Potential of Agarose for Biosorption of Cu(II) In Aqueous System

[1]Anurag Pandey, [2]Debabrata Bera, [1]Anupam Shukla and [2]Lalitagauri Ray
[1]Department of Biotechnology and Biomedical Engineering, National Institute of Technology,
Raipur- 492 010, India
[2]Department of Food Technology and Biochemical Engineering, Jadavpur University,
Kolkata- 700 032, India

Abstract: The ability of agarose gel as an adsorbent for Cu(II) ions in aqueous solution was studied. The experiments were done as batch processes. Batch kinetics and isotherm studies were carried out under varying experimental conditions of contact time, Cu(II) ion concentration, adsorbent dose, temperature and pH. Adsorption equilibrium of agarose gel was reached within 4 h for agarose gel when initial metal ion concentration was 25 mg/l, while at higher concentration 175 mg/l equilibrium was achieved in 6 h. Kinetics of adsorption obeyed a pseudo second-order equation. The optimum sorbent loading was found to be 1% for Cu(II) removal. The biosorption of Cu(II) ions by agarose gel decreased as the initial concentration of metal ions increased in the medium. The maximum Cu(II) ions adsorbed was found to be 238 mg/g agarose gel. The maximum uptake of metal ions was obtained at pH 2.0. At temperature 35 $^{\circ}$C, the biosorption of metal ions was found to be highest, with increase or decrease in temperature resulted in a decrease in the metal ions uptake capacity. The suitability of the Langmuir and Freundlich adsorption models to the equilibrium data were investigated and it was found that the sorption data conformed well to Langmuir isotherm model. The studies showed that the agarose gel can be used as an efficient adsorbent biopolymer for removal of Cu(II) ions from water and wastewater.

Keywords: Biosorption, Agarose gel, Biopolymer, Cu(II) adsorption, Aqueous system

INTRODUCTION

The presence of toxic heavy metal contaminants in aqueous streams, arising from the discharge of untreated metal containing effluents into water bodies, is one of the most important environmental issues[1]. Discharge and treatment of industrial wastewater containing heavy metals and precise identification of the actual sources of heavy metal contamination of water resources is urgent, due to the acute, severe, and persistent impacts of these pollutants on human health and on the sustainability of ecosystems are important issues in environmental protection.

A variety of methods are used to remove these toxic substances from effluents and industrial wastewaters before discharging into natural water bodies. The main treatment technologies include precipitation, coagulation, ion-exchange, membrane processes and electrolytic technologies. However conventional treatment technologies like precipitation and coagulation become less effective and more expensive when situations involving high volumes and low metal concentrations are encountered and the application of membrane processes and activated carbon are also restricted due to high costs [2]. As a result, cost-effective alternate technologies involving removal of heavy metals from wastewater are being sought to meet discharge standard.

Biological methods for remediation may provide the alternative[3-5]. Biosorption have been recommended as cheaper and most effective techniques[6]. Among the various biological systems, dead systems offer many advantages over live systems because they do not fall prey to toxicological effects of high concentrations of contaminants and can be obtained inexpensively[7]. Biopolymers are non-toxic, selective, efficient and inexpensive, and

Corresponding Author: Anurag Pandey, Department of Biotechnology and Biomedical Engineering, National Institute of Technology, Raipur- 492 010 India

thus highly competitive with ion exchange resins and activated carbon [8].

The aim of this study was to explore the possibility using agarose gel for removing Cu(II) ions from aqueous solution. The influence of various factors, such as adsorbent loadings, initial pH, temperature and initial metal ion concentrations on the sorption capacity were studied. The Langmuir and Freundlich models were used to analyze the adsorption equilibrium.

MATERIALS AND METHODS

Preparation of agarose gel: A desired amount of agarose gel was prepared by dissolving agarose in distilled water and keeping in a boiling water bath, and then plated into petri plates. The resultant polymerized gel was cut into pieces of approximately 3×3 mm^2 sizes.

Metal solutions: Metal stock solutions containing Cu(II) with a concentration of 1000mg/l were prepared using deionized distilled water and salts containing the metals. For biosorption experiments, concentrations ranging from 25-200 mg/l were prepared and pH of the metal solutions was adjusted to desired value using 0.1M citrate buffer.

Apparatus and glassware: All metal uptake experiments were carried out using 250 ml Erlenmeyer flasks. Metal ion concentrations were determined using Varian spectra A-220 atomic absorption spectrophotometer.

Biosorption studies: Biosorption experiments were carried out in 250 ml Erlenmeyer flasks by agitating pre-weighed amount of adsorbent with 50 ml of aqueous metal ion solution, in order to find out the optimum adsorbent loading, for a pre determined time interval at 150 rpm speed using a rotary shaker. The effect of pH of the suspending medium on metal removal was studied by performing equilibrium sorption tests at different pH values ranging from pH 1.0 and 4.0. In order to determine the effect of temperature variation on metal ion uptake by agarose gel, the temperature of the reaction was varied from 20^0C to 40^0C. After adsorption, the mixture was filtered through Whatman No-1 filter paper. Residual concentration of metal ion present in the clear supernatant was estimated. The amount of metal bound was taken to be the difference between the initial and final metal concentration. For isotherm analysis, adsorption experiments were conducted by varying the initial metal ion concentration from 25-200 mg/l and equilibrated for 6 h.

RESULTS AND DISCUSSION

Biosorption kinetic studies: Pseudo second-order equation was employed to model the sorption data over the entire time range. The pseudo second-order kinetic rate equation of Lagergren is generally expressed as follows [9]:

$$dq/dt = k_2 (q_e - q)^2 \qquad (1)$$

Where k_2 is the pseudo second order rate constant (g/mg/min). Integrating and applying boundary conditions as $t = 0$ and $q = 0$ to $t = t$ and $q = q_e$, Eq. (1) becomes

$$t/q = 1/q_e^2 k_2 + t/q_e \qquad (2)$$

The rate constant k_2 can be obtained from the intercept of the linearized pseudo second-order rate equation. If the pseudo second-order rate equation can fit the sorption data, there should be good linearity between t/q_t and t.

Fig.1 shows that the pseudo second-order equation was applicable to all the sorption data ($R^2 = 0.9972$), straight line obtained indicating that the process follows pseudo second-order kinetics, and k_2 value is 1.2 g/mg/min. This confirms that there is more than one mechanism involved in the adsorption process.

Effect of amount of sorbent on biosorption: The amount of adsorbent on the efficiency of adsorption was also studied. The results of biosorption experiments obtained by using gels with varying agarose load with 1-3% (w/v) are listed in Table 1.

Table 1: Biosorption capacity of agarose gel for Cu(II) at varying sorbent dose; 50 ml Single metal solution (50 mg/l) of Cu(II) was contacted with 1-3 % w/v of agarose for 6 h at pH 2.0 and temperature 35^0C

Agarose dose % (w/v)	% removal of Cu(II) ions
1	64
2	58
3	64

It was observed that 1% agarose concentration, was found to be optimum for Cu(II) removal. This can be attributed to the difference in porosity of the gels when a higher quantity of sorbent was loaded. The

Table 2: Langmuir and Freundlich isotherm constants

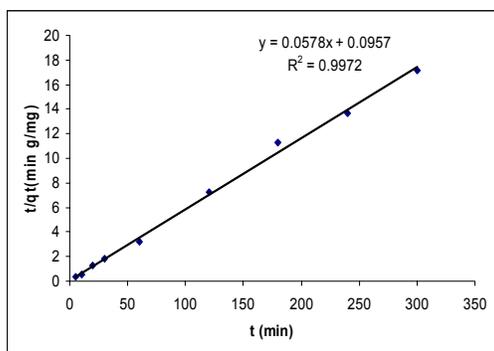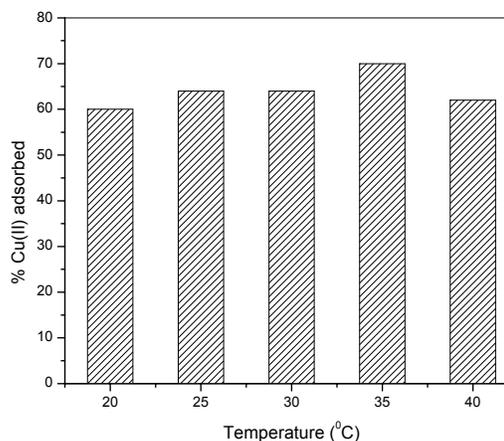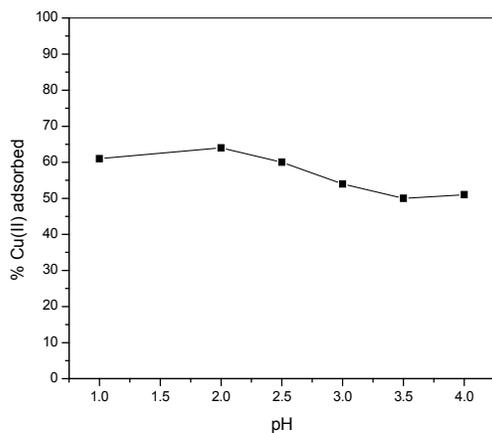| Type of Adsorbent	Langmuir isotherm			Freundlich isotherm		
	q_{max} (mg/g)	b (L/mg)	r^2	K_F	n	r^2
Agarose	238	0.0050	0.9668	1.1	1.0	0.9420

Fig. 1: Plot of t/q_t and t

Fig. 2. Effect of pH on metal uptake by agarose gel; 50 ml Single metal solution (50 mg/l) of Cu(II) was contacted with 1% of agarose for 6 h, temperature 35^0C

Fig. 3. Effect of temperature on metal biosorption of Cu(II) by agarose gel; 50 ml Single metal solution (50 mg/l) of Cu(II) was contacted with 1% of agarose gel for 6 h at pH 2
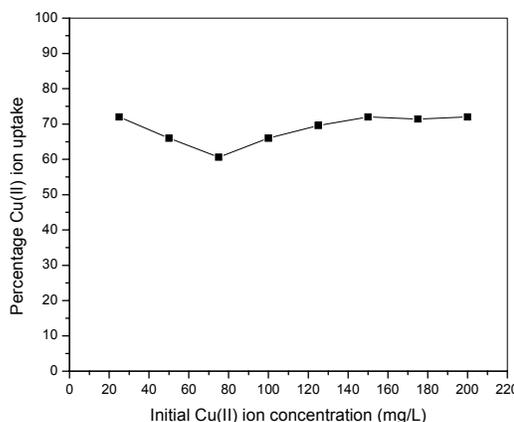

Fig. 4. Effect of initial metal ion concentration on biosorption of Cu(II) by agarose gel; 50 ml Single metal solution (25-200 mg/l) of Cu(II) was contacted with 1% of agarose gel for 6 h at pH 2 and temperature 35^0C

increase in dose of sorbent in relation to amount reduced the surface area of the gels [10]. As the sorbent dose was increased, the gels became less porous and the free transport of metal ions to the interior adsorption sites was affected. Because of the reduced porous nature, the total surface area of entrapped biosorbent particle, interacting with metal ions is reduced.

Freundlich Isotherm
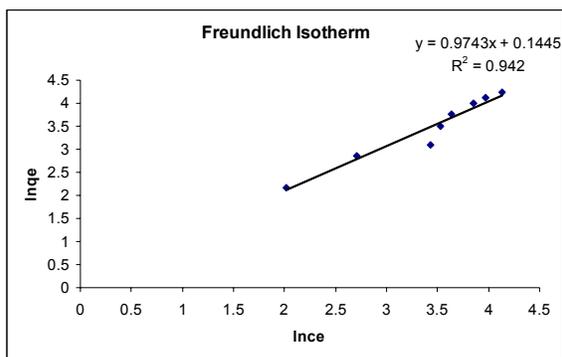
y = 0.9743x + 0.1445
R^2 = 0.942

Fig.5: Freundlich adsorption isotherms for Cu(II) biosorption by agarose gel, metal ion concentration range 25-200 mg/l, contact time 6 h at pH 2.0 and temperature 35^0C

Langmuir Isotherm

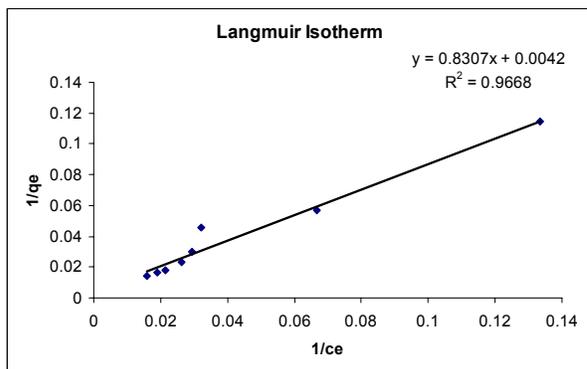y = 0.8307x + 0.0042
R^2 = 0.9668

Fig. 6: Langmuir adsorption isotherms for Cu(II) biosorption by agarose gel, metal ion concentration range 25-200 mg/l, contact time 6 h at pH 2.0 and temperature 35^0C

Effect of initial pH: The adsorption of Cu(II) from aqueous solution is dependent on the pH of the solution, which affects the surface charge of the adsorbent. It was therefore important to study the effect of pH on the adsorption of Cu(II). The effect of the pH of the suspending medium on metal removal was studied by performing equilibrium sorption tests at different pH values ranges from pH 1-4. Adjustments to pH were made with 0.1M citrate buffer. Metal uptake was affected by pH of the metal solution (Fig. 2). It is clear that maximum adsorption of Cu(II) occurred at pH 2, and decreased at lower and higher pH. Metal uptake by agarose gel decreases as the pH increases and the maximum removal for Cu(II) ions was 64 % at pH 2.0.

Effect of temperature: Results of metal sorption experiments carried out in order to determine the optimum reaction temperature for Cu(II) adsorption by agarose gel in solution, the metal sorption experiments was carried out at different temperatures ranging from 20^0C to 40^0C, when the amount of adsorbent in gel, pH and initial Cu(II) concentration were 0.1 g, 2.0 and 50 mg/l, using 50 ml solution in 250 ml Erlenmeyer flask are shown in Fig.3. It was observed that the extent of sorption of metal ions by the sorbent increased with increase in temperature upto 35^0C. Further increase in the temperature of the reaction mixture showed reduction in biosorption. It has been suggested that increase in metal uptake at increased temperature is due to either higher affinity of sites for metal or an increase in binding sites on relevant biosorbent [11].

Effect of initial metal ion concentration: The metal removal by agarose gels corresponding to different initial metal concentrations (25, 50,75,100,125,150,175,200 mg/l) are shown in Fig. 4. The parameters such as reaction temperature was fixed at 35^oC and pH was adjusted at 2.0, where as the amount of sorbent in gels were 1% are kept constant in 50 ml solution containing Cu(II) ions in 250 ml Erlenmeyer flask. As can be seen from Fig. 4, removal of Cu(II) ions is 70% at 25 mg/l concentration of Cu(II) ions in aqueous solution. The binding sites are limited keeping agarose loadings as constant. With increasing metal concentration, the percentage of metal removed was decreased to 125 mg/l and then stabilized with further increment in the metal concentration upto 200 mg/l. This could be because at higher concentrations, as more ions are competing for the available binding sites, the rate of adsorption decreased, resulting in lower adsorption percentage.

Analysis of adsorption isotherms: Analysis of equilibrium data is essential to develop an equation which precisely represents the results and which can be used for design purposes. Various isotherm models have been used for the equilibrium modelling of biosorption systems. The most widely used isotherm models to describe the biosorption process are Langmuir and Freundlich model.

The Langmuir isotherm assumes monolayer adsorption, and is presented by the following equation:

$$q_e = q_{max} \, b \, C_{eq} / (1 + bC_{eq}) \qquad (3)$$

Where q_e and q_{max} are the observed uptake capacity at equilibrium and maximum uptake capacities (mg/g biosorbent), C_{eq} is the equilibrium concentration (mg/l solution); b is the equilibrium constant (l/mg).

The linearized form of this equation is as

$$1/q_e = 1/q_m b \cdot 1/C_e + 1/q_m \qquad (4)$$

$1/q_e$ vs $1/C_e$ gives the straight line with slope $1/q_m b$ and $1/q_m$ as intercept. b is the sorption isotherm constant (l/mg).

The Freundlich isotherm equation is an empirical equation based on the sorption on a heterogeneous surface suggesting that binding sites are not equivalent and /or independent. The monocomponent Freundlich isotherm equation [5] is given below:

$$q_e = K_f \, C_e^{\ 1/n} \qquad (5)$$

where K_f is the Fruendlich isotherm constant, related to sorption capacity; n is the constant related to affinity of the metal ions on adsorbent.

A logarithmic plot linearized the equation

$$\ln q_e = \ln K_f + 1/n \ln C_e \qquad (6)$$

Where, q_e the amount of metal ions adsorbed per unit mass of adsorbent at equilibrium, mg/g, C_e equilibrium concentration of aqueous solution, mg/l, K_f constant related to adsorption capacity, $1/n$ constant related to adsorption intensity.

$\ln q_e$ vs $\ln C_e$ gives the straight line with slope $1/n$ and $\ln K_f$ as intercept.

It can be observed from Fig. 5 and 6 that both Freundlich and Langmuir isotherms model exhibited good fit to the sorption data of Cu(II). From Table– 2, it is concluded that the Langmuir isotherm model is slight better than Fruendlich isotherm model to fit Cu(II) sorption data well cover a concentration range 25 mg/l to 200 mg/l. Fig-5, shows the linear plot of $\ln q_e$ versus $\ln C_e$ giving a straight line ($r^2 = 0.9420$) and Fig-6, shows the linear plot of $1/q_e$ versus $1/C_e$ giving a straight line ($r^2 = 0.9668$), with slope $1/n$ and intercept $\ln k$ and the characteristic parameters q_{max} and b for Freundlich and Langmuir isotherm respectively. The values of the Langmuir and Freundlich constants are presented in Table-2, for the agarose gel adsorption system.

CONCLUSION

The results demonstrate the agarose gel can be successfully used as a biosorbing agent for the removal of heavy metal ions from aqueous solution. The characterization of Cu(II) uptake by agarose gel showed that the binding kinetics was found to be dependent on experimental conditions, particularly the medium pH, temperature and the initial concentration of metal ions. The Freundlich and Langmuir adsorption models was used to represent the experimental data and equilibrium data fitted very well to both the Freundlich and Langmuir isotherm model. The Langmuir isotherm represented the equilibrium data slightly better than Freundlich isotherm well cover a concentration range 25 mg/l to

200 mg/l. These studies show that agarose gel can be used as a filler material to build a permeable barrier to intercept the flow of groundwater. Heavy metal ions in the water will be adsorbed by the biopolymer and water passing through the barrier will free of metal ions.

REFERENCES:

1. Sudha Bai, R. and T. Emilia Abraham, 2003. "Studies on chromium(VI) adsorption-desorption using immobilized fungal biomass. Bioresource Technology*, 87: 17-26.
2. Kapoor, A. and T. Viraraghavan, 1995. Fungal biosorption an alternative treatment option for heavy metal cleaning wastewaters: a review. Bioresource Technology*, 53 : 195-206.
3. Tan, H., J.T. Champion, J.F. Artiola, M.L. Brusscan and R.M. Miller, 1994. Complexation of Cd by Rhamnolipid biosurfactant. Environ. Sci. Technol., 28: 2402-2406.
4. Chandra Shekhar, K., K.A. Natrajan, S. Subramanium and J.M. Modak, 1998. Removal of metal ions using an industrial biomass with reference to environmental control. Int. J. Miner. Process*, 53:107-120.
5. Jalali R., H. Ghafourian, Y. Asef, S.J. Davarpanah and S. Sepehr, 2002. Removal and recovery of lead using nonliving biomass of marine algae. J. Hazard. Mater., 92: 253-262.
6. Bolton, H. and C.P. Huang, 1996. Application of *Aspergillus oryzae* and *Rhizopus oryzae* for Cu(II) removal. Water Res., 30: 1985-90.
7. Kratochvil, D. and B. Volesky, 1997. Advances in biosorption of heavy metals. Trends Biotechnol., 16: 291-300.
8. Wilde, E.W. and J.R. Benemann, 1993. Bioremoval of heavy metals by the use of microalgae. Biotechnology Advances, 11: 781-782.
9. Ho, Y.S. and G. McKay, 1999. Pseudo-second order model for sorption processes. Process Biochem., 34: 451-65 .
10. Spiniti, M., H. Zhuang and E.M. Trujillo, 1995. Evaluation of immobilized biomass beads for removing heavy metals from wastewater. Water Environ. Res., 67:943-952.
11. Marques, A.M., X. Roca, M.D. Simon-Pujol, M.C. Fuste and F. Congregado, 1991. Uranium accumulation by *Pseudomonas* sp.EPS-5028. Applied Microbiology and Biotechnology*, 35:406-410.