

Adsorption and equilibrium studies on removal of copper(II) by chitin

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Manuscript received 14 October 2003, revised 9 March 2004, accepted 16 July 2004

The adsorption of Cu^{2+} ions by chitin was studied in alkaline, neutral and acidic media and also under different experimental conditions like contact time, particle size of the adsorbent, pH of the medium and temperature to establish the optimum conditions. The effect of temperature on the adsorption process was verified by batch equilibration method. The experimental results revealed that the adsorption occurred as a spontaneous one. The equilibrium and activation parameters of the adsorption reaction were determined to assess the nature of adsorption. The adsorption increased with temperature. The results imply that the adsorption process is endothermic and spontaneous.

Copper occurs in the earth's crust at an average concentration of approximately 50 mg/kg mainly as sulphate. The latter are easily soluble in water and release copper ions, especially in acid environments. Copper is regarded as an essential element in mammalian nutrition because of its key role in many enzymatic reactions. It is also one of the ions capable of being toxic when present beyond the tolerance level in water bodies. Such toxic metal ions inhibit the self-purification of rivers. They may also cause chromosome damage and interfere with the process of heredity. When copper is ingested at high concentration it can become toxic to humans, causing cancer and promoting oxidation. They are also toxic to fish and other aquatic life and micro-organisms. Copper in about 2 mg dm^{-3} of water is fatal to stickle backs¹.

This study deals with the removal of Cu^{2+} ions using chitin as an adsorbent. Chitin is one of the three most abundant polysaccharides in nature. It occurs in crustaceans, insects, crabs, prawns and shrimp wastes. Chitin is a non-toxic and biodegradable polymer of *N*-acetylglucosamine and glucosamine residues. The constituent monosaccharide units in chitin are linked together by β -1-4-glycosidic bonds and hence have a relatively rigid configuration. It is easily filmable and spinnable and the materials thus processed have very good mechanical properties^{2,3}. It is insoluble in water and alkali but soluble in strong mineral acids and in anhydrous formic acid. It forms complexes with transition metal ions⁴⁻⁶. A systematic study of the removal of copper(II) by chitin under different conditions has been carried out in order to establish the nature of the adsorption process.

Results and discussion

Effect of particle size :

As the rates of adsorption of Cu^{2+} ions by chitin were dependent on the availability of active surface sites on the adsorbent, the sorption studies were carried out using three particle sizes of the adsorbent to determine the most efficient sample. The results are shown in Fig. 1. There is a significant increase in the sorptive nature of chitin with a decrease in the particle size. The specific surface area available for adsorption is greater for smaller particles. Chitin of 0.21 mm particle size possesses the maximum adsorption capacity compared to the other two.

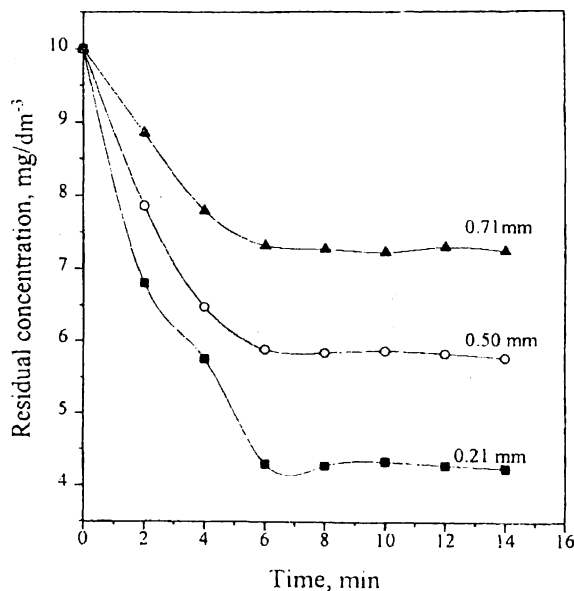


Fig. 1. Effect of particle size.

Effect of contact time :

The adsorption of Cu^{2+} ions by chitin increased at the initial stages, however, the process reached saturation after six minutes and thereafter it remained constant. No considerable increase in the sorptive ability of chitin was observed further. Hence it can be presumed that chitin requires a minimum contact time of six minutes to attain maximum adsorption capacity. The time variation is smooth and continuous, indicating the formation of monolayer coverage on the outer interface of the adsorbent⁷.

Effect of pH :

The adsorption nature of chitin was determined at four pH levels viz. 3, 5, 6 and 8. A plot of concentration of the adsorbate (mg dm^{-3}) versus time (min) at different pH ranges is shown in Fig. 2. Maximum adsorption of copper(II)

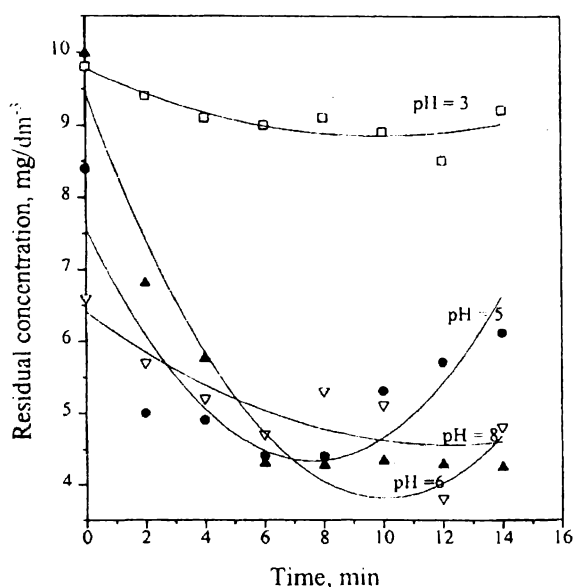


Fig. 2. Effect of pH.

occurred at pH 6. No appreciable changes in the pH of the reaction mixture were observed after the agitation process in all the batch experiments. The rate of adsorption is less at low pH range. This is because the metal ions that would coordinate with the lone pair of nitrogen of chitin have to compete with the H_3O^+ ions for active sites available on the surface of chitin⁸. The rate of adsorption is not appreciable at higher pH ranges (above 8). Copper(II), a divalent ion, is present essentially as Cu^{2+} in acidic medium, where sorption is highly favoured, but it gets converted to $\text{Cu}(\text{OH})^+$ in the pH range beyond 8. This results in a decrease in the adsorption rate on the active sites of chitin which was also reported by other workers⁹.

Effect of co-ions :

All the three co-ions Fe^{3+} , Zn^{2+} , Cr^{6+} were observed to hinder the removal of Cu^{2+} ions. However, the maximum inhibition was caused by Zn^{2+} ions.

Adsorption isotherm :

Quantification of the adsorption capacity of chitin for the removal of Cu^{2+} from the solution were studied using Freundlich and Langmuir adsorption equations.

Freundlich isotherm :

Batch isothermal data fitted to the linear form of the Freundlich isotherm. The fit of the data indicates that the intercept, K , is roughly an indicator of the sorption capacity and the slope $1/n$, of the sorption intensity¹⁰. The values of K and $1/n$ are calculated from the graph and the data are provided in Table 1. The linearity of the plots ($0.9962 < r < 0.9988$ and $0.0139 < sd < 0.0245$) at different temperatures supports the applicability of the Freundlich adsorption iso-

Table 1. Freundlich parameters

Temp. (K)	K	$1/n$
293	2.2897	0.6914
303	2.3132	0.6847
313	2.3316	0.6923
323	2.3567	0.7001

therm⁸ indicating that the forces of adsorption by chitin are governed by physisorption¹¹. The values of n for this system were calculated from the slope of the curve and are found to be between 1 and 2. Our findings are in satisfactory agreement with the findings of Treybal¹² who mathematically evaluated values of n for a number of mass transfer operations of systems and reported that the values of n between 1 and 10 would represent beneficial adsorption.

Langmuir isotherm :

The linear equation of Langmuir adsorption isotherm was applied in the form,

$$C_e/q_e = 1/Qb + C_e/Q$$

where Q and b are the Langmuir constants, indicating the adsorption capacity and energy of adsorption respectively. C_e and q_e have their usual significance. The linear plots ($0.9243 < r < 0.9626$ and $0.4286 < sd < 0.5843$) of C_e/q_e versus C_e at different temperatures indicate the applicability of Langmuir adsorption isotherm on the adsorption process. The Langmuir constants and thermodynamic parameters are given in Table 2, along with the K_0 values. An

Table 2. Langmuir constants and thermodynamic parameters

Temp. (K)	Langmuir constants		Thermodynamic parameters			
	b dm ³ mg ⁻¹	Q mg g ⁻¹	K_0	ΔG° kJ mol ⁻¹	ΔH° kJ mol ⁻¹	ΔS° JK ⁻¹ mol ⁻¹
293	0.1638	1.3357	5.48	-4.13	-	-
303	0.1684	1.3550	5.54	-4.31	0.8655	17.08
313	0.1696	1.4333	5.58	-4.48	-	-
323	0.1742	1.5033	5.66	-4.65	-	-

increase in K_0 value with temperature indicates the endothermic character of the adsorption process. The results reveal that the energy of adsorption (b) for trapping of Cu^{2+} ions by chitin increases with temperature. This explains the increase in adsorption of Cu^{2+} ions by chitin at higher temperatures¹³. Our findings are in good agreement with those of Annadurai *et al.*¹⁰ who studied the sorptive character of chitin on basic dyes. The influence of temperature on chitin and its enhanced adsorption behaviour at higher temperatures further adds on more emphasis to the phenomenon of swelling in the internal structure of the chitin molecules to accommodate more Cu^{2+} ions on its surface.

Equilibrium parameter :

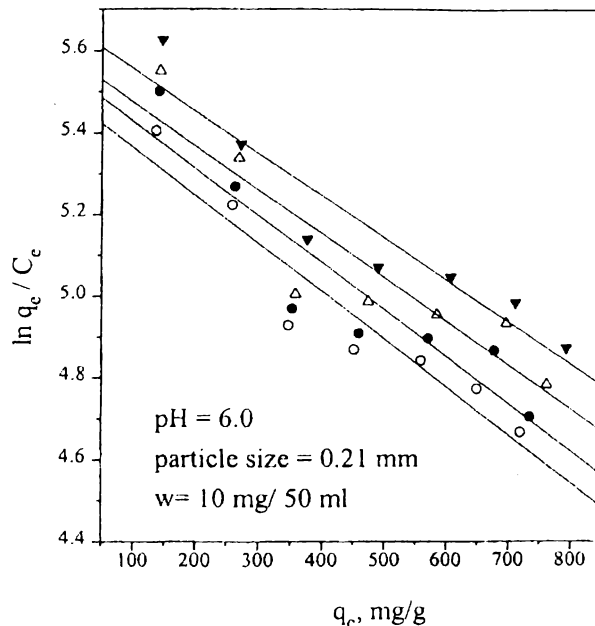
The dimensionless equilibrium parameter (R_L) is defined by $R_L = 1/(1 + bC_0)$ where b is the Langmuir constant and C_0 is the initial concentration of the metal ions¹⁴. The R_L values calculated at different temperatures for the initial concentrations of copper(II) are given in Table 3. The values lying between 0 to 1 indicate favourable adsorption at the four different temperatures.

Table 3. Equilibrium parameter (R_L)

Concen. of copper ion (mg dm ⁻³)	Temperature, (K)			
	293	303	313	323
2	0.753	0.748	0.747	0.742
4	0.604	0.598	0.596	0.589
6	0.504	0.497	0.496	0.489
8	0.433	0.426	0.424	0.418
10	0.379	0.373	0.371	0.365
12	0.337	0.331	0.329	0.324
14	0.304	0.298	0.296	0.291

Adsorption dynamics :

The plots of $\ln q_e/C_e$ versus q_e of the reactions are given in Fig. 3. The thermodynamic equilibrium constant, K_0 for the sorption reaction was determined from the plot $\ln q_e/C_e$ versus q_e and extrapolating to zero q_e ¹⁵. An increase in K_0


Fig. 3. Plot of $\ln q_e/C_e$ versus q_e , pH = 6.0, particle size = 0.21 mm, W = 10 mg/50 ml : (o) 293, (•) 303, (Δ) 313, (▼) 323 K.

value with temperature indicates that the adsorption process of Cu^{2+} ions over chitin is endothermic.

The thermodynamic parameters associated with the adsorption reaction viz. standard free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated using the conventional equations. A plot of $\ln K_0$ versus $1/T$ is found to be linear. ΔH° and ΔS° are determined from the slopes and intercepts of the plot¹⁶. The negative values of the standard free energy change (ΔG°) for this reaction suggest the sorptive nature to be spontaneous. This explains why the value of ΔG° is negative with the rise in temperature¹⁷. The positive value of ΔH° (0.8655 kJ mol⁻¹) indicates that the process of adsorption is endothermic and its irreversibility, probably due to its non-polar interactions. The positive value of entropy change ΔS° (17.08 JK⁻¹ mol⁻¹) suggests a high degree of disorderliness at the solid-solution interface during the adsorption process. This may be due to the fact that the adsorbed molecules, which are displaced by the adsorbate species, gain more translational entropy than what is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system. It also reflects the affinity of the adsorbent for the metal ions and suggests some structural changes in adsorbate and adsorbent.

Conclusion :

This study reveals that an optimum contact period of six minutes is required for maximum removal of Cu^{2+} ions

by chitin. The adsorption process depends on the particle size of the adsorbent, pH and also on temperature. The adsorption follows Langmuir and Freundlich adsorption isotherms. Thermodynamic parameters indicate that the reaction is spontaneous and endothermic which implies increase in sorption with temperature. The above results are supported by Langmuir constants and equilibrium constants.

Experimental

Commercially available chitin (Otto Kemi, C1904) was obtained in the form of flakes from M/s B. R. Corporation, Mumbai, India. The raw sample was pulverized with mortar and pestle and sieved into three sizes, viz. 0.21, 0.50 and 0.71 mm, using scientific test molecular sieves manufactured by ELITE Scientific Instruments Co., Mumbai. The separated chitin samples were further purified by first boiling in 0.1 N HCl for three hours. The solution was decanted and the residue was treated further by boiling in 0.1 N NaOH again for three hours. The purified samples were soaked in double-distilled water for sufficient amount of time (till it registered neutral pH), as swelling would make more sites available. Later the samples were dried in an oven. Only the chemically treated samples were used for the experiments.

Experimental solutions were prepared using double-distilled water. The adsorption experiments were carried out by batch equilibration method. All the chemicals employed for the analysis were AnalaR, G.R. or other high purity grade purchased from Qualigens and C.D.H. and were used without further purification. A stock solution of the adsorbate containing 1000 mg dm⁻³ of Cu²⁺ ions was prepared using cupric chloride (CuCl₂·2H₂O). From the stock solution, aliquots of the adsorbate containing the different concentrations viz. 2, 4, 6, 8, 10, 12 and 14 mg dm⁻³ of Cu²⁺ ions were measured out. 50 cm³ of the adsorbate of each concentration was mixed with 10 mg of chitin of all the three grades and the mixtures were agitated in a mechanical shaker. The samples were filtered at regular time intervals of 2 min and the concentrations of Cu²⁺ ions left over at each stage were determined. Adsorption experiments were conducted at 3, 5, 6 and 8 pH ranges and also at four temperatures viz. 293, 303, 313 and 323 K. All experiments were done in a thermostat attached with a shaker, TECHNO make which could maintain the constancy of temperature with an accuracy of ±0.5°C. Adsorption studies of Cu²⁺ ions in the presence of iron(III), zinc(II) and chromium(VI) were experimentally verified to study the effect of co-ions. This involved the determination of the residual Cu²⁺ ions in the mixture containing equal amounts

of Fe³⁺, Zn²⁺ and Cr⁶⁺ ions. Estimation of the Cu²⁺ ions in the residual solutions was carried out using Atomic Absorption Spectrometer (Model AA 100, Perkin-Elmer make) and the pH was measured using Elico LI 120 pH meter. Duplicate measurements were also conducted to ensure the reproducibility of the values of residual concentration within ±2%.

Acknowledgement

The financial support received from the Rajiv Gandhi National Drinking Water Mission, Ministry of Rural Development, Government of India is gratefully acknowledged.

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