Adsorption Studies of Copper on α-Alumina

SUMRA NAEEM, UZMA ZAFAR*, NASEEM ZAHRA AND GHULAM RASOOL
Materials Science Research Center, PCSIR Labs. Complex, Lahore-54600, Pakistan.

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Summary: In this investigation, adsorption of Cu^{2+} on α-Alumina has been studied by means of batch-technique. Percentage adsorption was determined for α-Alumina-Copper solution system as a function of contact time, pH, adsorbate concentration and temperature. Adsorption data has been interpreted in terms of Freundlich and Langmuir equations. Thermodynamics parameters for the adsorption system have been determined at three different temperatures. The value of ΔH^o=15.822KJ/mole and ΔG^o=-1.0775KJ/mole at 288K suggest that the adsorption of copper on α-Alumina is endothermic and spontaneous process. The desorption studies especially with 1 % NaOH, 1% $CaCl_2$and 1%HCl at given copper loadings on α-Alumina show that no significant percentage of the element is reversibly desorbed.

Introduction

Heavy metals produced and released by industrial activity represent a serious environmental problem. Interest in the fate of heavy metals has increased because of their potential toxicity to biota and humans. Soil, groundwater, plants and animals can be considered as potential source of contamination. Copper is an essential trace element and it can be toxic above moderate levels. The main sources of copper to surface water are the industrial and domestic wastes, mining and mineral leaching [1]. Adsorption and coprecipitation of copper by the hydroxides of iron and aluminum have been studied [2]. Adsorption behavior of Cu^{2+} on solid waste materials *i.e.* sea nodule residue (SNR), fly ash (FA) and red mud (RM) and chitosan has been investigated. The effect of various parameters, such as pH, contact time, temperature, adsorbate and adsorbent concentration and particle size of adsorbent were studied [3, 4]. Investigation has been made for the removal of Pb, Cd, Cu and Zn from aqueous using the adsorption process on bentonite [5]. The atomic absorption spectroscopy as an analytical method was used for assaying trace metals in environmental samples. Different kinds of clays for removal of metal ions from aqueous solution have been studied. Three major kinds of clays, including smectites (such as montmorillonite), Kaolinite and micas have shown good metal removal efficiency. Montmorillonite has the highest cation exchange capacity and is considered to be 20 times cheaper than that of activated carbon [6]. Likewise adsorptive removal of poisonous metals Pb(II), Cu(II), Mn(II), Hg(II) and CN− from water by using adsorbents such as active carbon, impregnated carbon and bentonite loaded fabric strip has been studied [7] . The present work describes the removal of copper in wastewater by adsorption process using alumina. The main object was to develop the low cost technique for water purification.

Results and Discussion

The adsorption of Cu^{2+} on the α-alumina powder was studied as a function of shaking time, pH, adsorbate concentration and temperature for known Cu^{+2} concentration at 32 ± 0.5 °C. The results are interpreted in terms of percentage adsorption, Adsorption of Cu^{2+} on the α-Alumina is rapid at room temperature because of the largest amount of copper attached to the adsorbent within 30 minutes and become constant subsequently .Similarly adsorption of Cu^{2+} as a function of its concentration was studied at 32 ± 0.5 °C by varying the metal concentration from 10ppm to 80 pmm, percentage adsorption values decreases with increasing metal concentration (Fig. 1) which suggest that at lower concentrations almost all the ions were adsorbed very quickly and further increase in initial metal ion concentrations led to saturation of adsorbent surface. The adsorption is pH dependent, a much greater adsorptive capacity for Cu^{2+} was observed in neutral solution *i.e.*, pH 7- 8 (Fig. 2). Because when the pH is reduced, surface charge of the particles becomes positive and competition of the hydrogen ions for the

*To whom all correspondence should be addressed.

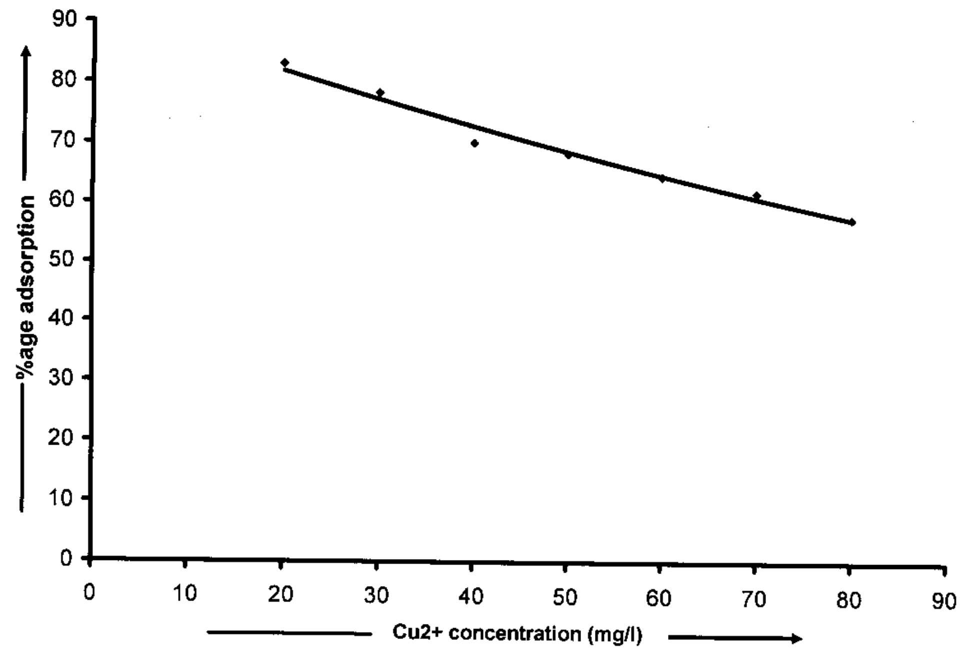

Fig. 1: Dependence of Adsorbate concentration relative to Cu^{2+} Adsorption on α-Alumina at $32 \pm 0.5\,^{\circ}C$ at pH 7.20.

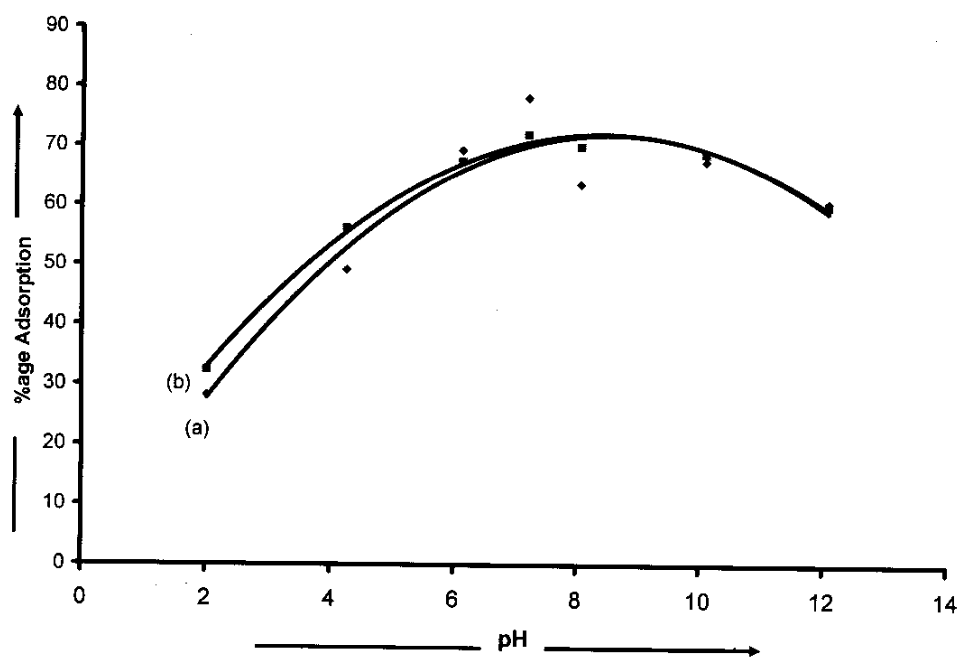

Fig. 2: Effect of pH on adsorption of Cu^{2+} (a) 30ppm and (b) 40 pmm on α-Al_2O_3 at $32 \pm 0.5\,^{\circ}C$.

binding sites, metal ions tend to desorb at low pH region as well a small decrease in copper adsorption was observed at pH higher than 9.0. This behavior may be due to the formation of soluble copper-hydroxide complexes, which remain in solution as dissolved component. Desorption studies at given Cu^{2+} loadings on α-Alumina showed that no significant percentage desorption of Cu^{2+} is observed. 1 % NaOH, 1 % $CaCl_2$ and 1 % HCl solution was used for the elution of copper.

The adsorption isotherms at three different temperatures (15± 0.5 °C, 32 ± 0.5 °C and 50 ± 0.5 °C) were obtained by plotting the amount of copper adsorbed on α-Alumina (g/g) against metal at equilibrium concentration (Fig. 3). Adsorption of Cu^{2+} increases with increasing temperature. Two models, Langmuir and Freundlich equations, were used to describe experimental data for adsorption isotherms. The linear form of the Freundlich isotherm model is given by the following relation:

$$\log X/m = \log K_F + 1/n \log Ce \quad (1)$$

where X/m is the amount adsorbed at equilibrium (mg/g), Ce is the equilibrium concentration of the adsorbate (mg/l) and K_F and 1/n are the Freundlich constants related to adsorption capacity and adsorption intensity respectively, of the sorbent. The values of K_F and 1/n can be obtained from the intercept and slope respectively, of the linear plot of experimental data of logX/m *versus* logCe.

The linear form of the Langmuir isotherm model can be represented by the following relation:

$$Ce/X/m = 1/K_L Vm + Ce/Vm \quad (2)$$

where Vm and K_L are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and slope of the linear plot of experimental data of Ce/X/m versus Ce.The linearized Freundlich and Langmuir adsorption isotherms are shown in Figs. 4 and 5. The related parameters of Langmuir and Freundlich models are summarized in Table-2. The results reveal that both the Langmuir and Freundlich isotherm models can adequately describe the adsorption data

Calculations of Thermodynamic Parameters

Thermodynamic parameters such as Gibbs free energy ΔG° (KJ/mol), change in enthalpy ΔH° (KJ/mol) and change in entropy ΔS° (KJmol⁻K⁻) for

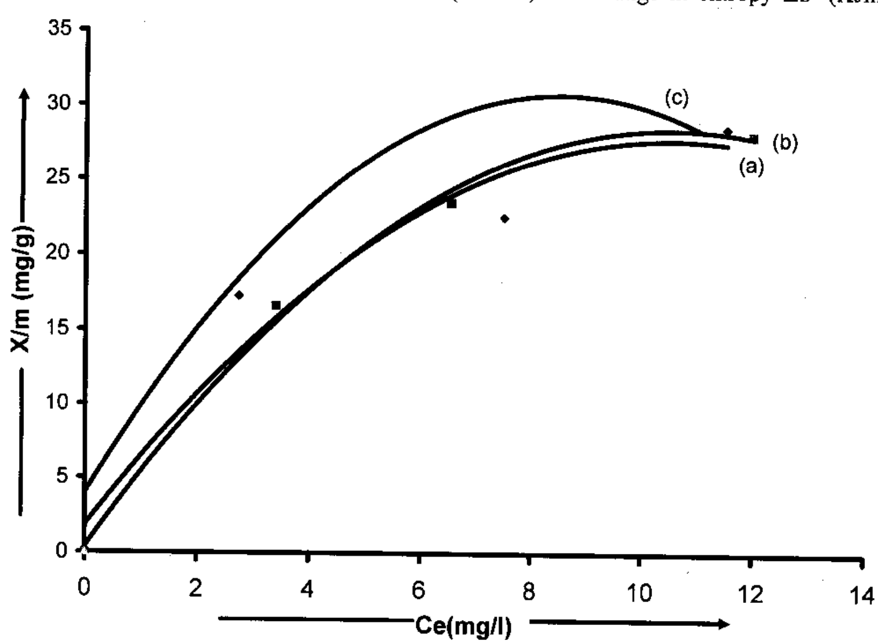

Fig. 3: Adsorption isotherms of Cu^{2+} on α-Alumin at different temperature (a) 288K, (b) 305K, (c) 323K.

Table-1: Dependence of Adsorbate concentration relative to Cu^{2+} Adsorption on α-Alumina at 32 ± 0.5 °C at pH 7.20.

Amount of Adsorbent Taken (mg)	Amount of Cu^{2+} Taken (ppm)	Amount of Cu^{2+} in Soln. at Equilibrium (ppm)	Amount of Cu^{2+} Adsorbed (ppm)	Adsorption (%)
1000.00	10.00	0.001	9.999	99.99
1000.00	20.00	3.400	16.60	83.00
1000.00	30.00	6.540	23.46	78.20
1000.00	40.00	12.00	28.00	70.00
1000.00	50.00	15.89	34.11	68.22
1000.00	60.00	38.65	21.35	64.42
1000.00	70.00	43.20	26.80	61.72
1000.00	80.00	46.00	34.00	57.50

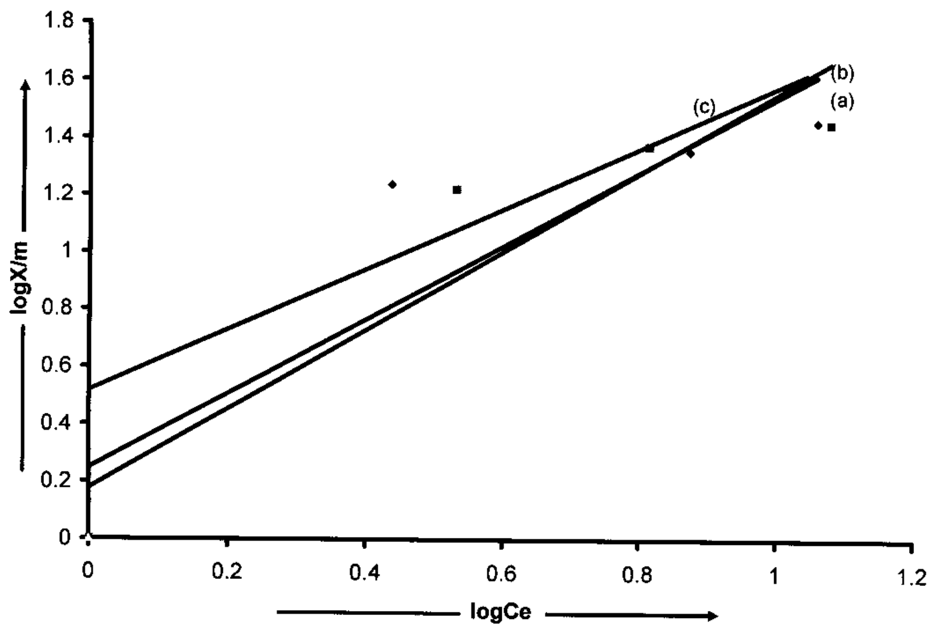

Fig. 4: Freundlich plots of Cu^{2+} adsorption on α-Alumina at solution to Alumina Ratio 50:1 at different temperature (a) 288K, (b) 305K, (c) 323K.

Cu^{2+} adsorption were calculated from the distribution constant K_L [8] by using the following relations:

$$\Delta G^\circ = -RT\ln K_L \quad (3)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (4)$$

$$\text{and } \ln K = -\Delta H^\circ/RT + \text{Constant} \quad (5)$$

Table-2 shows the values of thermodynamics parameters ΔH°, ΔS° ΔG°. The positive value of ΔH°=15.822KJ/mole, which is calculated from equation (3) and Fig. 6, confirms the endothermic nature of the overall adsorption process. The positive value of ΔS° suggests increased randomness at the solid/solution interface with some

Table-2: Freundlich and Langmuir Isotherm parameters for Adsorption of Cu^{2+} on α-Alumina.

Isotherm	T(k)	288	305	323
Langmuir	V_m	28.73	29.32	29.49
	K_L	1.001	0.830	1.803
	R^2	0.955	0.952	0.988
Freundlich	1/n	1.372	1.207	1.054
	K_F	0.753	0.606	0.400
	R^2	0.870	0.805	0.600

Table-3: Values of Thermodynamic Data for Adsorption of Cu^{2+} on α-Alumina.

Temperature K	ΔH^0 (KJ/mole)	ΔG^0 KJ/mole	ΔS^0 ($KJK^{-1}mol^{-1}$)
288	15.822	-1.0775	0.0586
305	15.822	-1.7490	0.0576
323	15.822	-3.1420	0.0587

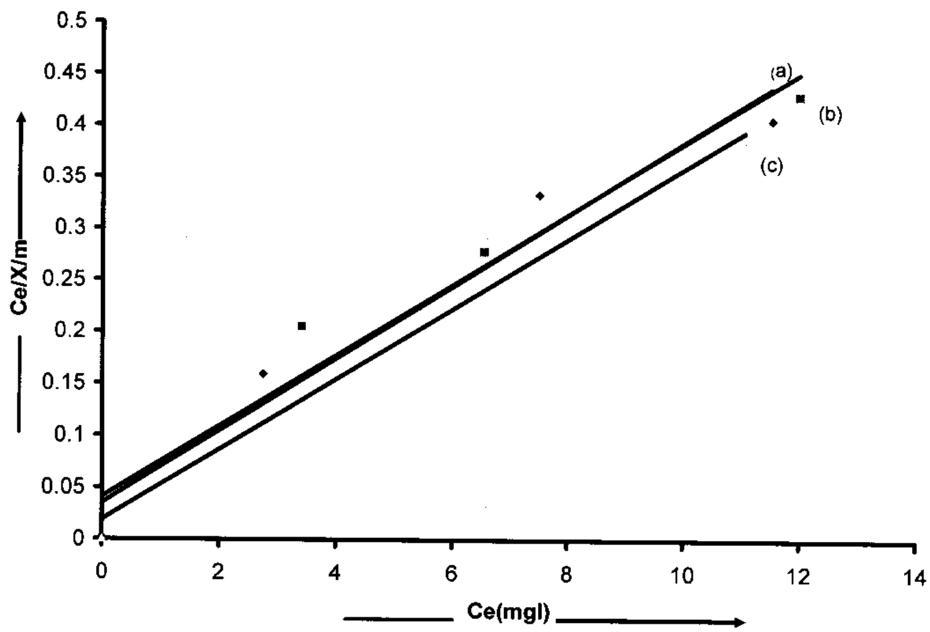

Fig. 5: Langmuir plots of Cu^{2+} adsorption on α-Alumina at solution to Alumina Ratio 50:1 at different temperature (a) 288K, (b) 305K, (c) 323K.

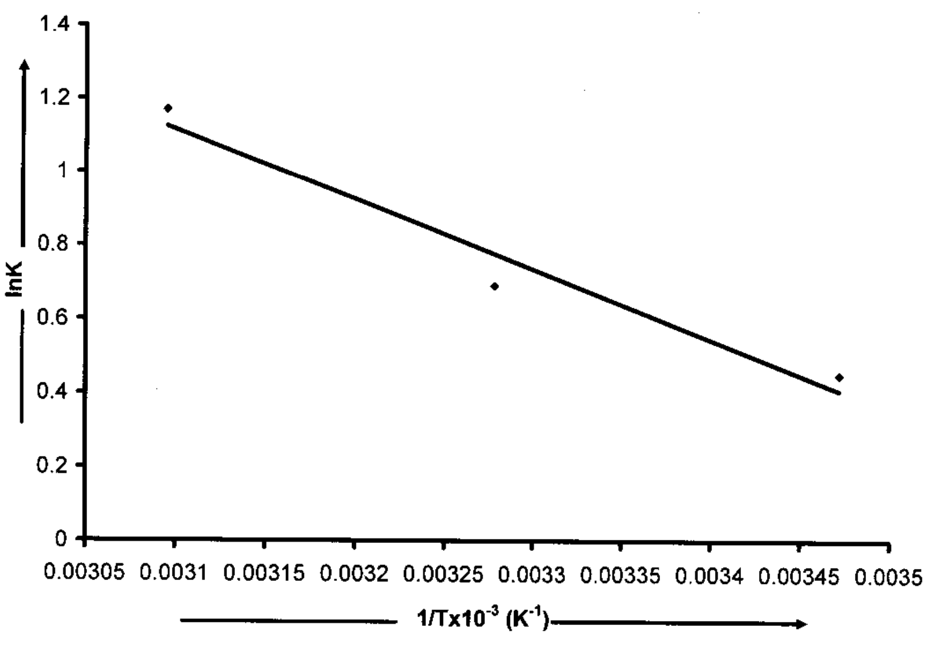

Fig. 6: Plot of lnK Vs.1/T for Cu^{2+} adsorption on α-Alumina.

structural change in the adsorbate and adsorbent and also affinity of the α-Alumina powder towards Cu^{2+} Negative value of ΔG° indicates the feasibility and spontaneity of the adsorption process, where higher negative value reflects a more energetically favorable adsorption process.

Experimental

Atomic absorption spectrometer Z8000 (Hitachi-Japan) was used to determine the Cu^{2+} initial and equilibrium concentrations [8]. All reagents used in the experimental work were of analytical grade (E.MERCK) ™; The following chemicals were employed: 1000 ppm $Cu(NO_3).3H_2O$ Stock solution, 1 % Hydrochloric Acid, 1 % $CaCl_2$ and 1 % NaOH. Various spiked standard solutions were prepared by taking a known aliquot of the stock solution in borosilicate 250 ml measuring flasks, making the volume up to the mark with deionized water. α-Alumina (E.MERCK) ™, with a BET area of 100 ± 30 m^2g^{-1}, density 3.970 g/cm^3 and a mean particle size 20 nm was used as an adsorbent without any heat and chemical treatment.

The adsorption of Cu^{2+} on α-Al_2O_3 (Alumina) was studied by batch-technique [9, 10]. All adsorption experiments except variable pH were carried at pH 7.20, which was obtained naturally at solution to adsorbent ratio of 50:1 and was measured by using pH meter (Model: 8417 Hanna Instruments). The pH of the suspension in one set of experiments was adjusted by using $NaOH/NH_4OH$ and HNO_3.The pH of solution was that of supernatant, which was obtained after equilibration. After equilibrium the suspension was centrifuged in a stoppered tube for 5 minutes at 4500 rpm, was then filtered through Whatman 41 filter paper. Adsorption of Cu^{2+} on α-Al_2O_3 (Alumina) was determined in terms of percentage extraction. Amount adsorbed per unit weight of theα-Al_2O_3(Alumina), X/m was calculated from the initial and final concentration of the solution, Adsorption capacity for the adsorption of Cu^{2+} species has been evaluated from the Freundlich and Langmuir adsorption isotherms [8] were studied at three different temperatures (*i.e.*, 15 ± 0.5 °C, 32 ± 0.5 °C and 50 ± 0.5 °C). The Cu^{2+} concentration studied was in the range of 10pmm to 80 ppm for 50:1 solution toα-Al_2O_3 (Alumina)) ratio.

Conclusions

Keeping the adsorptive nature of alumina it seemed better to select batch adsorption process for removal of copper from the industrial wastewater using alumina. The main advantages of the procedure are:

1. Cost of process is low as alumina is an indigenous material and easily available in country.
2. Ease and simplicity of preparation of the sorbent due to non-corrosive and non-poisonous nature of alumina.
3. Rapid attainment of phase equilibration and good enrichment.
4. The positive value of ΔH° and negative values of ΔG° indicate the endothermic and spontaneous nature of the adsorption process.

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