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Biosorption of Silver using Metal-Imprinted Thiourea-Modified Glutaraldehyde-Crosslinked O-Carboxymethyl Chitosan Beads

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Abstract

Chitosan, an abundant biopolymer obtained from deacetylation of chitin, has been proved to be a promising biosorbent for metal uptake. Grafting new functional groups on the chitosan backbone was also reported to be efficient in increasing either the sorption capacity or sorption selectivity for the target metal. In this study, silver-imprinted thiourea-modified glutaraldehyde-crosslinked O-carboxymethyl chitosan beads were prepared to selectively adsorb Ag (I) from a bimetallic aqueous solution. The biosorbent was synthesized by using prepared O-carboxymethyl chitosan beads to first absorb Ag (I) ion, then crosslinking with a polymeric Schiff's base of thiourea/glutaraldehyde. To obtain the best performance sorbent, the degree of carboxymethylation substitution, and the amount of crosslinking agent used were studied. Results indicated the highest selective uptake capacity of Ag (I) occurred when a molar ratio of amino group of chitosan to carboxymethylation agent to crosslinking agent of 6:15:16 is used in the synthesis.

Batch sorption tests were carried out for isotherm and kinetic studies using the sorbent which provides the best selective uptake capacity of Ag (I). All isothermal and kinetic experiments were performed at 25 ℃. The maximum uptake of Ag (I) was found to be 137.5 $\mathrm{mg \cdot g^{-1}}$ at pH 5.0 with the initial concentration of Ag (I) being 1.75$\mathrm{mmol \cdot L^{-1}}$. The sorbent demonstrated extremely good selectivity towards Ag (I) as equal mole of Cu (II) present in the solution was scarcely absorbed over a pH range from 1.0 to 6.0. The experiments also revealed that the biosorption process of Ag (I) fits well with a Langmuir model and Lagergren's Pseudo-second-order kinetic.

Keywords: Carboxymethylchitosan, Crosslinking, Imprinting, Silver, Thiourea.

Introduction

Silver is used extensively as a metal in the fields of aerospace, chemical porcelain, photographic, electroplating and medical industries, due to its excellent malleability, and extremely high electrical and thermal conductivity. Significant amounts of silver are discharged in the wastewater from such industries. In addition, mining effluents also contain appreciable amounts of silver since silver is usually distributed with relatively low contents in massive base metal ores. Development of novel and cost-effective technology to recover silver from dilute aqueous solutions is important.

In recent years, biosorption has been recognized as an effective method for the removal or concentration of metals from solutions. (Das, 2010) Biosorption is defined as a general property of non-living biomass to rapidly bind and concentrate inorganic and organic compounds from diluted aqueous solutions. (Kotrba et al., 2011) Biosorbents prepared from agricultural wastes, industrial wastes, and natural residues have been widely used to retain/remove heavy metals from wastewater due to their biodegradable, biocompatible, renewable and nontoxic nature. (Volesky and Holan, 1996) Among the large biomass resource pools, chitosan, a biopolymer obtained from the deacetylation of chitin, has been identified as an efficient metal scavenger due to the presence of reactive amino groups. However, the solubility of chitosan in dilute acid has limited its applications, as many industrial effluents tend to be acidic. Moreover, powder form of chitosan is not suitable to be packed in a column for applications at preparative scale because they may cause clogging problems, a huge pressure drop or serious hydrodynamic limitations. (Wang and Chen, in press) Gel beads are regarded as the best form as sorbents for sorption of metal ions from aqueous solution. (Eric, 2004) Immobilization of chitosan powders is therefore necessary for practical implementations.

Surface imprinting technology has attracted much attention in generating recognition sites, and has been successfully applied to prepare metal ion imprinted polymers. (Fan et al, 2011) This technology has been successfully applied to different polymeric materials, such as chitosan (Tao et al. 2012), poly(ethylene terephthalate) (Monier and Abdel-Latif, 2013), polyazomethine amides (Monier and Abdel-Latif, 2013), for the uptake of different kinds of target metal ions: Ag (Fan et al, 2011), Cu (Tao et al. 2012), Hg (Monier and Abdel-Latif, 2013), As (Liu et al, 2012), Pb (Jiang et al, 2011), Cd (Murugesan et al, 2011), Ni (Chen et al, 2011), Zn (Chen et al, 2011), and Mn (Guan et al, 2008).

Crosslinking has been used to improve the chemical resistance of chitosan in acid media, but when amino groups are involved in chemical crosslinking process, the uptake capacity of chitosan will decrease. (Wan Ngah and Fatinathan, 2008) To improve the capacity, grafting of certain function groups is necessary before crosslinking. (Donia et al, 2008) Carboxymethyl chitosan (CMC), which has amino group, carboxyl group, and hydroxyl groups at C-2 and C-3 position, can enhance the sorption capacity with various metal ions, (Hon and Tang, 2000) and the preparation procedure is considered to be simple and efficient for chitosan modification. (Chen and Park, 2003; Choong and Wolfgang, 2003) Precious metal ions have a preference for complexion with ligands with more electronegative donor atoms, such as N and S, based on the theory of hard and soft acids and bases (HSAB) theory defined by Pearsona. (Zhou, et al, 2009) Thiourea contains both N and S groups, so thiourea modification of CMC should effectively increase the capacity of crosslinked imprinted CMC beads towards Ag (I). (Chen et al, 2005)

In this study, an attempt was made to selectively uptake Ag (I) from a bimetallic solution using the silver-imprinted thiourea-modified glutaraldehyde-crosslinked O-carboxymethyl chitosan beads. Optimal conditions for the sorbent preparation has been found by varying the amount of carboxymethylation agent used, the amount of crosslinking agent used, and the use of imprinting technology. Effects of initial pH, initial concentration, and contact time on selective sorption of Ag (I) was also studied. Different kinds of kinetics and isotherm models were used to describe the selective uptake of Ag (I) on the prepared sorbent.

Materials and Methods

Materials

Chitosan with 80 mesh, 91.03% degree of deacetylation and average molecular weight of 2×10^5 $g\cdot mol^{-1}$ was purchased from Fisher Scientific. Acetic acid, sodium hydroxide, monochloroacetic acid, isopropanol, ethanol, hydrochloric acid, thiourea, glutaradehyde, acetone, silver nitrate, sulfuric acid, copper nitrate were purchased from Fisher Scientific as well and used without further purification. The deionized water was generated from Mili-Q water purification system in the lab.

Preparation of Imprinted Crosslinked CMC Beads

Preparation of Chitosan Beads. 5 g chitosan powder was dissolved in 100 mL of 5% acetic acid in a beaker, the mixture was left overnight to obtain a homogeneous chitosan solution before being added dropwise into 500 mL of 0.5 $mol\cdot L^{-1}$ NaOH solution. The NaOH solution was under a continuous stirring at 150 rpm for 24 hours to coagulate spherical chitosan gel beads and to neutralize the acetic acid within the beads. The chitosan beads were filtered, rinsed with deionized water, and then stored in deionized water for use.

Carboxymethylation of Chitosan Beads. Wet chitosan beads (containing 5 g dry basis of chitosan) was immersed in 100 mL of 1.69 $mol\cdot L^{-1}$ NaOH solution in a 500 mL Erlenmeyer flask to swell and alkalize for 12 hours. 7.5 g monochloroacetic acid dissolved in 20 mL isopropanol, was then added drop-wise into the flask over 30 min. The reaction mixture was left for 4 hours at room temperature and was stopped by adding 200 mL 70% ethanol. The solid was then filtered and rinsed with 70% ethanol. The beads were suspended in 100 mL ethanol, 50 mL of 37% HCl was added and the reaction shaken for 1 hour. Acid-form of O-carboxymethyl chitosan (CMC) beads were obtained after filtration, rinsing, and then stored in 70% ethanol.

Imprinting of CMC Beads. Wet CMC beads (containing 2 g dry basis of chitosan) were added into 200 mL of 10 $mmol\cdot L^{-1}$ silver nitrate ethanol solution in a 500 mL flask and shaken for 24 hours. The beads were filtered and excess Ag was removed by rinsing with 70% ethanol, then stored in ethanol for use.

Crosslinking Imprinted CMC Beads. 1.5 g of thiourea was dissolved in 30 mL of deionized water. The thiourea solution was then mixed with 8.5 mL of 50 wt% glutaraldehyde in a flask. The mixture was heated in an incubator at 50 ℃, shaking at 150 rpm for 3 hours. Wet imprinted CMC beads (containing 1.0 g dry basis of chitosan) and 70 mL ethanol were mixed with the thiourea/glutaraldehyde solution and heated at 70 ℃, shaking at 150rpm for 8 hours. The beads were then filtered and washed with dilute sodium hydroxide, deionized water, and finally acetone. The beads were air dried for 48 hours to remove the acetone then stored in deionized water.

Desorption of Ag (I) from CMC beads. Water solution containing 3.5 wt% of thiourea and 0.075 vol% of H_2SO_4 was used to desorb the imprinted Ag (I) from CMC beads. The solution was left for 1 hour with constant shaking at 150 rpm. 0.1 g of silver-imprinted crosslinked CMC was then added into 100 mL of desorbent. After shaking for 24 hours, the beads were filtered and rinsed with deionized water, then air-dried for 24 hours.

Batch Absorption Experiments

Bimetallic solution containing 1.0 $mmol\cdot L^{-1}$ $AgNO_3$ and 1.0 $mmol\cdot L^{-1}$ $Cu(NO_3)_2$ with a pH value of 5.0 was used for the sorption test. 100 mL bimetallic solution was mixed with 100 mg sorbent in a 500 mL Erlenmeyer flask under agitation of 150 rpm for 24 hours at room temperature. After filtration, the filtrate was analyzed by ICP-OES to determine the final concentrations of metal ions in the solution.

The experiments for adsorption isotherm were conducted at 25 °C and pH 5.0 for 24 hours in a working solution volume of 100 mL. The working solution contained equal mole of Ag (I) and Cu (II). The initial metal concentrations varied between 0.25–2.0 $mmol\cdot L^{-1}$.

200 mL $AgNO_3$ solution with an initial concentration of 1.0 $mmol\cdot L^{-1}$ at pH 5.0 was fully mixed with 100 mg sorbent at 25 ℃ and 300 rpm shaking speed in the incubator for kinetic study. Samples will be collected at different time intervals and filtered for later metal concentration measurement by ICP-OES.

Analytical Method

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the concentration of metal ions.

Results and Discussion

Sorbent Screening

Results of Ag (I) uptake by different biosorbents at 25 ℃ and pH 5.0 are shown in Table 1. Based on the data shown in the table, all prepared biosorbents show superb selectivity towards Ag (I) when equal molar concentration of Cu (II) exists in the solution. The most promising biosorbent with highest Ag (I) uptake was obtained when the molar ratio of amino group of chitosan to carboxymethylation agent to crosslinking agent of 6:15:16 is used (No.1 in the table below). Thus, the crosslinked imprinted CMC beads prepared under this condition have been chosen for further experiments.

Table 1. Selective sorption of Ag(I) on CMC beads

No.	Molar ratio of amino group to carboxymethylation agent	Molar ratio of amino group to crosslinking agent	Imprinted or Not	*Uptake*$_{Ag}$ $mg\cdot g^{-1}$	*Uptake*$_{Cu}$ $mg\cdot g^{-1}$
1	2:5	3:8	Y	79.65	0.37
2	2:5	3:8	N	43.91	0.49
3	2:5	3:16	Y	39.19	0.26
4	2:5	3:16	N	35.00	0.10
5	4:5	3:8	Y	44.59	0.50
6	4:5	3:8	N	32.53	1.25
7	4:5	3:16	Y	47.00	0.82
8	4:5	3:16	N	38.08	0.61

Effect of pH

Results of silver uptake by the selected biosorbent at different initial pH are shown in Figure 1. As seen from Figure 1, the selected biosorbent shows relatively high uptake towards Ag (I) over the pH range from 1.0 to 6.0. Compared with the uptake at pH 4.0, 5.0 and pH 6.0, the difference is less than 4%, which can be considered as a result of experimental error. Considering the pH of silver nitrate solution is around 5.0, further sorption tests were conducted at pH 5.0 instead of pH 4.0, because abolishing pH adjustment means less chemical were consumed during the sorption test, which is better both environmentally and economically.

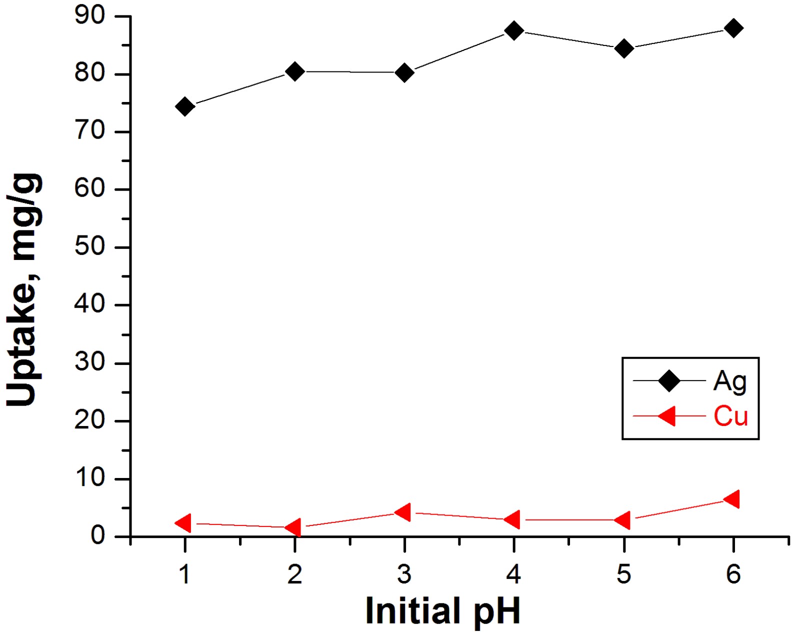

Figure 1. Effect of pH on uptake of Ag (I) and Cu (II)

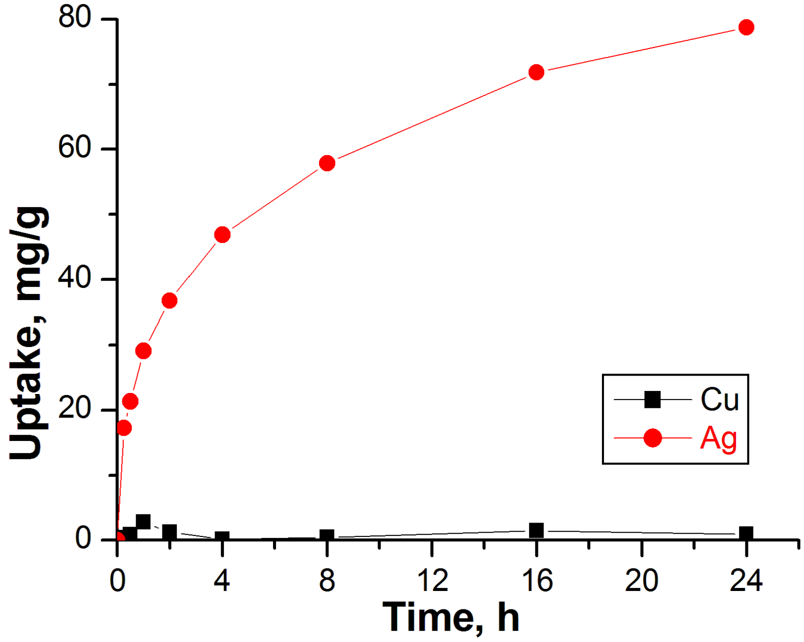

Figure 2. Effect of contact time on uptake of Ag (I) and Cu (II)

Table 2. Kinetic parameters of the biosorption of Ag (I) on silver-imprinted crosslinked CMC beads

Pseudo-first-order			Pseudo-second-order		
k_1 (h^{-1})	q_e, calculated ($mg\cdot g^{-1}$)	R^2	k_2 ($g\cdot mg^{-1}\cdot h^{-1}$)	q_e, calculated ($mg\cdot g^{-1}$)	R^2
0.133	58.585	0.994	0.007	81.169	0.985

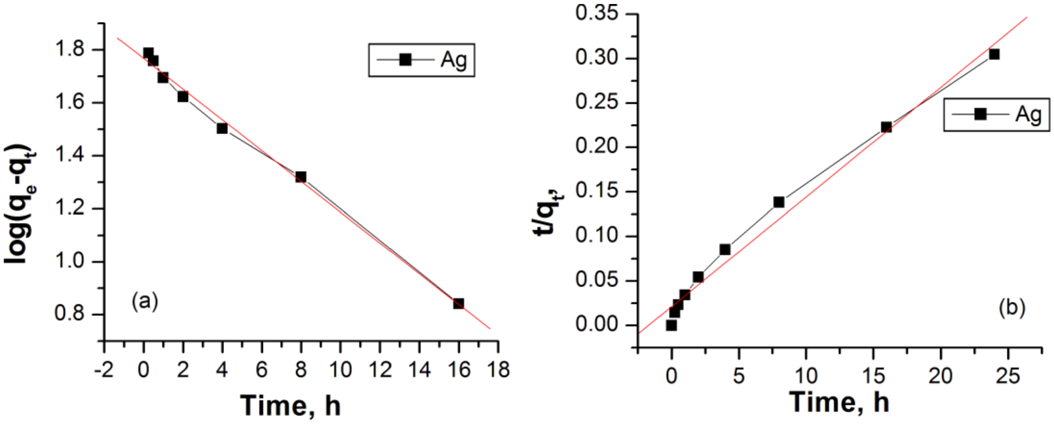

Figure 3. Pseudo-fisrt-order (a) and Pseudo-second-order (b) kinetics of the sorption of Ag (I) at 25 ℃ and pH 5.0.

Absorption Kinetics

The effect of contact time on the biosorption of Ag (I) and Cu (II) is demonstrated in Figure 2. Recurrently, the biosorbent showed superb uptake selectivity of Ag (I). Because Cu (II) is scarcely adsorbed by the prepared sorbent, kinetic rate constants for the biosorption of Cu (II) were not incorporated in this study.

The kinetic of biosorption is an important characteristic which defines the efficiency of sorption. In order to evaluate the kinetic mechanism that controls the biosorption process, pseudo-first-order and pseudo-second-order were employed to interpret the experimental data.

The pseudo-first-order equation is in the form of,

$$q_t = q_e(1-\exp^{-k_1 t}) \tag{1}$$

Its linearized equation is given below,

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \tag{2}$$

where k_1 (h^{-1}) is the pseudo-first-order biosorption rate constant, q_t ($mg\cdot g^{-1}$) is the amount absorbed at time t (h), and q_e ($mg\cdot g^{-1}$) is the amount absorbed at equilibrium.

The pseudo-second-order equation can be expressed by,

$$q_t = \frac{k_2 t}{1+k_2 q_e t} \tag{3}$$

The equation below is the linear form of pseudo-second-order equation,

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e}\right)t \tag{4}$$

where k_2 (g·mg^{-1}·h^{-1}) is the pseudo-second-order biosorption rate constant, while all the other parameters have the same physical meanings as those in the first order equation.

The kinetic parameters for the rate equations were determined from the linear plots of log (q_e-q_t) vs t (Figure 3) for pseudo-first-order and (t/q_t) vs t (Figure 3) for pseudo-second-order. The results are shown in Table 2.

From Figure 3, it is observed that biosorption of Ag (I) can be well described by both models since the high value R^2 were obtained in both cases as seen from Table 2. But pseudo-second order model is better with a more accurate calculated q_e.

Absorption Equilibrium Isotherm

Figure 4 shows the effect of initial concentration on the biosorption of Ag (I) on the prepared CMC biosorbent. Both Langmuir and Freundlich isotherm models were used to describe the amount of Ag (I) absorbed and its equilibrium concentration in aqueous solution.

The Langmuir and Freundlich equations are given in Eqs.5 and 6, respectively,

$$q_e = \frac{q_s b c_e}{1 + b c_e} \tag{5}$$

$$q_e = K_F c_e^{1/n} \tag{6}$$

where q_e (mg·g^{-1}) is the absorbed amount of Ag (I) at equilibrium concentration, c_e (mg·L^{-1}) is the equilibrium concentration of Ag (I) in solution, q_s (mg·g^{-1}) is the maximum biosorption capacity, b is the Langmuir binding constant, K_F is a constant indicative of the adsorption capacity of the sorbent, and 1/n is a measure of adsorption intensity.

Both Langmuir and Freundlich models can be converted into linear forms as shown in Eqs.7 and 8 and the isotherm parameters can be determined by linear regression. The determined Langmuir and Freundlich isotherm parameters can be found in Table 3.

$$\frac{c_e}{q_e} = \frac{c_e}{q_s} + \frac{1}{q_s b} \tag{7}$$

$$\log q_e = \log K_F + 1/n \log c_e \tag{8}$$

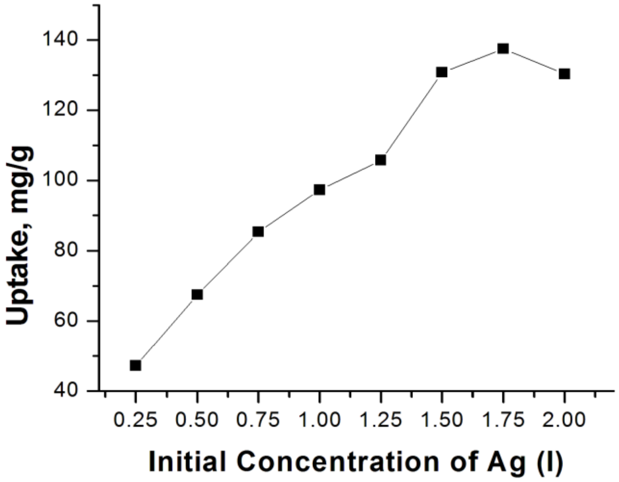

Figure 4. The uptake of Ag (I) at different initial concentrations at 25 ℃ and pH 5.0.

Table 3. Isotherm parameters of the biosorption of Ag(I) on silver-imprinted crosslinked CMC beads

Langmuir			Freundlich		
b mg^{-1}	q_s (mg·g^{-1})	R^2	K$_F$	n	R^2
0.02737	167.224	0.980	16.7656	2.3299	0.964

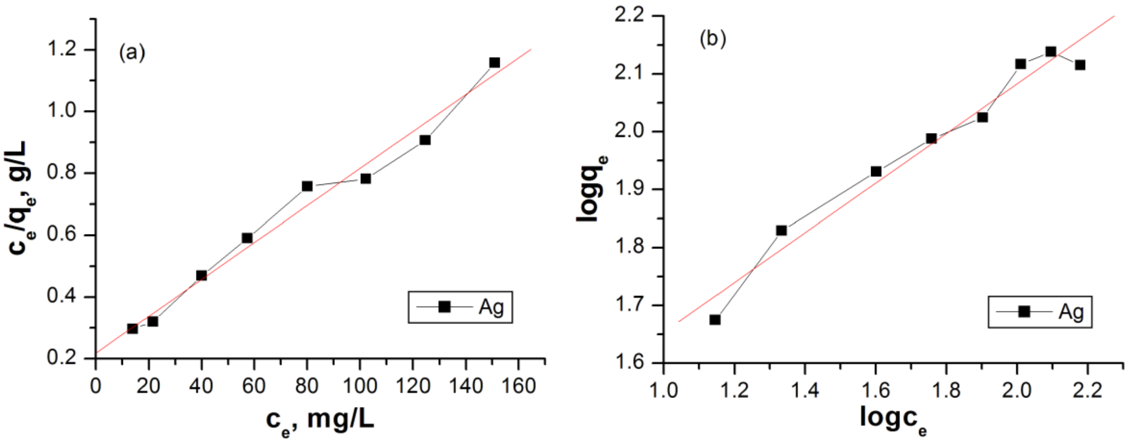

Figure 5. Langmuir (a) and Freundrich (b) isotherm.of the biosorption of Ag (I) at 25 ℃ and pH 5.0.

Results indicate that Langmuir model represents the experimental data better than Freundlich model. The Degree of suitability of the selected biosorbent towards Ag (I) was estimated from the values of the separation factor (R_L) using the following equation (Qi and Xu, 2004)

$$R_L = \frac{1}{1 + bc_0} \tag{9}$$

Different RL values have different physical meanings, for example $R_L>1$ means process unsuitable; $R_L=1$ linear, $0<R_L<1$ suitable, $R_L=0$ irreversible. The values of R_L for this study lie between 0.1446 and 0.5859 for all concentration ranges which indicate the selected biosorbent is suitable for the absorption of Ag (I) from aqueous solution under the conditions used in this study.

Conclusions

The biosorption of Ag (I) using silver imprinted thiourea modified glutaraldehyde crosslinked carboxymethyl chitosan was studied. The results indicated that all biosorbents prepared under different conditions have superb selectivity towards Ag (I) in all ranges of initial concentration, initial pH, and contact time. The maximum uptake of Ag (I), 137.5 mg·g^{-1}sorbent, was obtained at 25 ℃ and pH 5.0 when the initial concentration was 1.75 mmol·L^{-1}. The best performance biosorbent was prepared when the molar ratio of amino group of chitosan to carboxymethylation agent to crosslinking agent was 6:15:16. The isothermal and kinetic study revealed that the biosorption process of Ag (I) fits well with a Langmuir model and Lagergren's Pseudo-second-order rate equation.

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