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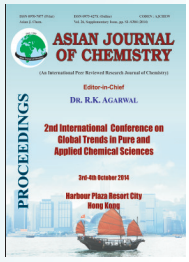

Sorption Efficiencies and Capacities for Removal of Cu^{2+} by Particles of Ignimbrite: Equilibrium and Thermodynamic Studies

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In this manuscript, Cu^{2+} uptake by the particles of ignimbrite from aqueous solutions was investigated using batch sorption techniques. The sorption equilibrium studies were performed as a function of contact time, initial Cu^{2+} concentration, sorbent dosage, pH, temperature and agitation rate. The removal efficiency of Cu^{2+} and maximum Cu^{2+} sorption capacity of the ignimbrite particles were 76 % and 1.64 (mg m^{-2}), respectively. To evaluate the sorption equilibrium, four isotherm models were fitted to experimental data. The best model was determined by taking into account the correlation coefficient (R^2). The best adjustment from isotherm models was observed to be the Langmuir (R^2 0.973). The activation energy (E_a) was determined as 9.9 kJ mol^{-1}. Thermodynamic parameters such as $\Delta H°$, $\Delta S°$ and $\Delta G°$ were calculated from the slope and intercept of linear plot of ln K_D *versus* 1/T. The $\Delta H°$ and $\Delta G°$ values of Cu^{2+} sorption on the particles of ignimbrite show endothermic heat of sorption. The results indicated that the particles of ignimbrite are suitable sorbents in the removal of Cu^{2+} ions from an aqueous solution.

Keywords: Cu^{2+}, Ignimbrite, Sorbent capacities, Isotherms, Activation energy.

INTRODUCTION

Heavy metal uptake from industrial wastewater is an significant environmental problem. The uptake of heavy metals from drinking water is a real challenge due to their trace quantities, formation of complexes with natural organic matter and toxic effect even at very low concentrations[1-3]. Atmospheric depositions, waste emissions and anthropogenic activities also contribute to the heavy metal contamination in aquatic environments. Among these heavy metals, Cu^{2+} is usually considered to be non-toxic for human at lower concentration ranges, although its presence at higher concentrations (> 5 mg L^{-1}) in the body has been linked to several health problems such as kidney damage, high fever, haemolysis, vomiting, *etc.*[4-6]. Consequently, high concentration levels of Cu^{2+} contamination in the industrial wastewaters must be reduced to acceptable levels before discharging them into the environment[7]. In order to minimise the adverse effects of these heavy metals, authorities and environmental agencies enforced stringent standards for the maximum allowable limits of heavy metals discharged into open landscapes and water bodies. These strict regulations and standards have encouraged researchers to investigate new environmentally friendly technologies that can reduce heavy metals concentrations in the discharged wastewater[8].

Conventional methods used to remove metal ions from industrial wastewater include chemical precipitation, electrochemical treatment, ion exchange process, membrane separation and evaporation[9,10]. However, some of these conventional technologies are ineffective and unfavorable since they are expensive, inadequate and cause a sludge disposal problem[11,12].

Biosorption as an alternative process is the uptake of heavy metals from aqueous solutions by biological materials. This approach is competitive, effective and economical[12-17]. Sorption of metals by biomass has been mostly explored in recent years. Different forms of inexpensive, non-living plant material such as rice husk[18], sawdust[19], pine bark and canola meal[20-22] have been widely investigated as the potential biosorbents for the removal of heavy metals. There have been numerous studies on the biosorption of metal ions from aqueous solutions by microbial and plant biomass[23-28].

Ignimbrite is an economical rock and is included in the light concrete category. The chemical components of ignimbrite consist of SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO, K_2O and other components[29]. An important advantage of ignimbrite is its occurrence in active fault zones all over the world. These rocks are widely used as building stone in low storeyed buildings and especially in important building in the past. Nowadays, they have an increasing usage in outer surface covering of the buildings, stairs, floorings, banisters, pools and their surroun-

dings, arches, columns, fireplaces, balcony decorations and restoration applications because of their decorative properties[30]. One of the main advantages of Cu^{2+} removal using ignimbrite over the other chemical treatment methods is that no chemical sludge is produced after sorption.

In this study, ignimbrite materials have been used to remove Cu^{2+} ions from aqueous synthetic solutions as a function of pH, temperature, agitation rate, sorbent and sorbate concentration. The values of well-known thermodynamic functions and isotherm studies have been performed to elucidate the equilibrium sorption behaviour of Cu^{2+} ions at different temperatures. In addition, the kinetic parameters as a function of agitation rate, pH, temperature and sorbent dosage have been investigated.

EXPERIMENTAL

Sorbent and sorbate preparation: The ignimbrite particles were cut into small pieces, grounded in a blender and sieved to obtain particle sizes of ($0.5 < x < 2$) mm. Ignimbrite samples were washed with distilled water and then dried at 298 K for two weeks. Samples of 3 g were taken for sorption studies.

The Cu^{2+} solutions were prepared by diluting 600 mg/L of $CuSO_4 \cdot 6H_2O$ (Merck) stock solution with deionized water to a desired concentration range between 50 and 100 mg L^{-1}. The initial concentration of Cu^{2+} and the samples following the sorption process were complexometrically determined.

The surface area of the shells of *Helianthus Annuus* was measured by BET method at 77 K using a Quantachrome QS-17 model apparatus[31]. The surface area of the particles of ignimbrite was defined as 2.9 m^2/g.

The zeta potentials of the particles of ignimbrite before and after biosorption were measured with a zeta-meter (zeta-meter 3:0+/542, USA).

Analysis of Cu^{2+}: A sample that has a concentration of less than 20 mg Cu/100 mL is mixed with diluted ammonia solution until formed hydroxide redissolves. Excess ammonia is avoided to keep pH under 8. After addition of 1-2 droplet indicator solution (murexide) the sample is titrated with 0.01 M ethylene diamine tetraacetic acid (EDTA) solution until its colour turns from orange yellow into dark violet. 1 mL, 0.01 M EDTA solution is equivalent[32] to 0.6354 mg Cu^{+2}.

Sorption studies: Sorption of Cu^{2+} on the ignimbrite particles was investigated in a batch reactor. The effect of pH (from 1.8 to 5), contact time (30 min), initial Cu^{2+} concentration (75 ppm), sorbent dosage (from 2 to 5 g), particle size ($0.5 < x < 2$ mm), agitation rate (from 3 to 8 rps) and temperature (from 293 to 313 K) on the sorption process were studied. The experiments were conducted by a batch reactor with a water-cooling jacket keeping the reactor at a constant temperature at 293 K. The solutions of 250 mL were used for each sorption process.

The solution initial pH of the particles of ignimbrite is 5. All of the sorption studies were realized at initial pH 5. pH adjustments have been done by using solutions of 0.1N HCl and NaOH. The pH values of solution were measured using an ORION (N1218001) model pH-meter.

All experiments were carried out in a 500 mL cylindrical batch reactor. The reactor had a glass water-cooling jacket to keep the reactor contents at constant temperature. The temperature adjustment was performed using a water circulator (Polyscience, 9006 Model) with the precision of ± 0.5 °C.

RESULTS AND DISCUSSION

Effect of the sorbent dosage on the sorption: The ignimbrite dosage is an important parameter because it determines the sorption efficiencies and capacities of the sorbent for a given initial Cu^{2+} concentration. Fig. 1 shows the influence of sorbent dosage for the Cu^{2+} sorption and it was examined by varying sorbent dosage from 8 to 20 g L^{-1} while keeping the volume of the Cu^{2+} solutions constant and at pH of 5.

The efficiencies of Cu^{2+} removal steeply increases with the sorbent loading up to 20 g L^{-1}. This result can be explained by the fact that the sorption sites remain unsaturated during the sorption whereas the number of sites available for sorption increases by increasing the sorbent dose. The efficiencies of Cu^{2+} removal and sorbent capacities were found as 47, 63, 71 and 81 %, 1.5, 1.35, 1.14 and 1.05 mg m^{-2} at sorbent dosage of 8, 12, 16 and 20 g L^{-1}. It is apparent that Cu^{2+} uptake increased with the increase of sorbent dosage for a given initial Cu^{2+} concentration. The sorbent capacities per surface area of sorbent decreased with the increase of sorbent dosages. These results were anticipated because an increase in the sorbent dosage provides greater surface area for sorbate. As shown in Fig. 1, it is evident that, a minimum sorbent dosage for an efficiency of 81 % was 20 g L^{-1}.

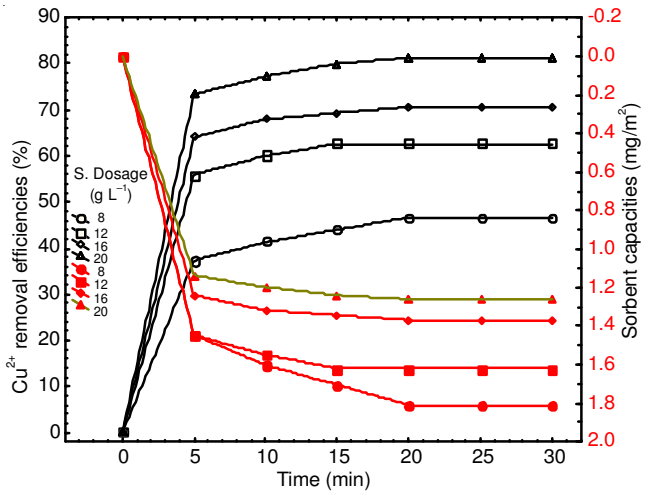

Fig. 1. Efficiencies of removal of Cu^{2+} and capacities of the sorbents as a function of sorbent dosage (pH 5, agitation rate 6 rps, temperature 293 K, Cu^{2+} concentration 75 mg L^{-1})

Effect of the sorbate concentration on the sorption: The effect of sorbate concentration on the removal of Cu^{2+} from aqueous solutions is presented in Fig. 2. Sorbate concentrations were varied from 50 to 100 mg L^{-1}. The Cu^{2+} removal efficiency decreased with the increasing sorbate concentration.

As result of a sorption of 30 min, the efficiency of Cu^{2+} removal for Cu^{2+} concentration of 100 mg L^{-1} was 81 %. However, the sorbent capacity at the equilibrium increased with the increasing sorbate concentration. As examined in Fig. 2, the sorbent capacities for different sorbate concentrations (50, 75 and 100 mg L^{-1}) were defined as 1.2, 1.35 and 1.58 (mg m^{-2}), respectively.

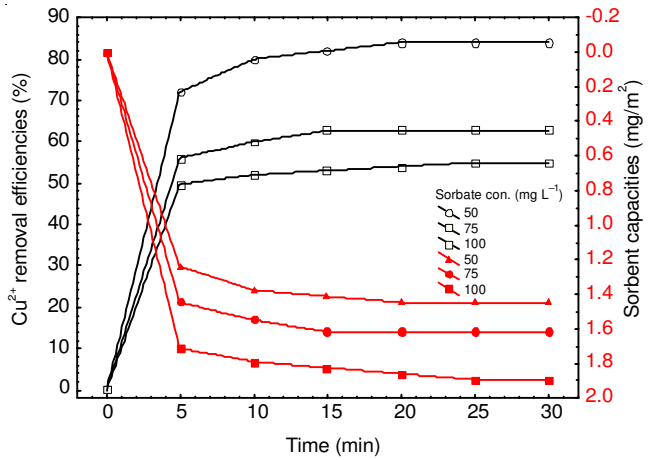

Fig. 2. Efficiencies of removal of Cu^{2+} and capacities of the sorbents as a function of sorbate concentration (pH 5, agitation rate 6 rps, temperature 293 K, sorbent dosage 12 g L^{-1})

Effect of the agitation rate on the sorption: The sorption studies in which were used an IKA (EUROSTAR DIJITAL) model mechanic mixer were carried out with a batch reactor at pH 5. The initial concentration of Cu^{2+} was 75 mg L^{-1}. The effect of agitation rate on the removal of Cu2+ was studied for various contact times. The results are given in Fig. 3.

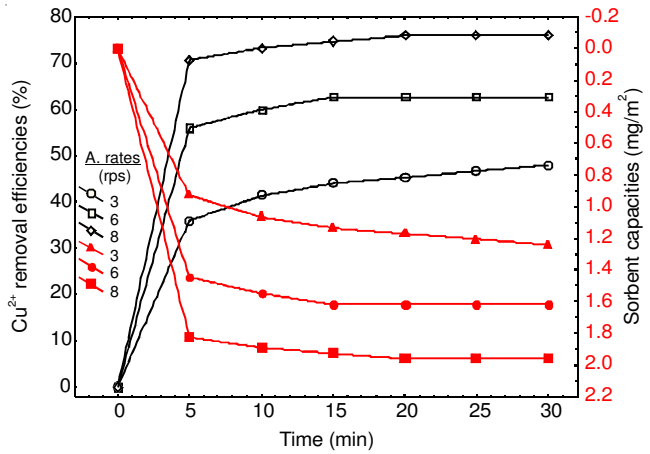

Fig. 3. Efficiencies of removal of Cu^{2+} and capacities of the sorbents as a function of agitation rate (pH 5, Cu^{2+} concentration 75 mg L^{-1}, temperature 293 K, sorbent dosage 12 g L^{-1})

This Figure shows that the Cu^{2+} removal efficiency has increased with increasing agitation rate and been 76 % at the 8 rps. It was thought that the diffusion of Cu^{2+} from the solution to the surface of sorbent and into the pores occurs easily and quickly. As result of sorption of 30 min, the Cu^{2+} sorption capacities at the agitation rate of 3, 6 and 8 rps were obtained as 0.95, 1.35 and 1.64 (mg m^{-2}), respectively.

Effect of the pH on the sorption: The removal of Cu^{2+} ions by the ignimbrite materials increased with the increase of pH from 1.8 to 5. The largest increase in the Cu^{2+} removal was observed at pH 5. The effect of pH on the sorption of Cu^{2+} is presented in Fig. 4. The pH of the aqueous solution is an important controlling parameter in the sorption process[28]. The Cu^{2+} ions are completely released under extreme acidic conditions[33].

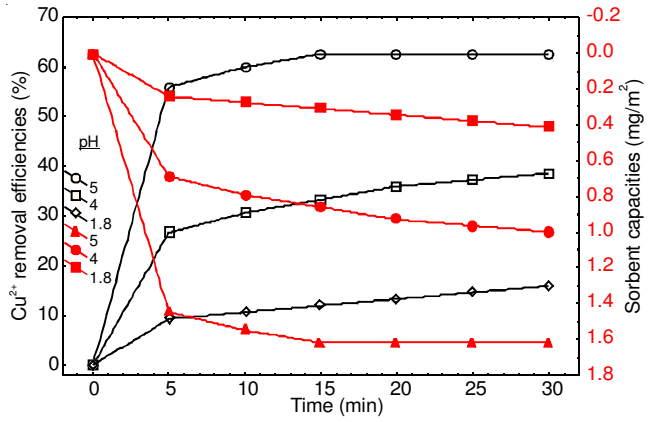

Fig. 4. Efficiencies of removal of Cu^{2+} and capacities of the sorbents as a function of pH (agitation rate 6 rps, Cu^{2+} concentration 75 mg L^{-1}, temperature 293 K, sorbent dosage 12 g L^{-1})

Fig. 4 showed that maximum the Cu^{2+} removal efficiency was at pH 5, which is the initial value of solution of ignimbrite. As result of a sorption of 30 min, the Cu^{2+} removal efficiency at pH 5 was 63 %. The Cu^{2+} sorption capacities at different values of pH (1.8, 4 and 5) were obtained as 0.3, 0.6 and 1.35 (mg m^{-2}), respectively.

At pH between 1.8 and 5.6, there are three species present in the solution as suggested by Ajmal *et al.*[28]. The dominant species between pH 2 and 5 were Cu^{2+}, $Cu(OH)^{+}$and $Cu(OH)_2$. These species are sorbated an electrostatically and chemical interaction on the surface of the particles. At low pH, the surface charge becomes positive due to high concentration of H_3O^{+} ions. Their presence inhibits sorption, as Cu^{2+} compete with protons to form a bond with active sites of functional groups on sorbent surface. As the pH decreases, the surface of ignimbrite particles exhibits an increasing positive characteristic.

As can be seen from Fig. 5, zeta potential values of the ignimbrite particles at pH (1.8-5) in the distilled water were smaller than these of Cu^{2+} solution. The dominant species in the Cu^{2+} solution were electrostatically affected by sorbent particles and then sorbated on the surface of sorbent. Sorption of Cu^{2+} on the sorbent caused an increase of the zeta potential values. The increase in the zeta potential values of the sorbent was a sign of sorption of Cu^{2+} from aqueous solutions.

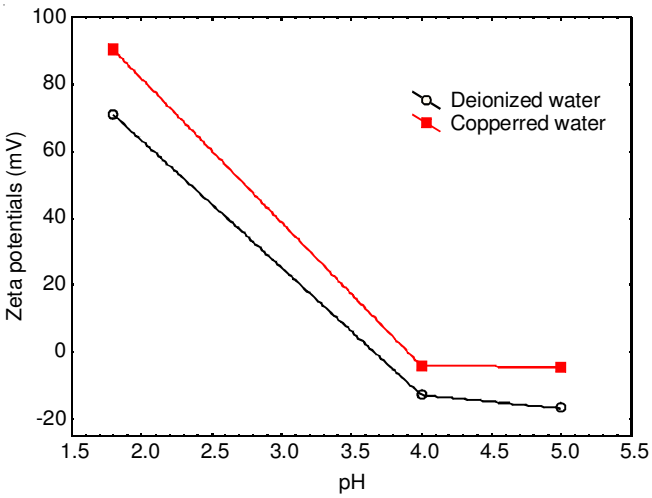

Fig. 5. Relation between zeta potentials and pH

Effect of the temperature on the sorption: The effect of temperature on the removal of Cu^{2+} was investigated as a function of contact time. The results are shown in Fig. 6. It has been thought that 15 min of contact time is enough to remove a considerable amount of Cu^{2+} present in aqueous solution at all temperatures. Fig. 6 shows also that the removal of Cu^{2+} depends on temperature ranges (293, 303 and 313 K). The kinetic energy of Cu^{2+} increased with the increase of temperature of the solution. As the collision frequency between sorbent particles and Cu^{2+} increased, the Cu^{2+} was electrostatically and chemical sorbated on the surface of the sorbent particles. Fig. 6 also shows that the Cu^{2+} sorption capacities per m^2 sorbent.

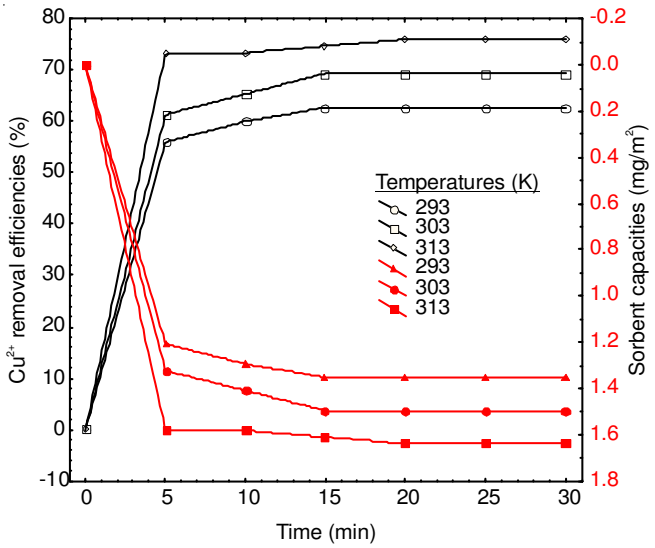

Fig. 6. Efficiencies of removal of Cu^{2+} and capacities of the sorbents as a function of temperature (agitation rate 6 rps, pH 5, Cu^{2+} concentration 75 mg L^{-1}, sorbent dosage 12 g L^{-1})

From Fig. 6, the Cu^{2+} sorption capacities at the different temperatures indicate that the removal of Cu^{2+} increases with increasing temperature. The Cu^{2+} sorption capacities at different temperatures (293, 303 and 313 K) were 1.35,1. 49. and 1.64 (mg m^{-2}), respectively.

Kinetics of Cu^{2+} sorption, equilibrium isotherms and thermodynamic parameters of Cu^{2+} ions onto the ignimbrite particles

Kinetics of Cu^{2+} sorption: In order to examine the mechanism of the sorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the rate data. The linear pseudo-second order equation is given[34,35] by eqn. 1:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \quad (1)$$

where k_2 is the equilibrium rate constant of pseudo-second order sorption (g mg^{-1} min^{-1}). Fig. 7 shows typical plots t/q_t *vs*. t of pseudo-second order equation for the Cu^{2+} sorption by the particles of ignimbrite.

The straight lines in the plot of the linear pseudo-second order equation show good agreement of experimental data with the pseudo-second order kinetic model for different initial pHs, agitation rates and temperatures. The correlation coefficients

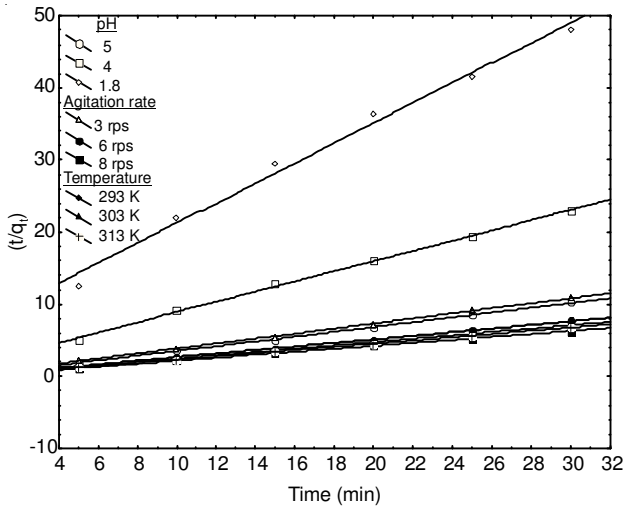

Fig. 7. Plot of the pseudo-second order equation for the sorption of Cu^{2+} on the particles of ignimbrite at the different experimental conditions

for the pseudo-second order equation were approximately 0.99 for all concentrations. This strongly suggests that the sorption of Cu^{2+} on the particles of ignimbrite is most appropriately represented by a pseudo-second order rate process. The values of k_{ads} and q_e calculated from the slopes and the intercepts of the straight lines according to pseudo-second order equation were shown in Figs. 8-10.

From Figs. 8-10, the values of k_{ads} and q_e at the different empirical conditions increased with increased agitation speed, pH and temperature. As seen in Fig. 10, the highest value of k_{ads} was obtained at 313 K.

Equilibrium isotherms: The procedure for the determination of the sorption isotherms of Cu^{2+} on the particles of ignimbrite was described in the first part of this study. The solution pH for the Cu^{2+} was 5. For the study of the effect of pH on equilibrium data, sorption isotherm experiments were carried out with accurately weighted amount of the particles of ignimbrite (8-20 g L^{-1}) that were continuously stirred at 6 rps. The temperature was controlled at 293 K. Agitation was provided for 30 min.

In order to optimize the design of a sorption system for the removal of metals from effluents, it is important to establish

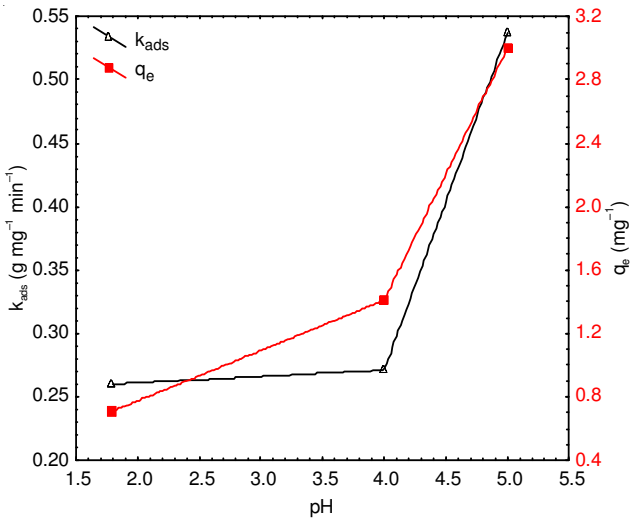

Fig. 8. Values of k_{ads} and q_e values at the different pHs

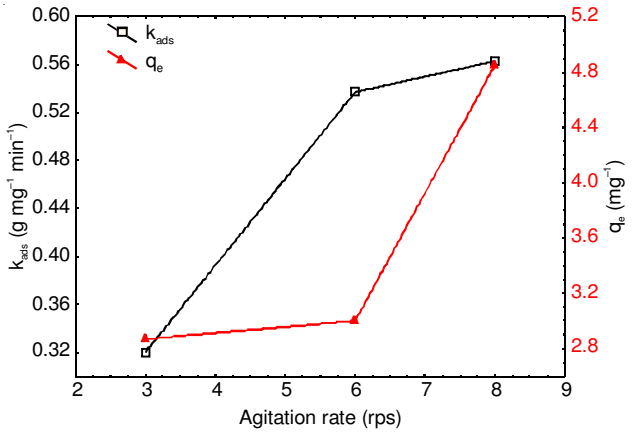

Fig. 9. Values of k_{ads} and q_e values at the different agitation rates

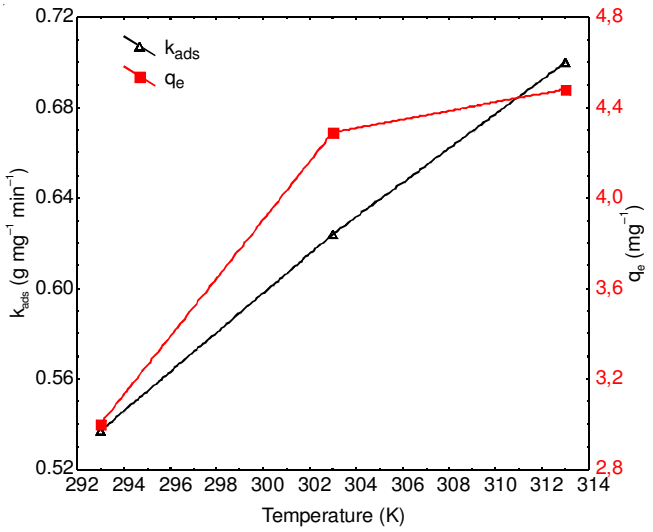

Fig. 10. Values of k_{ads} and q_e values at the different temperatures

the most appropriate correlation for equilibrium curves. Experimental isotherm data was fitted to Freundlich, Langmuir, BET and Dubinin-Radushkevich (D-R) models from two parameter isotherms.

According to Freundlich isotherm is an empirical model that is based on sorption on heterogeneous surface and the linear form of Freundlich isotherm is given by eqn. 2:

$$\ln q_e = \ln K + \frac{1}{n} \ln C_e \quad (2)$$

where K and n are the Freundlich constants which represent sorption capacity and sorption intensity, respectively. A plot of ln q_e *versus* ln C_e would result in a straight line with a slope of (1/n) and intercept of ln K.

Conversely, with the Langmuir model, sorption occurs uniformly on the active sites of the sorbent and once a sorbate occupies a site, no further sorption can take place at this site. The linearized Langmuir model was given by eqn. 3:

$$\frac{t}{q_e} = \frac{t}{Q} + \frac{1}{bQ}\frac{1}{C_e} \quad (3)$$

where Q and b, the Langmuir constants, are the saturated monolayer sorption capacity (mg g^{-1}) and the sorption equilibrium constant (L mg^{-1}), respectively.

A plot of $1/q_e$ *versus* $1/C_e$ would result in a straight line with a slope of (1/bQ) and intercept of 1/Q.

The BET isotherm model is:

$$\frac{C}{(C_s - C)(q_e)} = \left(\frac{1}{BQ}\right) + \left(\frac{B-1}{BQ}\right)\left(\frac{C}{C_s}\right) \quad (4)$$

where q_e is the sorbated amount per unit weight of sorbent (mg g^{-1}), C is the concentration of solute remaining in solution at equilibrium (mg L^{-1}), C_s is the saturation concentration of the solute (mg L^{-1}), Q is the amount of solute sorbated per unit weight of sorbent in forming a complete monolayer on the surface (mg g^{-1}) and B is the constant expressive of the energy of interaction with the surface. A plot of (C/C_s) *versus* $C/[(C_s\text{-}C)(q_e)]$ would result in a straight line with a slope of [(B-1)/(BQ)] and intercept of (1/BQ).

The linearized D-R equation was given by eqn. 5:

$$\ln q_e = \ln q_m - K\varepsilon^2 \quad (5)$$

where C_e is the equilibrium solution concentration, q_e is the amount of Cu^{2+} sorbated at the equilibrium, K is a constant related to the sorption energy, q_m is the theoretical saturation capacity, ε is the Polanyi potential, equal to RT ln (1+1/C_e). The values of q_m and K were deduced by plotting ln q_e *versus* ε^2.

Langmuir isotherm was found suitable because of the high regression coefficient (R^2 0.99). Isotherm studies indicated that Cu^{2+} sorption could not involve different mechanisms. Table-1 presents the constants of regression equations and the constants of sorption isotherm models for Cu^{2+} sorption.

TABLE-1
ISOTHERM CONSTANTS AND VALUES OF R^2 FOR THE IGNIMBRITE

Parameter	Value	R^2
Freundlich isotherm		0.672
K	34.46	
n	143	
Langmuir isotherm		0.997
Q	4.74	
b	0.2	
BET isotherm		0.918
Q	0.0426	
B	-126.24	
D–R isotherm		0.934
K (kJ^2 mol^{-2})	-0.001	
q_m (mol g^{-1})	0.0001	
E (kJ mol^{-1})	70.71	

Thermodynamic parameters of Cu^{2+} on the particles of ignimbrite: The changes in Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) for the sorption process were obtained using the following equations[36]:

$$\Delta G° = -RT \ln K_d \quad (6)$$

$$\ln K_d = \left(\frac{\Delta S°}{R}\right) - \left(\frac{\Delta H°}{R}\right)\left(\frac{1}{T}\right) \quad (7)$$

The values of log K_d were defined as fallow by eqn. 8:

$$K_d = \frac{F_e}{1 - F_e} \quad (8)$$

where F_e is the fraction sorbated at equilibrium, R is the ideal gas constant (kJ mol^{-1} K^{-1}) and T is the temperature (K). The

enthalpy change (ΔH°) and the entropy change (ΔS°) are calculated from a plot of ln K_d *versus* 1/T.

The activation energy (E_a) of the Cu^{2+} sorption on the particles of ignimbrite was calculated using Arhenius equation. It was found to be 8.56 kJ/mol. The results of these thermodynamic calculations were shown in Table-2.

TABLE-2
THERMODINAMIC PARAMETERS AND VALUES

C_o (mmol L^{-1})	ΔH^o (kJ mol^{-1})	ΔS^o (kJ $mol^{-1}K^{-1}$)	ΔG^o (kJ mol^{-1})		
			293 K	303 K	313 K
4.72	14.4	0.054	-1.3	-1.9	-2.3

The negative value for the Gibbs free energy for Cu^{2+} ions shows that the sorption process is spontaneous and the degree of spontaneity of the reaction increases with the increase of temperature. The sorption process seems to be endothermic (ΔH° 14.4 kJ/mol). This result also supports the observation that the sorption capacity of the particles of ignimbrite for Cu^{2+} increases with the increase in temperature. Table-2 also shows that the (ΔS°) values were positive (entropy increases as a result of sorption). This occurs as a result of redistribution of energy between the sorbate and the sorbent. Before sorption occurs, the Cu^{2+} near the surface of the sorbent will be more ordered than in the subsequent sorbent state. As a result, the distribution of rotational and translational energy among a small number of molecules will increase with the increasing sorption by producing a positive value of ΔS° and the randomness will increase at the solid-solution interface during the process of sorption. Sorption is therefore likely to occur spontaneously at normal and high temperatures because $\Delta H° > 0$ and $\Delta S° > 0$.

Conclusion

The results of this study indicate that ignimbrite sorbent is an effective sorbent for removal of Cu^{2+} from aqueous solutions. The removal efficiency of Cu^{2+} and maximum Cu^{2+} sorption capacity of the ignimbrite particles were 76 % and 1.64 (mg m^{-2}), respectively. It was found that the amount of Cu^{2+} sorbated on the particles of ignimbrite comparatively depends on pH, temperature and agitation rate of the solution. As the result of this study, it was thought that the removal of Cu^{2+} from solid/liquid interface by ignimbrite predominantly took place by precipitation mechanism, ion exchange and weak physical interactions between the surface of sorbent and the Cu^{2+}.

The isotherms, thermodynamic and kinetic investigations of Cu^{2+} sorption on the particles of ignimbrite were studied using the isotherm models of two parameters. The kinetic studies showed that pseudo-second-order equations were able to provide a realistic description of the sorption kinetics of Cu^{2+} ions. Langmuir isotherm was found suitable because of the high regression coefficient (R^2 0.99). Isotherm studies indicated that Cu^{2+} sorption could not involve different mechanisms.

The activation energy of the Cu^{2+} sorption was calculated using Arrhenius equation. The dependence of Cu^{2+} sorption on temperature was investigated and the thermodynamic parameters ΔH°, ΔS° and ΔG° were calculated. The result shows an endothermic heat of sorption, but a negative free energy value, indicating that the process of Cu^{2+} sorption is favoured at high temperatures.

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