Kinetic Modeling and Effect of Process Parameters on Selenium Removal Using Strong Acid Resin

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Abstract—**Heavy metal pollution due to the contamination of Selenium above the tolerable limit in the natural environment is a challenging issue that environmental scientists face. This study is aimed at identifying ion exchange technology as a feasible solution to remove selenium ions using 001x7 resin. Parametric experiments were conducted to identify the optimal pH, sorbent dose and speed of agitation. Selenium removal efficiency of 85% was attained at pH 5.0 with 100 mg/L selenium concentration. The increase in resin dose was found to increase removal efficiency. However, metal uptake decreased. The experiments on the effect of concentration proved the negative effect of higher concentrations of selenium on removal efficiency. The ion exchange process was proved to be optimal at an agitation speed of 200 rpm and a temperature of 35 °C. Pseudo second order model was found to fit the kinetic data very well compared to the pseudo-first order model and the pseudo second order rate constant was estimated as 8.725×10^{-5} g mg^{-1} min^{-1} with a solution containing 100 mg/L selenium.**

Keywords-metal removal; kinetics; selenium; acid resin

I. INTRODUCTION

Selenium is one of the metals which is present naturally in earth's crust with black shale, phosphate rocks and coal as major sources[1]. Selenium is distributed in many oxidation states and forms like selenite (Se_3^{2-}, Se(IV)),selenide (Se^{2-}) and selenite (SeO_4^{2-}, Se VI)), in different phases depending on the aquatic, terrestrial and atmospheric geological resources with Se(IV) and Se(VI) commonly found in aqueous media [2]. Se(IV) is reported to be more toxic than Se(VI).The threshold permissible limit of selenium is 10 µg/L according to World Health Organization (WHO) regulations while USEPA allows a maximum level of 50 µg/L [3]. Depending on the type of release sources, the selenium levels and forms vary. The choice of the appropriate method of treatment is dependent on the speciation of selenium and the presence of competing ions. Various physico-chemical methods like evaporation, chemical precipitation, coagulation and membrane processes are applied for the removal of metals [4]. But, the physical and chemical processes suffer from demerits like high operating costs, excessive usage of chemicals and production of secondary pollutants [5-6]. Biosorption has been proposed as an alternative method for the removal of metals with special attention to naturally available biomass as a sorbent material [7]. Biosorptive removal of selenium using dried biomass of Saccharomyces cerevisiae has been reported [8]. Studies on removal of Se(IV) and Se(VI) using Fe-based and Al-based coagulants were reported to achieve high removal percentages [2]. But the feasibility of biological methods was not investigated for high concentrations of selenium [6]. Among these various methods, Ion exchange offers a suitable choice for application. Ion exchange method utilizes the ion exchange resins which are high molecular weight polysaccharides in insoluble form and the resins possess the ability to exchange their mobile ions for ions of similar charges from the surrounding environment [9]. Removal of nickel and zinc using amberlite IR-120 resin has been reported and the kinetic data were presented [10]. Two macro porous resins, D-201 and D-301, have been utilized to remove mono butyl phthalate and physical adsorption was identified as the mechanism [11]. In this research study, the main objective was to investigate the feasibility of utilizing a strong acid cation exchange resin, 001x7, for the removal of selenium from aqueous solutions. The effect of process parameters, namely initial pH, selenium concentration, resin dose, shaking speed and operating temperature was studied. Kinetic modeling was performed using pseudo-first order and pseudo-second order models.

II. EXPERIMENTAL

A. Resin and chemicals preparation

In this experimental study, a strong acid cationic resin 001x7 containing sulphonic acid (SO_3H) as the functional group, was chosen. This resin consists of SO_3H groups on styrene based polymer and the acidity of this resin is similar to HCl and H_2SO_4. This cation exchange resin has moisture content in the range of 45–55% and was used for water softening applications. The particle size of the supplied resin was in the range of 0.42-1.2 mm in diameter. The resin was washed with deionized water repeatedly for several times and dried at 50 °C in a vacuum oven for 12 h. Selenium stock solution containing Se(IV) ions was prepared by diluting 1000 mg/L of Na_2SeO_3 standard solution (Aldrich, Germany) with deionized water. pH adjustments were performed using analytical reagent (AR) grade HCl, NaOH and buffer solutions (Merck, Germany). FTIR characterization of the resin have been reported in [12].

B.   Parametric Experiments

The parametric experiments were conducted under shaking conditions with pH studies as the primary step. Batch ion exchange studies were conducted using a sample of 100 ml of the metal solution and agitated in an orbital shaker at different experimental conditions based on the experimental design for an equilibrium time of 150 min which was fixed after preliminary experiments. The effect of pH was studied in the range of 2.0- 9.0 at fixed operating conditions. The adjustment of pH of the samples was done by adding either 0.1N HCl or NaOH as the buffering agent. Different resin quantities ranging from 0.25 to 2.0 g/L were tested at optimal pH and an initial metal concentration of 100 mg/L. The effect of different initial selenium concentrations on the percentage metal removal was studied in the range of 0-200 mg L^{-1} at a pre-determined optimal pH and resin quantity. The effect of agitation was studied in the range of 0-300 rpm while the temperature effect was investigated at 30, 35 and 40 °C respectively. At fixed time intervals, a sample of solution was withdrawn and filtered. The filtered sample was analysed for residual metal concentrations using inductively coupled Plasma – Optical emission spectrometer (Thermo Fischer scientific, Japan). In order to determine the mechanism of removal, kinetic studies were conducted. The experimental data were fitted to Pseudo-second order and intra particle diffusion models and linearity of fit is verified. The metal uptake was calculated by using the following equation:

$$q = (S_o - S_e)V/R \qquad (1)$$

Where q is the amount of metal adsorbed by the resin at any time, t (mg g^{-1}); S_o and S_e are the initial and final selenium concentrations (mg L^{-1}), respectively; V is the volume of sample solution (L) and R is the resin quantity (g). The percentage selenium removal is defined by:

$$\% \text{selenium removal} = \frac{(S_o - S_e)}{S_o} \times 100 \quad (2)$$

C.   Kinetic models

The pseudo-first order kinetic model is represented as:

$$\ln(q_e - q) = \ln q_e - k_1 t \qquad (3)$$

where q_e is the amount of metal adsorbed by the resin at equilibrium(mg/g) and k_1 is the first order rate constant (g mg^{-1} min^{-1}). The slope and intercept of the linear plot $\ln(q_e - q)$ vs time will give the values of the model constants.

The Pseudo-second order model [13] can be represented as:

$$\frac{t}{q} = \frac{1}{h_2} + \frac{t}{q_e} \qquad (4)$$

where, q_e, the amount of dye adsorbed at equilibrium (mg g^{-1}), $h_2 = k_2 q_e^2$, the initial exchange rate (mg g^{-1} min^{-1}) and the pseudo-second-order constant k_2 (g mg^{-1} min^{-1}) can be determined experimentally from the slope and intercept of plot t/q versus t.

III.   RESULTS AND DISCUSSION

A.   Effect of pH

Ion exchange studies were strongly influenced by pH conditions as the speciation of ions are restricted by pH variations. Moreover, pH changes were reported to induce precipitation of compounds. The fraction of free ions is dependent on the pH conditions [10]. In this set of experiments, the initial pH of the solution was varied in the range of 2.0–9.0 and the selenium removal percentages were estimated. Figure 1 presents the influence of pH on the selenium removal efficiency studied at fixed initial metal concentration of 100 mg/L. The maximum removal of selenium was determined as 91% obtained at a pH of 5.0. In the acidic pH range of 2.0-4.0, the removal efficiencies attained were low which could be due to the competition posed by hydrogen ions with selenium ions for exchange with the resin. The reduction in removal efficiency when the pH was greater than 5.0 was related to precipitation phenomenon. Nickel removal using the 001x7 resin reported a similar influence of pH [12]. Zinc, copper and lead removal using Dowex 50W resin reported similar observation. Most of the studies reported poor metal removal when pH<4.0 [14]. In addition, high acidity was reported to be unfavorable for efficient metal removal [15].

B.   Effect of resin dosage

Resin dosage, which is defined as the quantity of resin added per unit volume of sorbate solution, is an important process variable. The effect of 001x7 resin dosage was studied in the range of 0.25–2.0 g/L while the initial metal concentration was fixed at 100 mg/L and pH at optimal value of 5.0 and presented in Figure 2. The metal removal efficiency depends on the availability of free sites for exchange and thus increased with increase in resin dose. The efficiency increase was considerably high in the resin dose range of 0.25 to 1.0 g/L and the increase was not proportionate at the higher dosages of 1.5 and 2.0 g/L. The optimal resin dosage was identified as 1.0 g/L and used further in all other parametric experiments. Excessive presence of actives sites could be the reason. The metal uptake exhibited a contrary behaviour with increase in resin dosage leading to decrease in selenium uptake. The split in the flux and aggregation of sites were reported to be responsible for the decrease in metal uptakes with increase in sorbent dose [7].

C.   Effect of initial selenium concentration

The selenium concentrations reported in various industrial effluents were found to be in the range of 0 -74 mg/L [6]. With reference to this range, the effect of concentration study was conducted in the selenium concentration of 50-200 mg/L. The experimental conditions were fixed at pH=5.0 and resin dose=1.0 g/L with an equilibrium time of 150 min. Figure 4 presents the effect of the initial metal concentration on the removal efficiency of selenium. The equilibrium removal efficiencies attained at lower selenium concentrations of 50 and 100 mg/L were found to be 95% and 85% respectively. With an increase in initial selenium concentration, the removal efficiency is decreased. Limitations on the availability of ion exchange sites for different concentration and free surface with

the cation exchange resin could be the reasons for this effect [12]. The equilibrium efficiencies were attained at 150 min for all the concentrations except 50 mg/L. Various studies on the removal of metals by ion exchange and adsorption report a similar relationship between concentration of metal and efficiency [7, 12, 16].

D. Effect of agitation speed

Ion exchange is a surface exchange process where an efficient contact between the ions to be exchanged is very vital. The agitation speed, found to be responsible for effective contact, was varied in the range of 0-400 rpm and its effect on selenium uptake are presented in Figure 4. The initial concentration of selenium and pH were maintained at 100 mg/L and 5.0, respectively. The metal uptake increased from 5.4 to 74.0 mg/g when the speed increased from 0-300 rpm. The change in uptake was appreciable in the range of 0–200 rpm whereas no significant increase was observed at 300 rpm. The stirring velocity in the rpm range of 0-200 rpm was much more beneficial and resulted in better uptakes. At a very high speed of 400 rpm, a decrease in uptake was observed which could be contributed by the excessive shear force. Similar effects of high agitation speeds on metal uptakes have been reported in studies on mercury removal [7]. The controlling mechanism in an ion exchange process could be either chemical rate or intraparticle diffusion or both. Since no appreciable increase in uptake was observed at high speeds, the optimal agitation speed was chosen as 200 rpm. Reduced or no influence on metal uptake at speeds greater than 150 rpm confirms the presence of more than one rate controlling mechanisms. Copper(II) ions removal using Purolite C 100: MB resin reported identical observations [17].

E. Influence of temperature

Separation processes are temperature dependent as diffusion and solubility are influenced by temperature effects. The studies on effect on temperature on the selenium removal was conducted at 30, 35 and 40 °C respectively at uptake at constant experimental conditions of initial metal concentration 100 mg/L, pH 5.0 and speed of agitation 200 rpm. From Figure 5, it can be observed that the metal uptake capacities increased with an increase in temperature which proves the endothermic nature of the ion exchange process. Surface energy of the resin was reported to be influenced by the surrounding temperature. Similar effects on ion exchange studies using Dowex resin [14] and 001 x7 resin have been reported [12].

F. Kinetic studies

Kinetic experiments are performed to identify the chemical or physical nature of the removal mechanism. The following ionic stoichiometry represents the ion exchange process mechanism [18] as given in:

$$Si_s^{4+} + 4R\text{-}Na \rightarrow R_4Si + 4Na^+ \qquad (5)$$

Figures 6 and 7 depict the linearized forms of equations of the pseudo-first order and pseudo-second order models. The linearity of the data was verified using correlation coefficients and the pseudo-first order model was found to fit the results

with values of $R^2 > 0.950$. The kinetic model constants, namely the rate constants (k_1, k_2) and uptakes (q_e), were determined form the slopes and intercepts of the kinetic plots. The values of the kinetic constants for the two models selected are presented in Table I at different initial metal concentrations. The variation in the pseudo second order model (the best fit model) rate constant with respect to the metal concentration are presented in   Figure 8 and an inverse proportionality was found to exist between the rate constant and initial metal concentration. Gulipalli et al [19] reported the suitability of pseudo-second order model for the removal of selenium by adsorption using rice husk ash. Similar observations on rate constant variations have been reported [12].

TABLE I.   KINETIC MODEL CONSTANTS

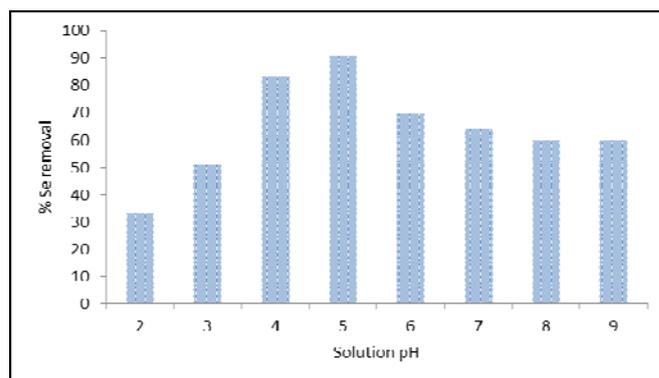| Kinetic model	Initial selenium concentration(mg/L)			
	50	100	150	200
Pseudo first order				
q_e (mg/g)	2.28	2.26	1.689	1.849
$k_1 \times 10^3$(g mg^{-1} min^{-1})	11.9	14	13.6	12.5
R^2	0.821	0.806	0.797	0.892
Pseudo second order				
q_e (mg/g)	108.7	113.6	122.0	129.9
$k_2 \times 10^5$(g mg^{-1} min^{-1})	9.36	8.725	8.25	7.72
R^2	0.984	0.952	0.983	0.962

Fig. 1.   Effect of pH on selenium removal using   resin 001x7 (t =150 min, C_0 = 100 mg/L).
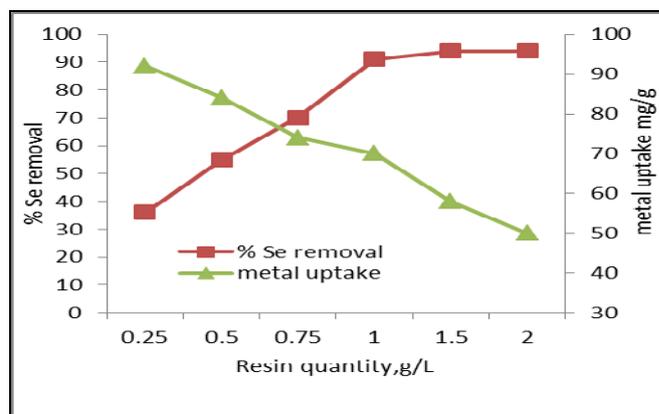

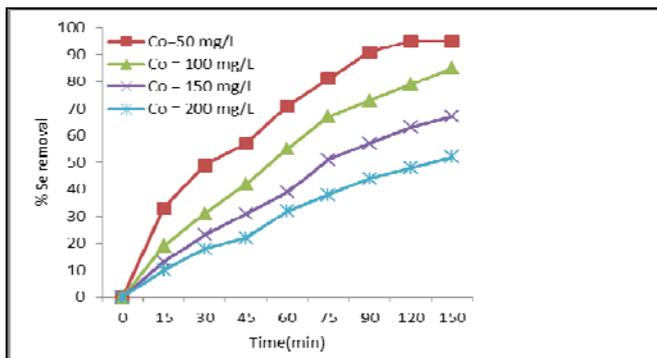Fig. 2.   Effect of resin dosage on % selenium removal and uptake (t =150 min, C_0 = 100 mg/L).

Fig. 3.   Effect of initial selenium concentration on % metal removal using resin 001x7(t=150 min, pH =5.0)
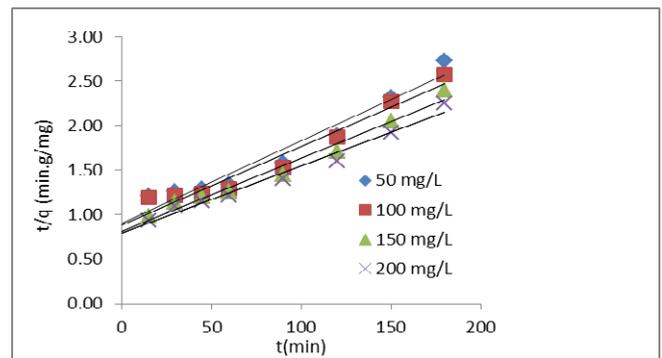

Fig. 4.   Effect of speed of agitation on metal uptake (t =150 min, C_0 = 100 mg/L)

Fig. 5.   Effect of temperature on   metal uptake using resin 001x7 (t =150 min, C_0 = 100 mg/L)

Fig. 6.   Pseudo-first-order kinetic model plot for the removal of selenium

Fig. 7.   Pseudo-second-order kinetic model plot for the removal of selenium

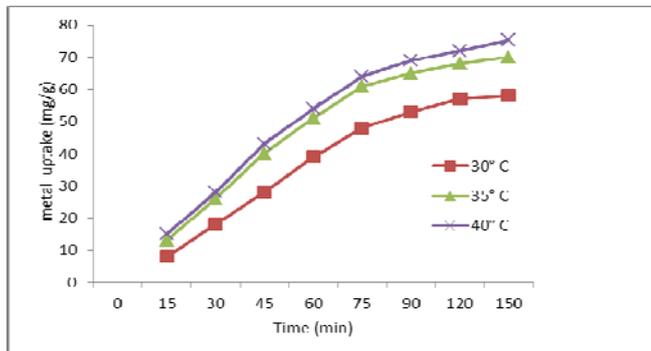
Fig. 8.   Effect of selenium concentration on the pseudo second order rate constant
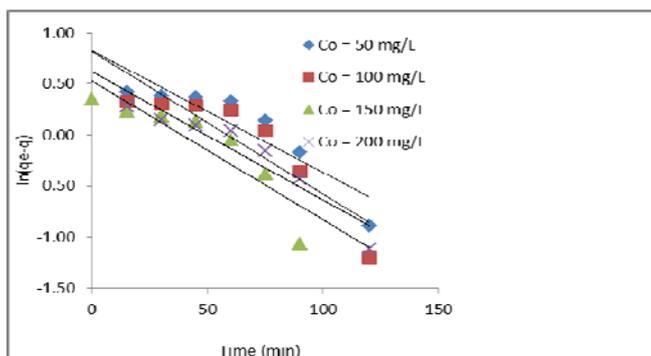
IV. CONCLUSIONS

The strong acid cation resin 001x7 was utilized for the removal of selenium ions from its aqueous solution. The optimal operating conditions were determined as: pH 5.0, resin dosage 1.0 g/L, agitation speed 200 rpm and temperature 35°C. Highly acidic conditions were found to decrease the metal removal efficiency. The selenium uptake was estimated as 70 mg/g at an optimal pH of 5.0 and initial selenium concentration of 100 mg/L. The selenium uptake decreased with increase in resin dosage and the ion exchange process was found to be endothermic as higher temperatures led to better removal. The correlation coefficients for the pseudo second order model was higher (>0.95) and the model constants were estimated at different selenium concentrations. Thus, the feasibility of utilizing 001x7 for selenium removal was validated and the kinetic mechanism was investigated.

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