

SHALLOW SHELL RESIN VERSUS TRADITIONAL RESIN: A CASE STUDY FOR Cu(II) REMOVAL

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ABSTRACT

A comparative study on Cu²⁺ removal by shallow shell resin (Purolite SST 60) and traditional strongly acidic cation exchange resin (Purolite PFC 100) was performed. Batch experiments were carried out as a function of resin dosage, solution pH and contact time. Ion exchange reaction showed a pH dependent feature. Maximum removal of Cu²⁺ achieved pH from 2 to 5. Sorption isothermal data is well interpreted by the Langmuir equation. Additionally, kinetic experiments showed that the pseudo first-order model was suitable for such resins. Thermodynamic parameters such as ΔG° , ΔS° and ΔH° of the ion exchange Cu²⁺ on cation exchange resins were also calculated. The regeneration performance of shallow shell technology (SST) resin is better than PFC 100. A solution of 2M H₂SO₄ performed complete regeneration of SST 60 resin. On the other hand, maximum regeneration reached 80% for PFC 100 resin.

Keywords: Cation exchange, Copper, Shallow Shell resin, SST 60, Traditional resin

1. INTRODUCTION

Ion exchange consists of interchanging of ions between two phases. With ion-exchange resins, the resin cross-linked polymer networks is the insoluble phase to which an ion is electrostatically bound; when contacted with a solution containing ions of the same charge, an exchange can take place, the extent to which depends on the concentration of the ion(s) in solution and the affinity of the ion(s) for the insoluble phase relative to the solution phase [1]. The most common ion exchange materials (IEMs) are ion exchange resins (IERS), manufactured as polymeric beads, which have particle sizes ranging from 0.3 to 1.2 mm, that reversibly exchange ions in solutions. Such reversibility allows IERS to be regenerated and reused, thus resulting in substantial cost savings over non-recyclable metal removal systems [2]. Chemical properties of functional groups define the characteristics of ion exchange materials. Cation and anion exchangers are the two types bearing respectively that are negatively and positively charged groups, therefore such materials are able to exchange cations or anions. Due to different dissociation properties of functional groups, strong and weak ion-exchangers are recognized similar to strong and weak electrolytes [3]. Ion exchange (IX) technology has various applications in various industrial fields, such as industrial water treatment, food and beverage, pharmaceuticals, petrochemicals, and hydrometallurgy. IX also plays an important role in the removal of impurities from process solutions to improve their purity which leads increase in the value of the final products [4]. The efficiency of ion exchange operation is determined by the amount of excess chemical used to drive the regeneration reaction. Regeneration efficiency not only drives the economics of the ion exchange process but increasingly, has become a limitation on new ion exchange considerations because of the restrictions on regenerant waste disposal [5]. Overall ion exchange efficiency is limited by the rate at which regeneration takes place. Decreasing the length of the regenerant work path by partial (surface) functionalization, leaving an inert core (shallow shell technology), allows ion exchange resins to higher regeneration efficiency, substantially reducing excess chemical usage with no sacrifice in capacity or leakage. The advent of shallow shell resins allows co-current regenerated systems to offer similar capacities and leakages previously only achieved in counter-current regenerated systems [6]. Shell-core ion exchange resins have been used for years in pellicle form in which the functionalized shell is very

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shallow and is used for high speed analytical chromatography. Additionally, shell-core resins have been made by grafting copolymers onto the surface of inert beads, such as glass. The result of the latter has always been that the functionalized shell peels from the inert core when cycled normally [7].

In this work, a shell-core resin (Purolite SST 60) was compared with traditional ion exchange resin (Purolite PFC 100) for removal of Cu^{2+} . The effect of resin dosage, solution pH, speed rate, temperature as well as the kinetic of such resins were compared. In addition, regeneration of resins was also tested.

2. EXPERIMENTAL

2.1. Materials

This research was performed using the commercially available ion exchange resins, Purolite SST 60 and PFC 100 which are strongly acidic cation exchange resins were obtained from Purolite Int. Co., Italy. The physicochemical properties of these resins were summarized in Table 1.

Table 1. Physico-chemical properties of ion exchange resins

	PFC 100	SST 60
Matrix	Crosslinked Gel Polystyrene	Polystyrene crosslinked with Divinylbenzene
Functional Group	Polystyrene sulphonate	Polystyrene sulphonate
pH limits	0-14	0-14
Physical Form and Appearance	Dark Amber Spherical beads	Clear Spherical beads

Cu^{2+} solutions of different concentrations were prepared from analytical grade $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Merck, Germany). The solutions utilized for pH control (1 Molar) were prepared from HNO_3 (Merck, Germany) and NaOH (Merck, Germany). pH meter (Mettler Toledo, FG2) was calibrated by using pH 4.0 and 7.0 buffers (Merck, Germany).

2.2. Pre-Conditioning of Ion Exchange Resins

Before using the ion-exchange resin; ion-exchange resins were converted to H-form. For this, 100 ml of ion exchange resin was contacted with 150 mL of 2.0 M HCl for 24 h in a shaker. The consumed HCl solution was decanted and then resins were thoroughly washed with deionized water till the pH effluent raised to 4 or higher. The washed resins were air dried and used in experiments.

2.3. Batch Experiments

2.3.1. Effect of resin dosage

Batch experiments were conducted in 50 mL square plastic bottles using 50.0 mL of Cu^{2+} solutions (10.0 mg Cu^{2+} /L, pH 4.0) in a temperature controlled shaker at 25 °C (Nüve ST 402). The various resin amounts (0.01 to 0.05 g) added to the solution and stirred for 24 hours. Following this, the resins were separated by decantation and solution was then analyzed for Cu^{2+} content by atomic absorption spectrometer (Varian SpectrAA 220 model) at a wavelength of 324.7 nm. The standard deviation of each measurement is < 2.0% (Samples were analyzed in triplicates).

The removal efficiency (Re) and ion exchange capacity (q) were calculated according to equations 1 and 2, respectively:

$$q = V \frac{C_0 - C_i}{m} \quad (1)$$

$$\text{Re} = \frac{C_0 - C_i}{C_0} \times 100 \quad (2)$$

In these equations, V is the volume of solution (L); C_0 and C_i are the initial and final concentrations of Cu^{2+} in the solution (mg/L) respectively; and m is the mass of resin (g).

2.3.2. Effect of solution pH

The pH of solution varied from 1 to 5 and it was adjusted by using 1 molar of HNO₃ or NaOH solutions. The optimum resin amounts (0.02 gram) were added to the 25.0 mL solution (10 mg/L of Cu²⁺); then the solutions were stirred in a temperature controlled shaker at 25 °C for 24 hours. Ultimately, the resins were separated and Cu²⁺ concentration in the solution was found out by analyzing the solution.

2.3.3. Equilibrium experiments

Sorption studies of Cu²⁺ were performed as follows: The optimum resin amounts were added to 25.0 ml of solution. The solutions were shaken in a temperature controlled shaker at 25 °C. 24 hours later, solutions were filtered and the Cu²⁺ concentrations were measured. The initial Cu²⁺ concentrations varied from 50 to 1000 mg Cu²⁺/L.

2.3.4. Ion-exchange kinetic

Kinetic tests were performed by implementing optimum resin dosages (0.8-gram resin/L) with 1.0 L of Cu²⁺ solution at pH 4.0. Solution was stirred with an overhead mixer at 400 rpm speed rate. Cu²⁺ concentrations were monitored by taking the samples at prescribed time intervals. The experiments were carried out at 25 °C in temperature controlled water bath.

2.3.5. The effect of different stirring speed

In this series of experiments; the stirring speed varied from 100 to 400 rpm while keeping all other parameters constant (10 mgCu²⁺/L, pH 4, 0.8-gram resin at 25°C).

2.4. Regeneration Experiments

The 2.0 grams of resin was contacted 450 ml of Cu²⁺ solution (1000 mg Cu²⁺/L, pH 4) for 24 hours. Later, the resins were separated from solution by decantation and washed with deionized water then dried in oven at 40 °C. The Cu²⁺ amount in feed and effluent was analyzed and loaded amount of Cu²⁺ on ion exchange resins were calculated. An 0.1 g of dry resin was contacted with 25 ml different regeneration solutions, then the mixture was shaken at room temperature for 24 hours and after this period Cu²⁺ concentration in the solution was determined.

Each experiment (except kinetic experiments) was performed two times and the presented results are the mean of the individual results.

3. RESULTS AND DISCUSSIONS

3.1. Effect of Resin Dosage on Cu²⁺ Removal

The effect of resin amount on the removal of Cu²⁺ was investigated under the same concentration of metal ion solution containing 10 mg Cu²⁺/L. Figure 1 shows the removal of Cu²⁺ versus resin dosage as a function of resin type. According to Figure 1, when the resin dosage was increased, removal of Cu²⁺ increased and after 0.02 gram resin, removal rate reached a plateau. Increase of resin dosage leads to an increase in ion exchange site for Cu²⁺ thus, removal of Cu²⁺ increased. Both resins showed similar trends and optimum resin dosage found 0.02 gram for such resin.

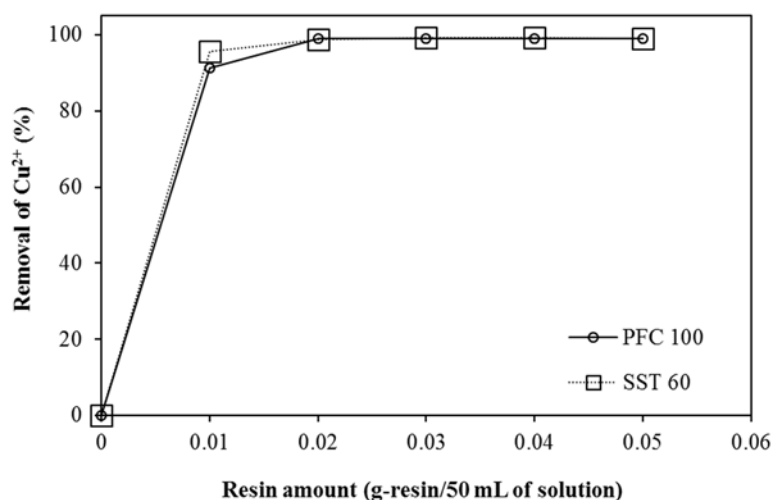
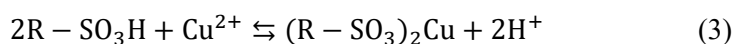


Figure 1. Effect of resin dosage on the removal of Cu²⁺

3.2. Effect of Solution pH

The pH of the aqueous solution is a significant controlling factor in ion exchange mechanism. In order to optimize the pH for maximum removal efficiency, pH of solution varied from 1 to 5. Figure 2 shows the effect of solution pH on the removal of Cu²⁺ by ion exchange resins. The removal rate increases by increasing the pH of the solution. This may be explained as follows: the ion exchange reaction between resins and Cu²⁺ is shown in Equation 3.



It follows from the Le Chatelier principle that, at a given pH in the solution, the exchange rate is increased when the concentration of H⁺ ion in the solution decreased [8]. On the other hand; the sulfonate groups binding Cu²⁺ through a nonspecific electrostatic interaction. The increase in Cu²⁺ removal from solution as the pH increases can be explained on the basis of decrease in competition between protons (H⁺ ions) and metal cations (Cu²⁺ ions) for the same functional groups (-SO₃⁻). According to Figure 2 the removal of Cu²⁺ is optimum in range of 2 to 5. In order to avoid the precipitation of Cu²⁺, high pH values were not studied.

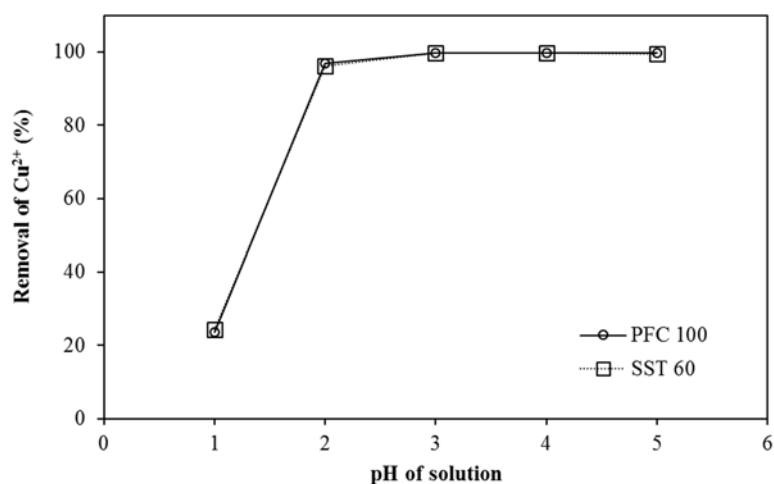


Figure 2. The effect of solution pH on removal of Cu²⁺

3.3. Sorption Isotherms As A Function of Initial Metal Concentration

Several models have been published in the literature to describe experimental data of sorption isotherms and it was noted that the Langmuir and Freundlich models are the most frequently used models [9]. The isotherm graphs were shown in Figure 3-4 and calculated constants were shown in Table 2. As can be seen from Figure 3 and 4, the amount of Cu^{2+} ions sorbed per unit mass of the resin increased with the initial concentration of Cu^{2+} and then reached to plateau which represents saturation of active points.

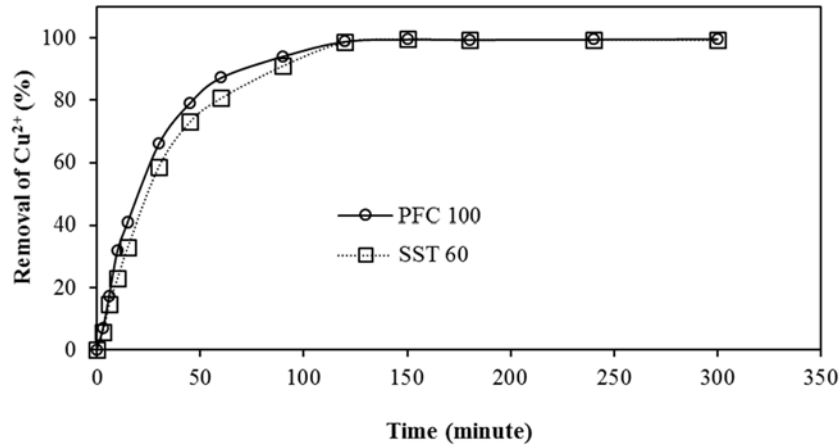


Figure 3. Sorption isotherm for Purolite SST 60 resin

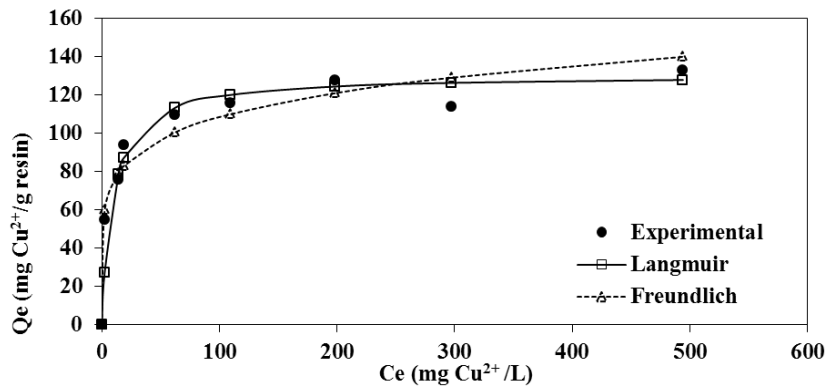


Figure 4. Sorption isotherm for Purolite PFC 100 resin

3.3.1. Langmuir model

The Langmuir isotherm is a commonly applied model for adsorption on completely homogenous surfaces with negligible interaction between adsorbed molecules. The model assumes uniform adsorption energies onto the surface and maximum adsorption depending on saturation level of monolayer [10]. Langmuir model can be represented with the following linear equation 4:

$$\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (4)$$

Where Q_e (mg/g) is the amount of Cu^{2+} sorbed per gram of dry resin at equilibrium, C_e is the equilibrium concentration of Cu^{2+} in the solution (mg/L), Q_0 (mg/g), and b (L/mg) are the Langmuir constants related to the capacity and energy of sorption, respectively.

3.3.2. Freundlich model

The Freundlich model is known as the earliest empirical equation and is shown to be consistent with exponential distribution of active centers, characteristic of heterogeneous surfaces [11]. Freundlich equation is

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

where K_f and n are the Freundlich constants which are indicative of relative capacity and adsorption intensity, respectively. From the obtained results; the regression correlation coefficients (R^2) for Cu^{2+} for both resins are very high (0.99) for the Langmuir model. Langmuir adsorption model assumes that the molecules are adsorbed at a fixed number of well-defined sites, each of which can only hold one molecule. These sites are also assumed to be energetically equivalent, and distant to each other so that there are no interactions between molecules adsorbed to adjacent sites [12].

Table 2. Isotherm constants for Cu^{2+} sorption on the ion exchange resin

Resin	Langmuir Isotherm Constants			Freundlich Isotherm Constants		
	Q_0 ($\text{mg}\cdot\text{g}^{-1}$)	b (L/mg)	R^2	K_f (mg/g)	n	R^2
Purolite PFC 100	130.30	0.11	0.99	51.84	6.24	0.91
Purolite SST 60	139.56	0.08	0.99	49.95	5.65	0.95

3.4. Kinetic of Ion Exchange Resins

The sorption of Cu^{2+} on cation exchange resin was investigated as a function of contact time at 400 rpm speed rate. It was clear from the Figure 5 that the removal of Cu^{2+} was rapid at the beginning time, then increased slowly until the plateau was reached. The fast sorption rate at the incipient stage could be attributed to the increase of driving force provided by the concentration gradient of Cu^{2+} in aqueous solutions and the existence of the great number of available active sites on the ion exchange resins [13]. Complete removal of Cu^{2+} achieved in two hours for such resins. Figure 5 also shows that the kinetic of resins are close to each other and only there is small difference at the beginning of the sorption. It should be noted that variations in the synthesis procedure which resulted in variations in the structure of the matrix, degree of cross linking, density of functional groups, proportion of functional groups and also the particle size affect the performance of resin [14].

The effect speed rate on Cu^{2+} removal was also studied. The speed rate varied from 100 rpm to 400 rpm. As shown in Figure 6 and 7, removal of Cu^{2+} increased when the stirring speed was increased. The quality of the dispersion of the resin in sorption on a batch reactor is a significant factor as in all processes of mass transfer. Stirring influences, the distribution of the aqueous solution and can also act on the formation of an external film of separation. The results show that increases in stirring speed from 100 to 400 rpm significantly modify the coefficient of diffusion of metal ions on the resin. It can be concluded that liquid film thickness decreases with increasing stirring speed [15].

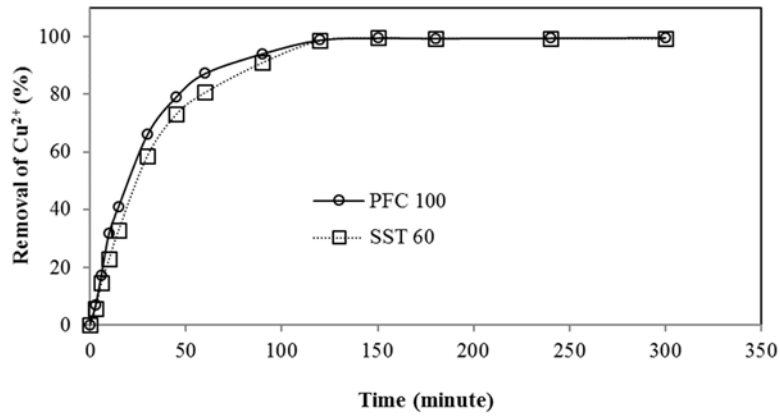


Figure 5. Removal of Cu²⁺ versus time as a function of resin type (speed rate: 400 rpm)

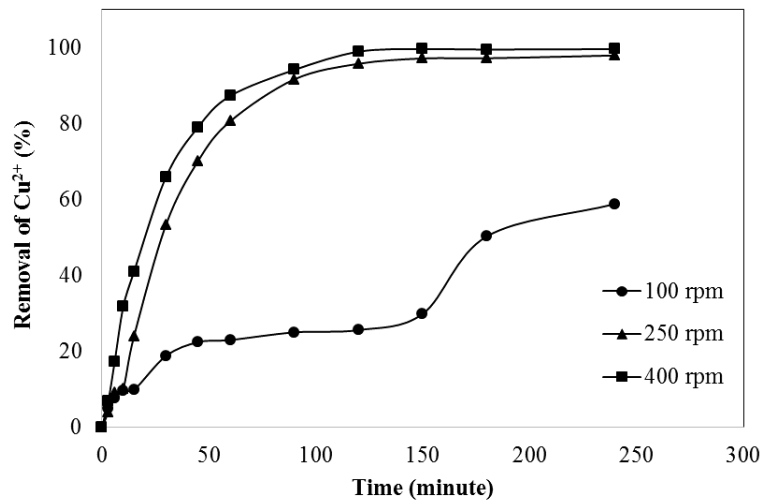


Figure 6. The effect of stirring speed on Cu²⁺ removal by PFC 100 resin [(10 mgCu²⁺/L, pH 4, 0.8-gram resin/L at 25°C)]

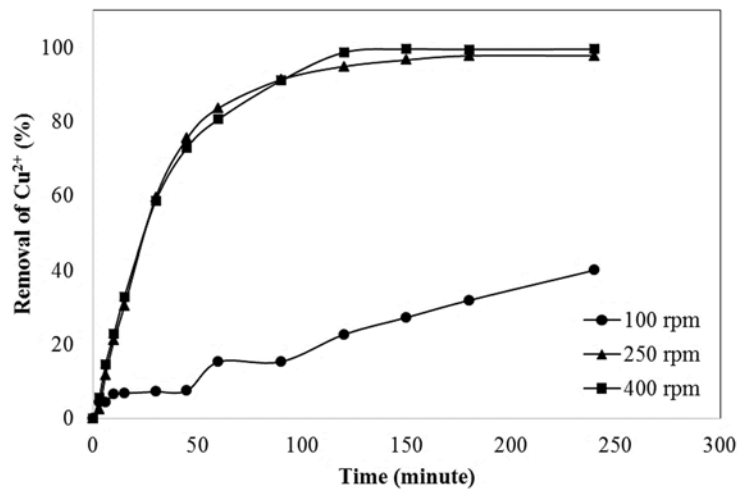


Figure 7. The effect of stirring speed on Cu²⁺ removal by SST 60 resin [(10 mgCu²⁺/L, pH 4, 0.8-gram resin/L at 25°C)]

The two main types of sorption kinetic models, reaction-based and diffusion-based, were adopted to fit the experimental data

3.4.1. Reaction based model

The experimental results were evaluated by using pseudo first order and second order reaction model. The linear form of pseudo first order rate equation was given by following equation 6, [16].

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (6)$$

Sorption rate constant k_1 (min^{-1}) can be calculated from the plot of $\log(q_e - q_t)$ versus time (Figure 8). If the rate of sorption is a second order mechanism, the pseudo-second order chemisorption kinetic rate equation is expressed as equation 7 [17].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (7)$$

If pseudo-second order kinetics is applicable, the plot of t/q_t against t of Eq. (7) should give a linear relationship, from which q_e and k_2 (g/mgmin) can be determined from the slope and intercept of the plot (Figure 9). Constant k_2 is used to calculate the initial sorption rate r ; at $t \rightarrow 0$, as shown in equation 8 [18].

$$h = k_2 q_e^2 \quad (8)$$

The results were summarized in Table 3. Removal of Cu^{2+} by such resins showed good compatibility with pseudo first order kinetic model and also R^2 value is found out to be 0.99. The Figures 8 and 9 also supports these findings.

3.4.2. Diffusion – based models

The intraparticle diffusion model proposed by Weber and Morris in 1963 was also taken into account in the experiments. They concluded that the sorption is proportional to the square root of the contact time [19]:

$$q_t = k_{id} t^{1/2} \quad (9)$$

where k_{id} is the intraparticle diffusion rate constant ($\text{mg}/(\text{g min}^{0.5})$). When the intraparticle diffusion model controls the sorption, the graph of q_t against $t^{0.5}$ should be a straight line passing through the origin. The rate constant can be calculated from the slope of the line. The liquid film diffusion equation is shown as

$$-\ln(1 - F) = k_{fd} t \quad (10)$$

where F is the fractional attainment of equilibrium $F = (q_t/q_e)$, k_{fd} ($1/\text{min}$) is the rate constant. A linear plot of $-\ln(1 - F)$ vs. t with zero intercept would suggest that the adsorption process was controlled by liquid film diffusion [19].

The experimental data fitted in the equations 9 and 10; and obtained results were summarized in Table 3. The R^2 revealed that the retention process is film diffusion controlled mechanism, since such plot provides a better straight-line plot than the intraparticle diffusion controlled mechanism.

Table 3. The calculated parameters of kinetic models

Kinetic model	Parameter	PFC 100	SST 60
Pseudo First order	k_1 (min^{-1})	0.03	0.03
	q_e (mg/g)	10.66	11.36
	R^2	0.99	0.99
Pseudo Second order	k_2 (g/mg min)	0.001	0.001
	q_e (mg/g)	16.19	18.79
	h (mg/gmin)	0.38	0.29
	R^2	0.93	0.92
Intraparticle diffusion model	R^2	0.95	0.94
	k_{id}	1.19	1.13
Diffusion model	R^2	0.99	0.99
	k_{fd}	0.034	0.029

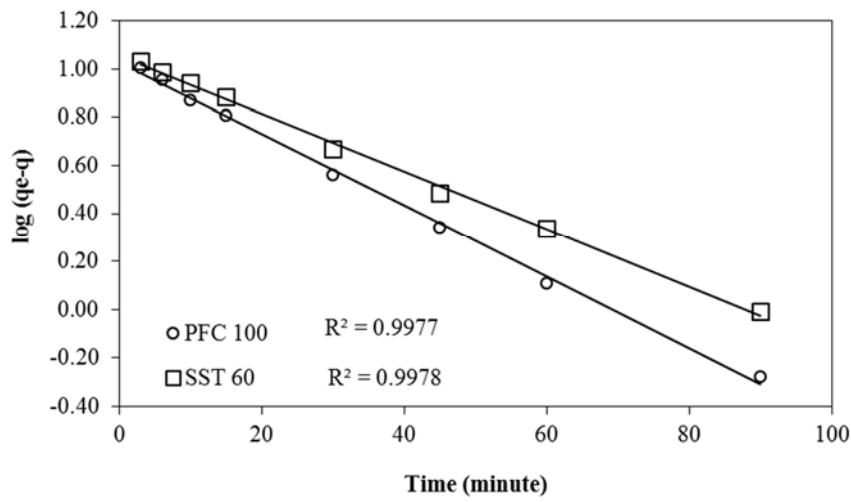


Figure 8. Pseudo-first-order reaction kinetics for the sorption of Cu^{2+} onto ion exchange resins (speed rate: 400 rpm)

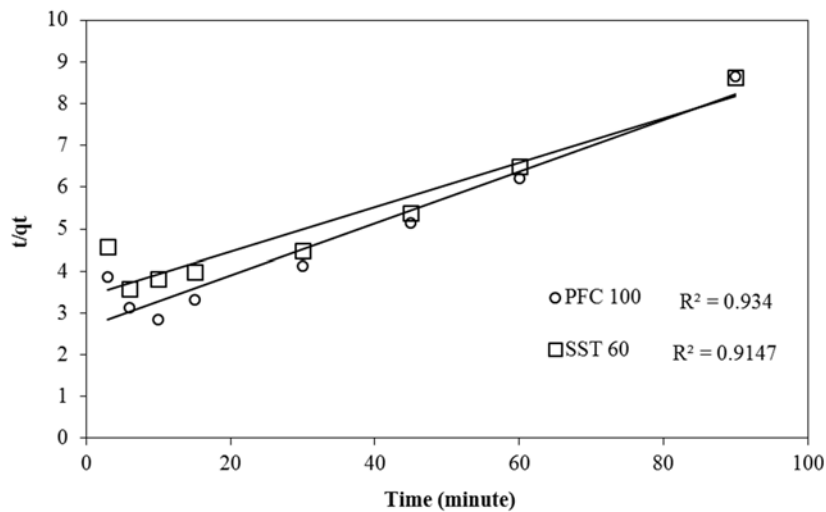


Figure 9. Pseudo-second-order reaction kinetics for the sorption of Cu^{2+} onto Purolite PFC 100 and Purolite SST 60 (speed rate: 400 rpm)

3.5. Thermodynamic Study

Thermodynamic parameters like change in free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) were calculated by using following equations [20]:

$$\Delta G = -RT \ln k_d \quad (11)$$

$$\ln k_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (12)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (13)$$

In these equations, k_d is the equilibrium constant was calculated by q_e/C_e , R is the universal gas constant (8.314 J/mol K), and T is the temperature (K). Parameters change in enthalpy (ΔH^0) and change in entropy (ΔS^0) are calculated from the slope and the intercept of the linear plot of $\ln k_d$ vs. $1/T$ presented in Figure 10 and calculated parameters are presented in the figure and also Table 4 along with values of change in free energy (ΔG^0).

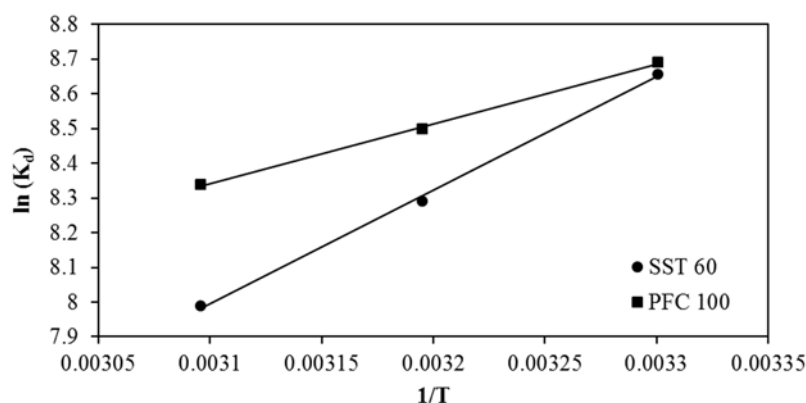


Figure 10. Plot of $\ln K_d$ vs $1/T$ for estimation of thermodynamic parameters for the sorption of Cu^{2+} on SST 60 and PFC 100 resin

The negative value of heat of adsorption (ΔH^0) suggests that the sorption of Cu^{2+} onto ion exchange resins is an exothermic process. The negative values of free energy change (ΔG^0) indicate the spontaneous nature of the sorption process. The ΔS^0 value is positive for PFC 100 resin which mean that the reaction is spontaneous. On the other hand; ΔS^0 is negative for SST60 resin but ΔH outweighs $T\Delta S$ and sorption becomes spontaneous [21].

Table 4. Thermodynamic parameters

	ΔS^0 (kJ/(mol K))	ΔH^0 (kJ/mol)	ΔG^0 (kJ/mol)
SST 60	-0.010	-24.9	-21.8 (303 K) -21.7 (313 K) -21.6 (323 K)
PFC 100	0.025	-14.3	-21.9 (303 K) -22.1 (313 K) -22.4 (323 K)

3.6. Regeneration Performance of Resins

Evaluation of resin regeneration with different regeneration solution (HCl, HNO₃ and H₂SO₄) was performed. Regeneration efficiency (RE, %) was calculated using Equation (14) and obtained results were summarized in Table 5.

$$RE (\%) = \frac{\text{Amount of eluated Cu}^{2+}}{\text{Amount of loaded Cu}^{2+}} \times 100 \quad (14)$$

Table 5. Percentage recovery of Cu²⁺ by different regeneration solution

Regenerated by	Regeneration (%)	
	PFC 100	SST 60
0.5 M HCl	66	63
1 M HCl	73	84
2 M HCl	79	95
0.5 M HNO ₃	58	80
1 M HNO ₃	66	92
2 M HNO ₃	63	93
0.5 M H ₂ SO ₄	60	82
1M H ₂ SO ₄	72	92
2 M H ₂ SO ₄	80	100

As can be seen from Table 5, the SST 60 resin regeneration performance is higher than PFC100 and with 2 M H₂SO₄ solution it can be completely regenerated. The shallow shell technology brings shorter the diffusion path to resin. This is particularly important during regeneration. Reducing the depth of penetration required to cleanse the resin allows for a more complete regeneration and provides a higher, more efficient utilization of the regenerant [22]. As presented in Figure 11; SST resin has inert center and only the outer shell is functionalized. Shortening the diffusion path (S path in Figure 11) leads to more efficient use of regenerant therefore, better regeneration.

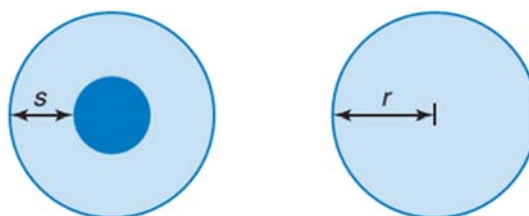


Figure 11. The diffusion path of SST resin (on the left) and standard resin (on the right)

4. CONCLUSIONS

The removal of Cu²⁺ from water by traditional strongly acidic cation exchange resin and SST resins was investigated. The resin dosage and pH of solution have the same effect on such resin's performance. When the resin dosage was increased the removal performance of resins increased. The 0.8 g resin/L was optimum amount for Cu²⁺ removal. The maximum removal of Cu²⁺ was found to occur pH between 2-5. At pH 1 only the 24% of Cu²⁺ removed from solution. The obtained results showed that ion exchange removal of Cu²⁺ is pH depended. The ion exchange kinetic of both resins are close to each other. In two hours, complete removal of Cu²⁺ is achieved. When the speed rate was increased from 100 to 400 rpm; removal of Cu²⁺ is increased for both resins. The ion exchange capacity of resins for Cu²⁺ are calculated by using Langmuir model. The maximum sorption capacity (Q₀) of resins are 130.30 mgCu²⁺/gram resin for PFC 100 and 139.36 mgCu²⁺/gram for SST 60 resin. The ion exchange reaction between resin and Cu²⁺ is spontaneous and exothermic for such resins. The regeneration performance of resins is different from each other. The SST60 resin has better regeneration performance than the

standard PFC 100 resin. 2 M H₂SO₄ completely regenerated the SST 60 resin but only 80% of sorbed Cu²⁺ recovered from PFC 100 resin. As a conclusion, the shallow shell technology improved the resin regeneration performance without losing the ion exchange capacity.

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