.15, and 313.15 K. Figure 4 depicts the adsorption behavior of PQ on Mg-Bentonite. With the rise of temperature the entropy and enthalpy of the system increases which opposes the adsorption of PQ on Mg-Bentonite, because thermodynamic studies established that the reaction is exothermic and decrease in entropy takes place with the adsorption processes. Adsorption capacity of Paraquat was also found to decrease with increasing temperature in the adsorption removal of the adsorbate onto Mg-Bentonite. Based on the results of the effect of temperature on the adsorption capacity, the basic mode of adsorption of Paraquat onto Mg-Bentonite should be physical adsorption, which is an exothermic process.

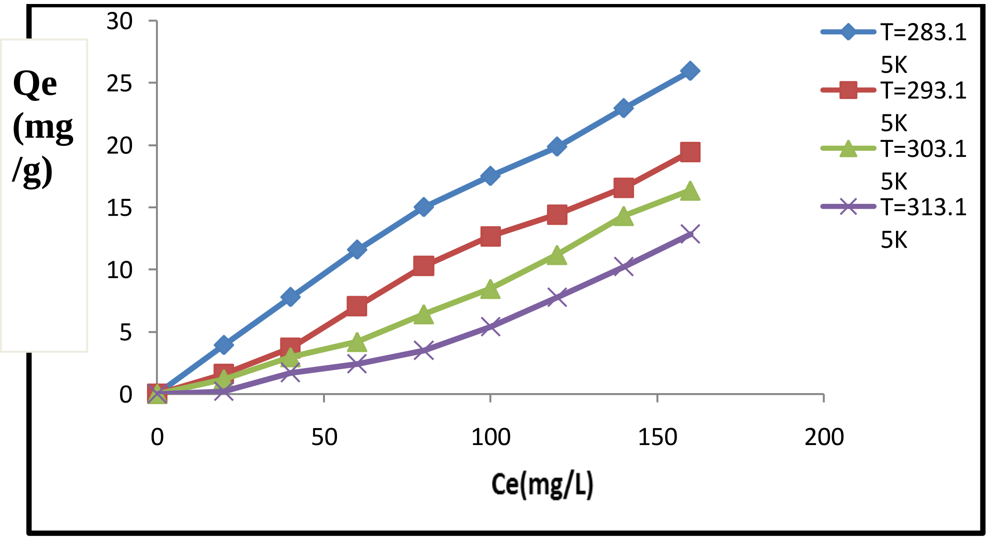

Fig 4: Effect of Temperature on adsorption capacity of PQ by the adsorbent, dose of adsorbent 0.5g, 300 mesh, pH 6 and contact time 30min.

Effect of Adsorbent dosages: The effect of adsorbents dosage on the Paraquat adsorption process is shown in figure 5. Removal of Paraquat increases with an increase in the adsorption dosage. The percentage removal increases by increasing the adsorbent dosage from0.25 to 2 g. The increased percentage adsorption of paraquat dichloride with increasing Mg-Bentonite clay may be due to increase in the surface negative charge and degrease in the electrostatic potential near the solid surface that the favors sorbent-solute interactions. However the adsorption capacity showed a decreasing trend with increasing adsorbent dosage. [21].

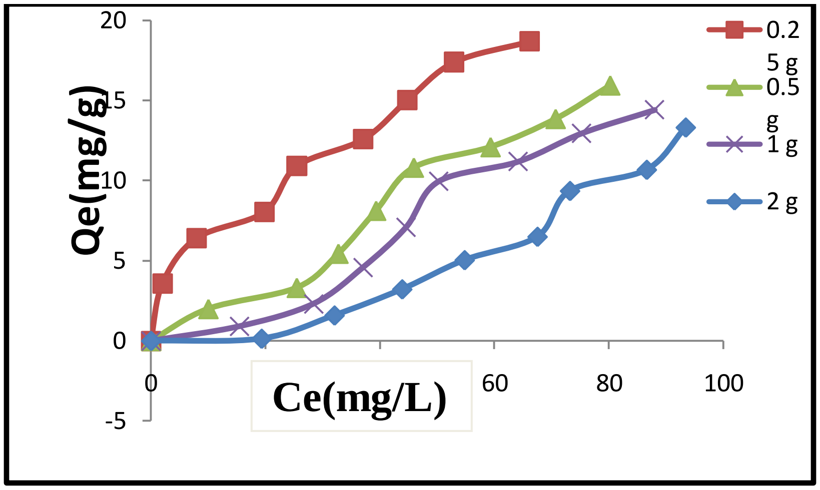

Fig 5: Effect of Adsorbent dosages on adsorption capacity of PQ by the adsorbent, pH 6 and contact time 30min

Adsorption isotherms: The adsorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the adsorbent. Adsorption isotherms can be generated based on theoretical models where Langmuir and Freundlich models are the most commonly used ones [22,23]. The relation ship between the equilibrium concentrations of the PQ and the amounts adsorbed on Mg-Bentonite clay surface was studied at pH 6. The applying the Freundlich adsorption isotherm equation showen in Fig.6, the experimental data is satisfactorily fits and give a straight line relationship between log (Xm/m) and log Ce for PQ in aqueous solution at pH 6, the Freundlich isotherm equation can be expressed as:

$$\mathbf{Log\ Q_e = 1/n\ log\ C_e + log\ K_f} \qquad (1)$$

Where Qe =Xm/m, X = the amount of PQ adsorbed. m = weight of adsorbate.Thus X/m = amount of adsorbed per unit weight. 1/n = constant.Ce = equilibrium constant of PQ. K_f = constant.

The figure 6 illustrated that the value n>1 represent a favorable adsorption condition Kf and 1/n can be determined from the linear plot of log Qe vs log Ce as shown in table 2. The adsorption isotherm fits quite well with the experimental data (correlation coefficient) $0.854 < R^2 < 0.930$.

Table 2: Coefficient isotherm parameters of Freundlich equation by adsorption of PQ on Mg-Bentonite.

Substance	**1/n**	**K_f(mg/g)**	**R^2**
Paraquat dichloride	1.3269	0.077	0.930

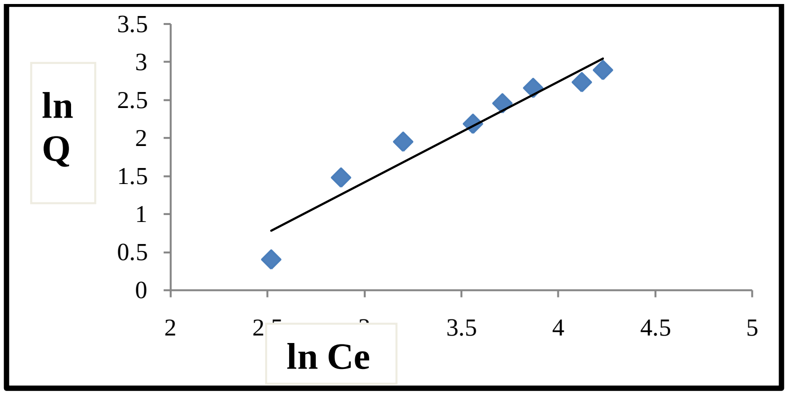

Fig. 6: Freundlich adsorption isotherm of PQ in adsorbent pH 6.

The adsorption isotherm data were applied to the Langmuir isotherm equation, can be expressed as

$$\frac{Ce}{Qe} = \frac{1}{KXm} + \frac{Ce}{Xm} \qquad \textbf{(2)}$$

Where K = constant related to the energy or net enthalpy.
Straight lines were obtained by plotting Ce/Qe against Ce for the adsorption of PQ on Mg-Bentonite clay illustrated in Figure 8. The value of Xm and K calculated from the slope and intercept and the Langmuir plot, the present data does not fit with Langmuir isotherms $R^2 < 0.2690$.

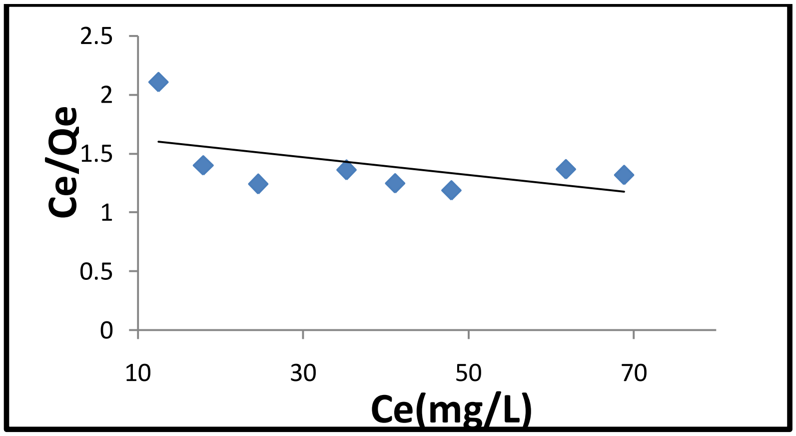

Fig. 7. Linear plots of Langmuir isotherm of PQ on Mg-bentonite at 20C□ temperature.

Desorption: Desorption studies can help elucidating the mechanism of an adsorption process. If the pesticide adsorbed onto the adsorbent can be desorbed by water, it can be concluded that the attachment of the PQ onto the adsorbent is by weak bonds. If the strong acids, such as HCl can desorb the PQ, it can be concluded that the attachment of the PQ onto the adsorbent is by ion exchange or electrostatic attraction [24]. Hence, distilled water of different temperature was used in the elution of PQ from PQ- Bentonite. As a general result of the PQ desorption study, the process is found to be endothermic, since an increase in desorption is observed with increasing temperature (Fig.9).

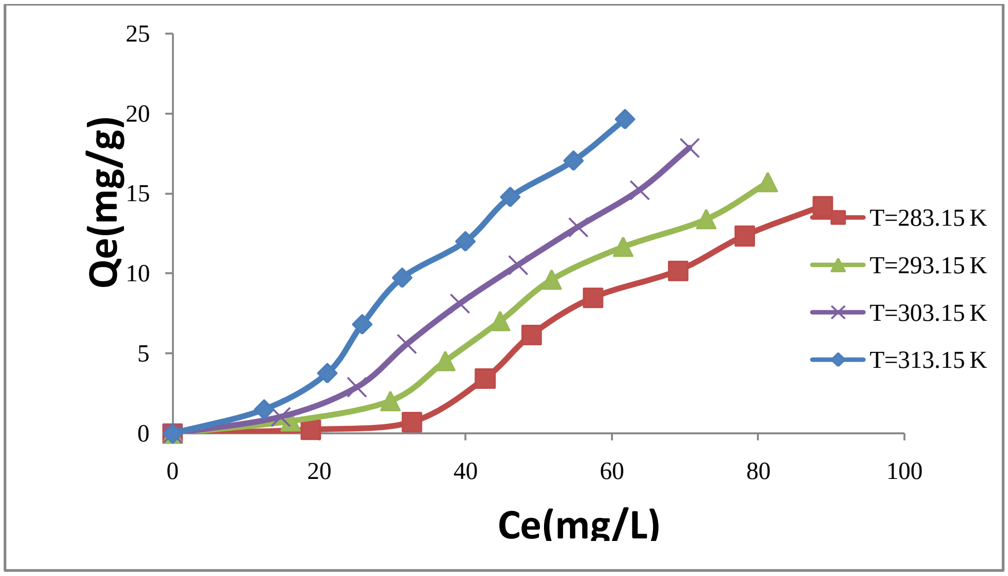

Fig. 9 Desorption of PQ at different temperature, t- 30min, dose of adsorbent 0.5g.

Thermodynamic Study of Adsorption: The thermodynamic parameters which help us to understand the nature of the sorption of Paraquat on adsorbents are change in Gibbs free energy (ΔG^0) change in entropy(ΔS^0) change in enthalpy (ΔH^0) these can be determined by using the following equations [25]

$$\Delta G^0 = -RT\ln K_C \qquad (5)$$

where, R: gas constant, T: temperature in kelvin, K_C: equilibrium constant, Similarly, the enthalpy change ΔH^0 from 283.15 to313.15K was computed from the following equation:

$$\ln K_C = -\frac{\Delta H0}{RT} + \frac{\Delta S0}{R} \qquad (6)$$

Plot of ln K_C vs 1/T (Figure 10) gives the values of ΔH^0 and ΔS^0.

Table 1 lists the values of thermodynamic parameters mentioned above. The negative value of ΔG^0 at various temperatures shows the spontaneous nature of the sorption process. It is clear from Table 3 that the negative values of ΔH^0 shows the sorption to be of exothermic nature and it is evident from the temperature experiment that with the rise in temperature adsorption of Paraquat decrease. Moreover, the negative values of ΔS^0 points out some structural changes as a result of the interaction of Paraquat with the active sites of adsorbents especially hydroxyl groups in cellulose and lignin, decrease in entropy signs of the Paraquat getting some fixed sites on the adsorbents which leads decrease in entropy.

Table3: The thermodynamic parameters for the adsorption of Paraquat on the Mg-Bentonite**.**

T/K	-ΔH^0 (KJ/mole)	-ΔG^0 (KJ/mole)	ΔS^0 (J/mole.K)
283.15	18.54	19.08	1.9
293.15		19.35	2.76
303.15		19.31	2.53
313.15		19.12	1.85

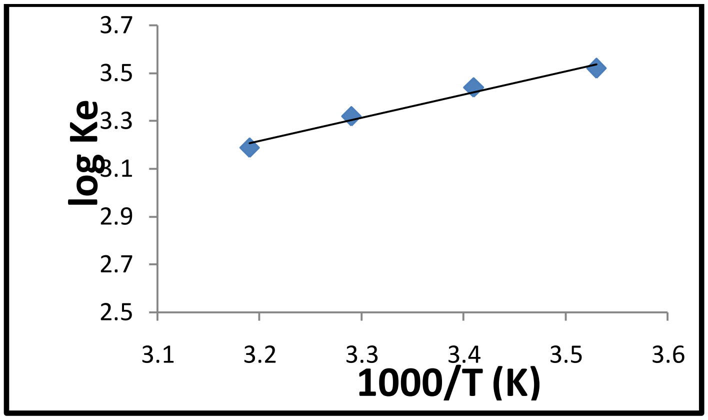

Fig. 10 Plot of logKe versus 1/T for adsorption of PQ on Mg-Bentonite.

APPLICATIONS

From these adsorption studies, the Bentonite may be used as an adsorbent for adsorption or removal of some compounds such as dyes and pesticides from waste water solutions.

CONCLUSIONS

The experiments on Mg-Bentonite for Paraquat removal from aqueous solution has been examined. The following conclusion can be drawn from the study:
-Adsorption of Paraquat has been influenced by the pH of the solution with the attraction between cationic Paraquat and anionic charged developed Mg-Bentonite.
-The effect of initial concentration, temperature, and pH plays a significant importance on adsorption rate of Paraquat.
-Thermodynamic studies confirms the adsorption is of exothermic and spontaneous in nature.

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