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## Treatment of Rice Husk Ash to Improve Adsorption Capacity of Cobalt from Aqueous Solution

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Equilibrium, kinetics and thermodynamics parameters of adsorption of cobalt using silica gel, (Si-Cl-RHA) (RHA = rice husk ash) were investigated. The sorption experimentation work were carried out at pH 6 for 2 h. It was found that the sorption process follow the model of pseudo second-order and the intra-particle diffusion was not the sole of the rate principal step. Adsorption data were perfectly described by Dubinin-Radushkevich, Langmuir and Freundlich models with a highest sorption capacity 123 mg/g according to D-R model at 25 °C which increased to 256 mg/g at 65 °C. From the calculation of the thermodynamic parameters ( $\Delta G^\circ$ ), ( $\Delta H^\circ$ ) and ( $\Delta S^\circ$ ) it can be concluded that the adsorption is spontaneous, a chemical and endothermic process. The presence of phosphate anions in solution, leads to the increase of adsorbability of Co(II) ions. The regeneration and recovery of Si-Cl-RHA was achieved by 99.50 (%) using H<sub>2</sub>SO<sub>4</sub> (0.5 M). Finally, the applicability and effectiveness of the preparations Si-Cl-RHA for removal of cobalt from simulates of low level liquid waste and process wastewater that might arise in research laboratories, show an efficiency of 93 and 99.5 % for <sup>137</sup>Cs and <sup>60</sup>Co removal, respectively.

**Keywords:** Cobalt, Rice husk ash, Silica gel, Adsorption models, Low level liquid waste, Process wastewater.

### INTRODUCTION

Discharge of heavy metal ions from diverse industrial and research activities, form one of the most important reasons of water pollution. Residues of toxic heavy metal in polluted habitats may be accumulates in aquatic plant, microorganisms and living creatures, which successively, may get in the food concatenation of human resulting to health problems [1]. Compounds containing cobalt is used excessively in numerous industrial applications such as metallurgical, mining industry, paints, metal electroplating and electronics [2]. Also, in nuclear power plants wastewater cobalt is present. The allowable limits of Co(II) in the wastewater and irrigation ditch water are 1.0 and 0.05 mg L<sup>-1</sup>, respectively [3]. In humans, the acute cobalt toxicity dose may cause dangerous health effects, *e.g.*, heart, thyroid and liver damage; asthma like allergy. An increase in risk of developing cancer is associated with exposure to ionizing radiation. Due to the problems related with cobalt, research studies correlating to the methods of cobalt removal from polluted water have drawn increasing attention [3]. Chemical precipitation, ion exchanger, adsorption using active carbon, membrane filtration and co-precipitation are most widely used methods for removal of cobalt ion [4]. Simplicity of design

and operation and cost are the most important reasons which causes the adsorption process to be the most encouraging technologies in wastewater pollution control [5]. Because of their abundant availability and low-cost, agro-residue is currently receiving wide attention for utilization as adsorbents due to comparatively high fixed carbon content, functional groups and existence of porous structure.

Many developing countries have accepted and followed the concept of “no waste” and all such materials are termed as “new resources” for new material development through value addition. Rice covers 1 % of the earth’s surface and is a most important source of food for billions of people. After detachment of the rice from the paddy, one-third of the mass remnants as a waste material. Many researchers have tried to use these agricultural byproducts to produce useful materials such as activated carbon, silicon carbide, silica gel, sodium silicate, silica and zeolite [6]. The husk created from the dealing out of rice is either burnt or dumped as waste in various countries producing rice [6]. Numerous industries such as power plant based on biomass and a rice mill has been used rice husk as an energy source. Rice husk ash is obtained by rice husk burning which contains over 60 % silica and is used for the production of silica gel and solar grade silicon [7,8]. The advantages of

silica gel are its local availability, high surface area of about 600 m<sup>2</sup>/g and high thermal resistance. Silica gels could efficaciously remove amount of trace elements such as Fe, Cu, Zn, Pb, Cd, Mn and Co from contaminated water as preliminary studies reported [9-11]. The present research used silica gel (Si-Cl-RHA) prepared from rice husk ash (RHA) for removal Co(II) ion from aqueous solution.

## EXPERIMENTAL

**Preparation of the silica gel:** Sample of the rice husk (RH) was gained from Kafr Blabsa, Kafr El Sheikh, Egypt. The sample of rice husk ash (RHA) was obtained by introducing the husk into the tube furnace. Then, the temperature was increased with the rate of (5 °C/min) to the desired temperature. The combustion process was performed at 650 °C for 1.5 h. 100 g of rice husk ash (RHA) was soaked in 4 % NaOH, mixed well, boiled for 1.5 h then left for 24 h. The mixture was filtered, then, the filtrate was precipitated by addition of 20 % of either HCl, citric acid, HNO<sub>3</sub> and acetic acid, until the pH reached 6-7; the formed gel was heated at 110 °C and stocked in a stopper bottles.

TABLE-1  
DIFFERENT TYPES OF PREPARED SILICA GEL

S. No.	Notation of sample	Condition of preparation
1	RH	Rice husk
2	RHA	Carbonized at 600 °C for 90 min
3	Si-Cl-RHA	Silica gel precipitated by HCl
4	Si-N-RHA	Silica gel precipitated by HNO <sub>3</sub>
5	Si-Ci-RHA	Silica gel precipitated by citric acid
6	Si-Ac-RHA	Silica gel precipitated by acetic acid

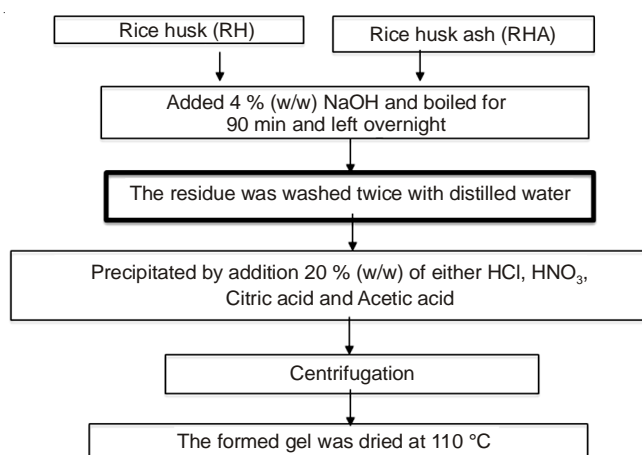


Fig. 1. Preparation of silica gel from RH and RHA

**Characterization of silica gel:** The BET surface area measurement was done by nitrogen adsorption at -196 °C using (NOVA 1000e Quantacrome, USA). Functional groups on the surface of Si-Cl-RHA sample (before and after adsorption of Co(II)) was characterized by a FTIR-100, Shimadzu in the range of 4000-500 cm<sup>-1</sup>. The pH of a suspension of some prepared silica gel was measured in distilled water. In this concern, one method entails preparing mixture of 1g adsorbent in 50 mL distilled water. The suspension was heated approximately to 90 °C and stirred for 20 min [12]. The suspensions of some

prepared silica gel were cooled to 25 °C and the pH was measured by initially calibrated pH meter. Energy dispersive X-ray characterization of selected adsorbents was carried before and after adsorption by using SEM-EDX (SEM: LSMT 20 JOEL, JAPAN). The density, ash and moisture content analysis of Si-Cl-RHA were determined.

**Adsorption experiments:** Experiments of adsorption were performed to investigate kinetic data by shaking 0.01 g Si-Cl-RHA in 10 mL Co(II) solutions (100 mg/L) in the flask using waterbath shaker at 25 °C for 24 h. The solution then filtered using Whatman 44 filter paper after an interval time. Using ammonium thiocyanate as chelating agent, the residual concentration of Co(II) in the filtrates was measured by UV spectroscopy. About 0.01 g of Si-Cl-RHA sample was agitated with different concentrations of Co(II) solutions to equilibrium for the adsorption isotherm studies. For the investigation of the effect of pH on the adsorption capacity and mechanism, 0.01 g of Si-Cl-RHA was shaken with 100 mg/L Co(II) solutions at the pH range of 1 to 8 and measured using a pH meter (Ecoscan, EUTECH Instruments, Singapore). Also, the adsorption of Co(II) at different temperatures (25, 45 and 65 °C) was studied. In all experimental runs, the uptake (q<sub>e</sub>) mg/g and removing (%) were computed from eqns. 1 and 2:

$$q_e = (C_o - C_e) V/M \quad (1)$$

$$\text{Sorption (\%)} = (C_o - C_e)/C_o \times 100 \quad (2)$$

C<sub>o</sub> and C<sub>e</sub> are the solute initial and residual concentration (mg/L), respectively; V is volume of solution (L) and M is the mass of Si-Cl-RHA used (g).

## RESULTS AND DISCUSSION

**Adsorbability of prepared silica:** Preliminary tests were performed to investigate the absorptive capacity of the prepared silica gel. The following figure (Fig. 2) shows the higher capacity of Si-Cl-RHA for adsorption of Co(II) than the another rice husk or rice husk ash prepared silica gel.

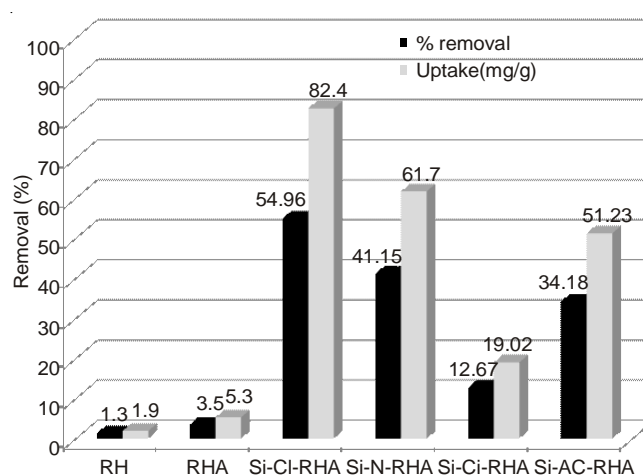


Fig. 2. Uptake (q<sub>e</sub>) and % removal of Co(II) onto rice husk, rice husk ash and prepared silica

Due to the highest uptake and % removal of Si-Cl-RHA, it was selected to investigate its characterization and study the factors affecting the adsorption of Co(II) ions.

TABLE-2  
PHYSICO-CHEMICAL CHARACTERIZATIONS OF THE PREPARED ADSORBENTS

Samples	Yield (%)	pH <sub>sol</sub>	Moisture (%)	Density		Solubility (%)		Ash (%)
				Apparent	Packed	Base	Acid	
RH	100	8.2	2.05	0.27	0.38	–	–	17
RHA	42.2	9.3	2.28	0.34	0.42	–	–	41.08
Si-Cl-RHA	31.4	9.8	6.43	0.67	0.92	9.2	38	43
Si-N-RHA	41.6	9.8	3.94	0.77	0.99	11.4	24.4	39.4
Si-Ci-RHA	44.5	9.8	5.40	0.95	1.17	25.8	30	44.8
Si-AC-RHA	43.4	9.4	12.2	0.57	0.82	14.8	24.4	31.4

### Characterization of prepared Si-Cl-RHA silica gel:

Some of the physicochemical characterizations of Si-Cl-RHA are tabulated (Table-2) which refer the variation in their properties depending on the method of preparation. The prepared silica gel from our precursor materials rice husk and rice husk ash exhibit basic surfaces and this may be due to inorganic (ash) content comes from the raw materials or from chemicals added in the preparation processes as reported by Hassler [13].

The correlation between the pH and the ash values is stable. This means that the ash is not soluble in water, so the prepared adsorbents have good applications and are suitable in water treatment. Surface area analysis of Si-Cl-RHA sample gives the BET surface area ( $S_{\text{BET}}$ ) = 3.20 m<sup>2</sup>/g, total pore volume ( $V_{\text{total}}$ ) = 1.24 e<sup>-03</sup> cc/g, average pore radius (nm) = 5.43 e<sup>+00</sup> and Langmuir surface area = 6.50 m<sup>2</sup>/g at the optimum conditions.

**Surface functional groups:** The FTIR spectra for RH, Si-Cl-RHA and Si-Cl-RHA sample loaded with Co(II) are presented in Fig. 3. In the sample RH a strong peak at 3345.9 represents the -OH stretching group of cellulose and lignin [14]. For Si-Cl-RHA and Si-Cl-RHA sample loaded with Co(II) 3451.6 and 3479.7 cm<sup>-1</sup> ascribes to Si-OH asymmetry stretching vibration [15]. At 2928 cm<sup>-1</sup> a sharp band is refer to vibrations stretching of the -CH of a CH<sub>2</sub> group of biomass. At 2361 and 2336 cm<sup>-1</sup> the bands come usually from finite types of functional groups and triple bonds. This band was approximately absent in sample RH and strongly appeared in the Si-Cl-RHA sample and approximately disappeared in the Si-Cl-RHA sample loaded with Co(II). The peak at 1736 cm<sup>-1</sup> is attributed to stretching >C=O of carbonyl groups in hemicelluloses [16] but this peak disappeared in the sample Si-Cl-RHA and Si-Cl-RHA sample loaded with Co(II).

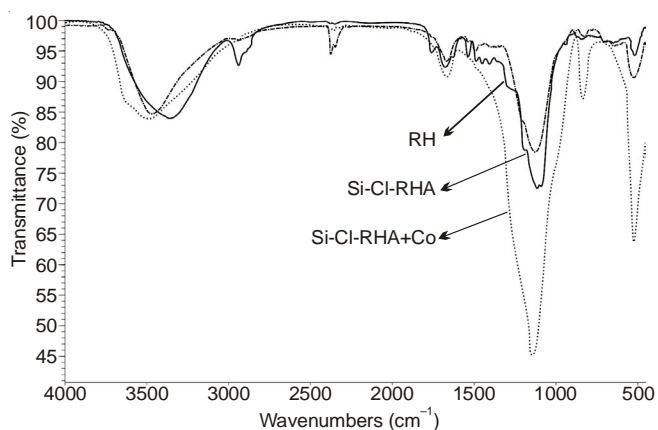


Fig. 3. FTIR of the RH, Si-Cl-RHA and Si-Cl-RHA sample loaded with Co(II)

The peak at 1512 cm<sup>-1</sup> is due to aromatic >C=C stretch vibration as in the sample RH [17] whereas this peak is weak in the sample Si-Cl-RHA and disappeared in the Si-Cl-RHA loaded with Co(II). The peak at 1075 is referred to stretching -CH and again is an indication of lignin presence in the RH and in Si-Cl-RHA correspond to asymmetric vibrations in siloxane bond, ≡Si-O-Si≡ while asymmetric vibration appears in Si-Cl-RHA sample loaded with Co(II) at 1088 cm<sup>-1</sup> [18]. At 1644 and 1654 cm<sup>-1</sup> in RH, Si-Cl-RHA and Si-Cl-RHA sample loaded with Co(II), the peaks are an indication of carboxylic groups [19]. The presence of a band at 794.4 cm<sup>-1</sup> in the Si-Cl-RHA sample loaded with Co(II) may be due to the ≡Si-Co or ≡Si-O bond. At 477 cm<sup>-1</sup> band is assigned to the Si-O symmetry stretching vibration [15].

In present study, FTIR analysis shows that there are oxygen containing surface functional groups like carboxyl, carbonyl and other surface groups. The peaks are strong in RH and weak in Si-Cl-RHA and Si-Cl-RHA sample loaded with Co(II). This phenomena may be attributed to the preparation conditions or Co(II) adsorption confirming that these active functional groups take part in the Co(II) ions adsorption.

**Analysis of Si-Cl-RHA by SEM-EDX:** Scanning electron micrographs and EDX spectra of Si-Cl-RHA before and after sorption of Co(II) are shown in Fig. 4. It shows the peak that suggesting the presence of silicon, oxygen, sodium and chloride before adsorption. If we compare the spectra of Co(II) loaded Si-Cl-RHA with that of unloaded one, the cobalt peak could be observed whereas sodium and chloride peak disappeared. It is suggested that Co(II) had been adsorbed on the surface of Si-Cl-RHA successfully.

**Factors affecting the sorption of Co(II) using Si-Cl-RHA:** According to our investigation, there are many factors affecting on the sorption capacity of Co(II) onto prepared Si-Cl-RHA.

**Initial pH of the solution:** The pH of the solution exerts a great effect on the capacity of the adsorbate most probably due to its effect on the surface characteristics of the adsorbent and dissociation or ionization of the adsorbate [20]. The adsorption of Co(II) onto (Si-Cl-RHA) was investigated in the pH range of 1-8 as illustrated in Fig. 5. The % removal of cobalt using Si-Cl-RHA increases as the pH increase appreciably to pH = 8. There is an increase in the amount of adsorption till pH 7, above this pH value Co(II) begins to hydrolyze to Co(OH)<sup>+</sup> and finally precipitate as Co(OH)<sub>2</sub> as shown in Fig. 5(B) and therefore the further increase of % removal above pH = 7 is almost due to precipitation as reported also by other authors [21]. The remaining sorption experiments of Co<sup>2+</sup> were performed at pH 6 before the beginning of Co(II) hydrolysis.

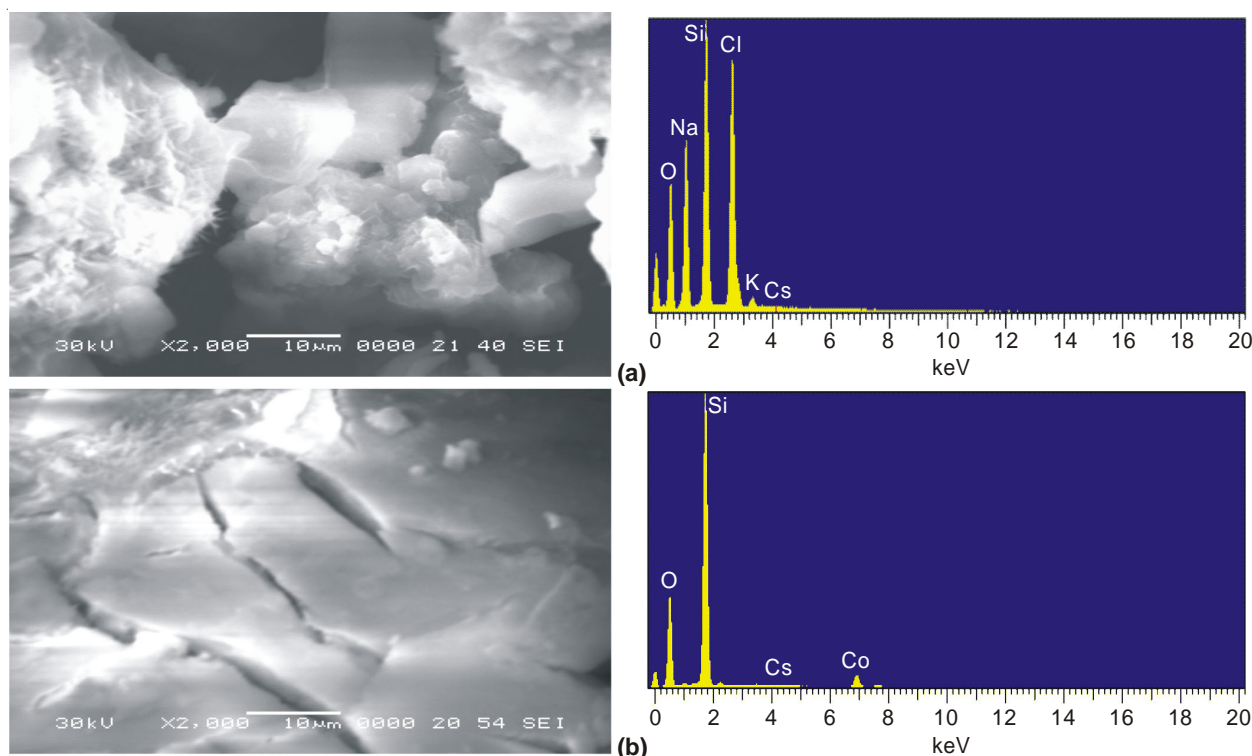


Fig. 4. (a) SEM micrograph and EDX spectra of Si-Cl-RHA before loading with Co(II) and (b) after loading with Co(II)

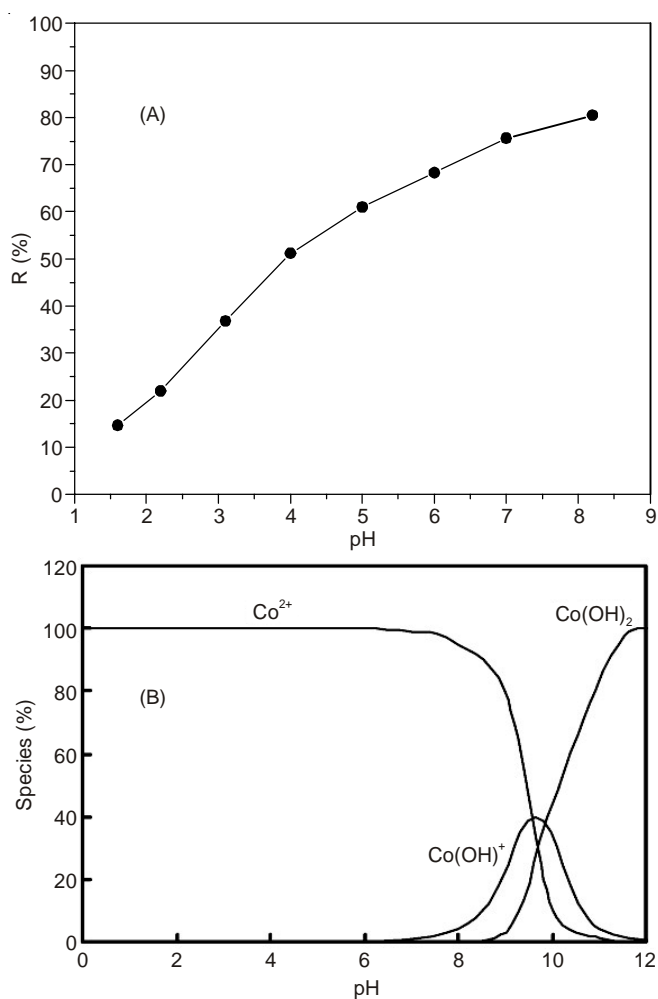
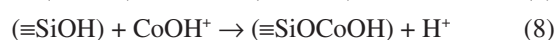


Fig. 5. (A) Effect of pH on the % removal of cobalt by Si-Cl-RHA, (B) Speciation diagram for Co(II) in aqueous solution

**Mechanism of cobalt ion adsorption:** Based on the results discussed above, it is still difficult to propose a mechanism for metal ion sorption. Nevertheless, from the limited data concerning the forms of adsorbed species and the knowing of metal chemistry in aqueous solutions, a preliminary mechanism for sorption can be proposed. The ion-exchange mechanism on the surface of silica is carried out by the substitution of hydrogen of the silanol surface groups with metal ions from solution, as follows:



$\text{M}^{n+}$  referring to the adsorbed metal ion of  $n^+$  charge,  $\equiv\text{SiOH}$  is the silanol group and  $x\text{H}^+$  is the amount of released protons. This mechanism of cation-exchange is expected in Si-Cl-RHA sorbent. Besides, since the electrostatic attractiveness was not reasonable between similar positive charge of adsorbent surface metal ion species, it appears that non electrostatic force that called "specific adsorption" was included in the adsorption process [22,23]. The potential mechanism of adsorption for cobalt ions includes the following:



where  $\equiv\text{SiO}^-$  denotes the negatively charged surface and  $\text{SiOH}$  denotes neutral surface.

**Weight of adsorbent:** It ascertains the adsorbent capacity for a given concentration of metal ions in aqueous solution. Fig. 6 showed that as the dose of adsorbent increased the % removal rapidly increased. However, even though the Co(II) % removal was enhanced, the adsorption capacity (mg of metal adsorbed/g of adsorbent) decreased with increasing adsorbent

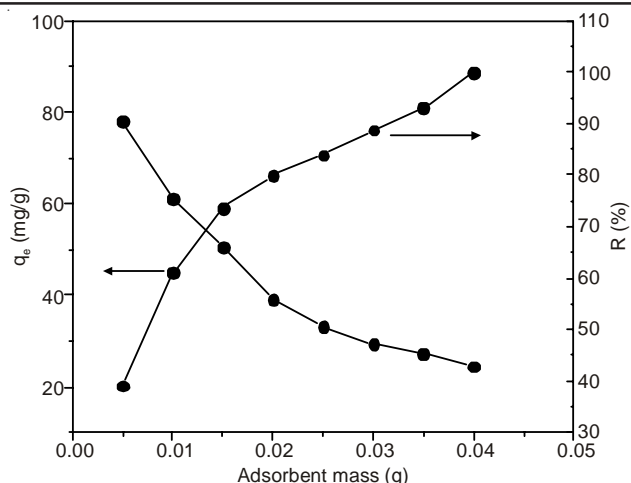


Fig. 6. Effect of weight of adsorbent on the uptake ( $q_e$ ) and % removal of Co(II)

dosage reaching a fixed value after the decisive dose. As the adsorbent weight increased from 0.005 to 0.040 g, the % removal of Co(II) increased from 39 to 100 %. An increase of metal ions % removal may be due to an increase in the availability of sorption surface area and consequently the availability of more sorption sites [24].

**Shaking time:** Adsorption of cobalt was found to increase with shaking time reaching equilibrium after 1.5 h. The fast adsorption is essential for any adsorbent, as it permits short contact time for solution-adsorbent and will admit the use of much shallow-minded contact beds of adsorbents in column application [25]. Besides, short contact time is one of the most essential considerations for economical applications in wastewater treatment. From the results obtained, the optimum agitation period of 2 h was selected for Co(II) removal for the subsequent experiments in the batch adsorption measurements to make certain that equilibrium is obtained.

The curve shown in Fig. 7 indicates that two steps are incorporated in the adsorption process: a much slower step comes after a rapid initial one. About 50 % of cobalt was adsorbed by Si-Cl-RHA within 40 min, accompanied with another 45 min to reach equilibrium. Similar observations were reported by Awval *et al.* [26].

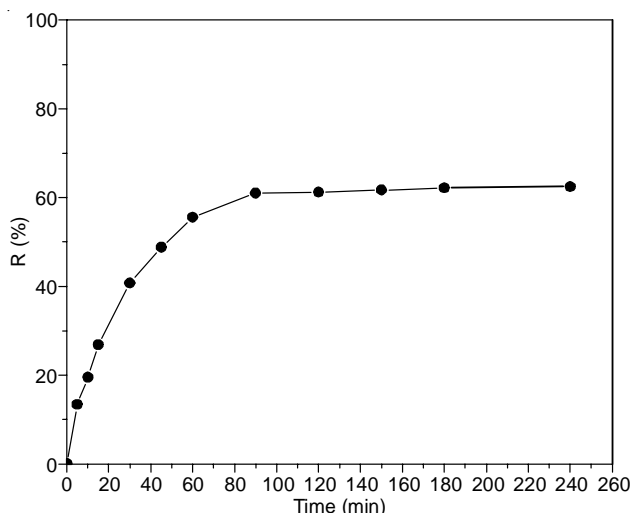


Fig. 7. Effect of shaking time on the Co(II) % removal using Si-Cl-RHA

Maleki *et al.* [27] explained this two-stage adsorption during the first stage the metal ion is sorbed at external surface and macropores of the prepared silica gel where the resistance towards metal ions to reach these surfaces is small. As the adsorption proceeds more and more metal ions diffuse through macropores, mesopores and micropores to arrive the whole surface area within the adsorbent grains. However, the rate of diffusion in such pores decreased with time and consequently the adsorptive capacity increased more slowly as time elapsed until equilibrium was attained.

**Kinetic rate parameters:** As it supply the data about the adsorption mechanism, which is essential for the adsorption process, a kinetic investigation of adsorption is required. In our study, three kinetic equations were used to prove which of them gives the best fit with experimental data. The kinetic model of pseudo-first-order is used in our kinetic investigations [28]. It is stated by the next equation:

$$\log (q_e - q_t) = \log q_e - K_1 (t \times 1/2.303) \tag{9}$$

where  $q_t$  and  $q_e$  are the adsorbed Co(II) at time  $t$  and at equilibrium of adsorption, respectively. The constant  $K_1$  can be calculated from the slope obtained from the straight line of plotting  $\log (q_e - q_t)$  vs. time.  $K_1$  and  $R^2$  (the correlation coefficients) are calculated and summarized in Table-3. The kinetic model of pseudo-second-order [29] is expressed as:

$$t \times 1/q_t = 1/K_2 q_e^2 + t \times 1/q_e \tag{10}$$

$K_2$  is the rate constant of the second-order which is used for calculation of the initial sorption rate, that is given by:

$$h = K_2 q_e^2 \tag{11}$$

$K_2$ ,  $h$  and  $R^2$  are investigated and summarized in Table-3. The second-order correlation coefficient is higher compared to kinetic first-order model. In addition, the experimental and theoretical values of  $q_e$  are in a good agreement with each other. Therefore, it can be supposed that the sorption of cobalt by Si-Cl-RHA follow the kinetic model of the pseudo second-order. There is a general grasp that the pseudo-second order provides best experimental data fitting for the sorption process when chemisorption mechanism seems considerable in the rate determining step [29]. These results are confirmed by the FTIR which indicates that there some peaks of functional groups disappeared and others are found in the spectrum of Si-Cl-RHA loaded with cobalt as shown in Fig. 3.

TABLE-3 KINETIC PARAMETERS ADSORPTION OF COBALT ION ONTO Si-Cl-RHA		
Model	Parameter	Cobalt
Pseudo first order	$q_{e, \text{exp}}$ (mg g <sup>-1</sup> )	62.4
	$K_1$ (min <sup>-1</sup> )	0.05
	$q_{e, \text{cal}}$ (mg g <sup>-1</sup> )	50.9
	$R^2$	0.908
Pseudo second order	$K_2$ (g mg <sup>-1</sup> min <sup>-1</sup> )	$7.3 \times 10^{-4}$
	$h$ (mg g <sup>-1</sup> min <sup>-1</sup> )	3.5
	$q_{e, \text{cal}}$ (mg g <sup>-1</sup> )	65.1
	$R^2$	0.996
Intra-particle diffusion	$K_p$ (mg g <sup>-1</sup> min <sup>-1</sup> )	7.4
	$R^2$	0.993

**Intra-particle diffusion:** Transport of an adsorbed substance from the solution to the substrate surface take place in different steps. The process of adsorption may be controlled by one or different steps, *e.g.* film diffusion, surface diffusion, pore diffusion or cooperation of more than one of these steps. The adsorption rate factor which dominates the batch process is the diffusion in the intra-particle of adsorbents. The potential of intra-particle diffusion resistance was reconnoitered by using Weber & Morris equation [30]:

$$q_t = K_{pt}^{0.5} + C \quad (12)$$

$C$  is the frontier layer surrounding of the adsorbent particle and the rate of intra-particle diffusion ( $k_p$ ) for adsorption of cobalt was computed from diagram of  $q_t$  vs.  $t^{0.5}$  as illustrated in Fig. 8A. If intra-particle diffusion was the rate-determining step, then the obtained straight line should be passes over the origin. As shown from the diagram, there is a curved portion at initial of the plot, followed by straight portion and then a plateau. The first part of this plot may be due to exterior solute transfer, the second linear part is owing to intra-particle diffusion and finally the plateau is due to the stage of equilibrium [28].

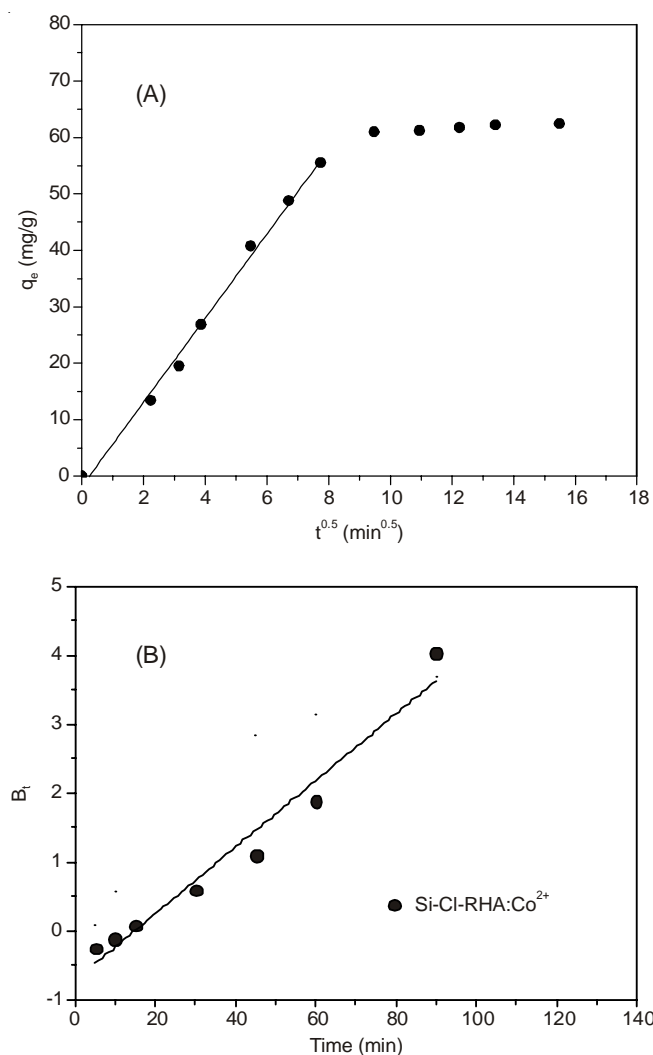


Fig. 8. (A) Diagram of intra-particle diffusion. (B) Boyd diagram of kinetics of adsorption of cobalt onto Si-Cl-RHA

Intra-particle diffusion rate constant ( $k_p$ ) has been obtained from the slope of linear part and its value was  $7.4 \text{ mg g}^{-1} \text{ min}^{-0.5}$  for cobalt. Also, the boundary layer calculated from the intercept of the plot. The greater the intercept, the higher is the donation of the sorption at the surface in the rate controlling step [32].

Ghasemi *et al.* [33] has proven that it is important for the plot to go along the origin if the intra-particle diffusion is the sole rate controlling step. As this is not the case in our work, the plot has intercept, it may be concluded that the diffusion in the intra-particle was not the sole rate limiting step. The mechanism of adsorption of cobalt is a complicated process, probably a combination of external mass transfer and diffusion in the intra-particle which participate in the rate limiting step [34].

Boyd kinetic equations were further analyze the kinetic data in order to predict the actual slow step involved in the adsorption processes. The Boyd kinetic expression is given by Boyd *et al.* [35].

$$F = 1 - (6/\pi^2)e^{-Bt} \quad (13)$$

$$\text{and} \quad F = q_t/q_\infty \quad (14)$$

where,  $q_t$  is the quantity of adsorbed solute ( $\text{mg g}^{-1}$ ) at time  $t$ ,  $q_\infty$  is the quantity of adsorbed solute at infinite time ( $\text{mg g}^{-1}$ ),  $F$  is the fraction of metal adsorbed at time  $t$ .

$B_t$  is a arithmetical function of  $F$  and calculated using Reichenburg equation [36]:

$$B_t = -0.4977 - \ln(1-F) \quad (15)$$

The obtained  $B_t$  value was drawn against  $t$  as seen in Fig. 8B. The linearity of plot was used to differentiate between the particle and film diffusion controlled adsorption. If the plot is a straight line crossing the origin, then the rate of adsorption is controlled by mechanism of particle diffusion otherwise it is limited by film diffusion [37]. This behaviour is anticipated when an initial fraction of the reaction is intra-particle diffusion controlled.

**Effect of cobalt concentration:** It was investigated using various metal ion concentrations ranging from 50-350 mg/L. In Fig. 9, it is clear that as the concentration of Co(II) increased the uptake  $q_e$  increased until equilibrium was achieved. This suggests that the adsorption procedure appears to proceed rapidly when a number of available sites is much higher than the metal ion species that will be adsorbed. As metal concentration increases, high-affinity sites begin to reach saturation and energetically less favourable ones (low affinity surface sits) become involved in the adsorption process causing reduction of removal efficiency [24]. In diluted solutions, the movability of cobalt is fast, probably for this behaviour, the reaction of these ions with the Si-Cl-RHA increased [38]. By increasing the Co(II) concentration, hydrolysis of its ions can increases which cannot reach the active sites of the Si-Cl-RHA [39] leading to a decrease of % R. These results suggest that the % removal is dependent on the concentration of Co(II) ions in solution. It may be accomplished that high % removal at low concentrations is essential in case of industrial applications.

**Adsorption isotherm:** Adsorption isotherms of Co(II) were obtained in an attempt to get a more comprehensive insight into mechanism of adsorption and maximum adsorption

capacity of cobalt onto prepared silica gel. In this concern, the results acquired for cobalt adsorption using Si-Cl-RHA silica gel are given in Fig. 9. Frist the isotherm rapidly rose through the initial adsorption stage where low  $q_e$  and  $C_e$  values subsisted.

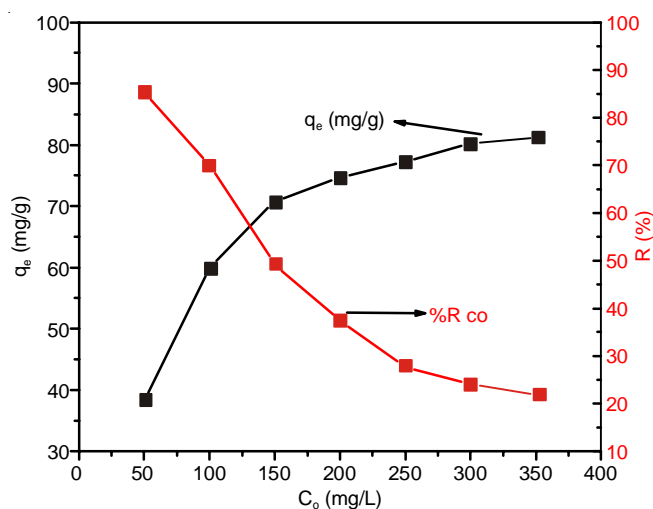


Fig. 9. Effect of cobalt concentration on the uptake and % removal using Si-Cl-RHA

**Freundlich and Langmuir isotherm:** From the adsorption isotherm, the data obtained was fitted to linear forms of Freundlich equation (eqn. 16) and Langmuir equation (eqn. 17):

$$\log q_e = \log K + \log C_e \times 1/n \quad (16)$$

$$C_e/q_e = 1/b q^0 + C_e/q^0 \quad (17)$$

whereas  $q_e$  is uptake at equilibrium ( $\text{mg g}^{-1}$ );  $C_e$  is the concentration at equilibrium ( $\text{mg L}^{-1}$ ); and  $K$  and  $n$  are Freundlich constants,  $n$  refer to favourableness of adsorption (intensity of adsorption),  $k$  is the adsorbent capacity (capacity of adsorption);  $q^0$  and  $b$ : are constants of the Langmuir gives an indication of maximum adsorption capacity in agreement with complete monolayer coverage of the surface and adsorption energy, respectively.

Adsorption parameters were listed in Table-4 along with corresponding correlation coefficients. It is clear that the value of  $K$  and  $n$ , show at ease uptake of  $\text{Co(II)}$  ions. As the values of  $n$  lie between 1 and 10, it interprets good and well-disposed adsorption and high value of  $K$  indicates high affinity [40].

Constant of Langmuir 'b' reverberates binding strength of adsorbate to adsorbent. From the table, a value of  $b$  is high for cobalt onto Si-Cl-RHA indicating strong bonding of cobalt with Si-Cl-RHA.

Maximum adsorption capacity ( $q^0$ ) of cobalt is  $75.7 \text{ mg g}^{-1}$ . By comparison the  $R^2$ , calculated correlation coefficients,

for both models, it may be inferred that the data obtained from experimental studies fit better to model of Langmuir than Freundlich one, over whole range of studied concentration.  $R^2$  of Langmuir model is higher than 0.994. The high fitting to the Langmuir model supposes that as the ions of metal perch a site, no additional adsorption can occur at the same site, then adsorption is restricted with a monolayer coverage and the adsorbent surface is comparatively homogeneous in expression of functional groups [41] with a chemical type of adsorption interaction [42].

**Effect of isotherm shape:** Favourable or unfavourable sorption system can be predicted from the isotherm shape. The important characters of Langmuir isotherm can be stated in expression of a dimensionless separation factor,  $R_L$ , which is expressed using the next relationship [43]:

$$R_L = 1/1 + bC_o \quad (18)$$

where,  $C_o$  the solute initial concentration ( $\text{mg L}^{-1}$ ),  $b$  is constant of Langmuir equation ( $\text{L mg}^{-1}$ ). The shape of isotherm can be indicated by this parameter as follow: unfavourable,  $R_L > 1$ ; Linear,  $R_L = 1$ ; favourable,  $0 < R_L < 1$ ; irreversible adsorption,  $R_L = 0$ . By processing above equation,  $R_L$  value for  $\text{Co(II)}$ : Si-Cl-RHA system is 0.061 indicating favourable sorption of  $\text{Co(II)}$  on Si-Cl-RHA with the conditions used in this study. There is a reverse relation between the value of Langmuir constant 'b' and  $R_L$  for cobalt *i.e.* if there is an increase in the  $b$  value, the value  $R_L$  decreases, these values support each other so the reaction for  $\text{Co(II)}$  ions is irreversible.

**Dubinin and Radushkevich isotherm:** The data of adsorption can be additionally discussed by Dubinin–Radushkevich (D–R) isotherm [44] to differentiate between physical and chemical adsorption. It does not assume a homogenous surface or a constant adsorption potential [45] therefore, it is more general than Langmuir isotherm:

$$q_e = q_0 \exp(-B\varepsilon^2) \quad (19)$$

$$\text{and} \quad \varepsilon = RT \ln(1 + 1/C_e) \quad (20)$$

where  $q_0$  is the solute maximum amount adsorbed;  $B$ : refer to the energy of adsorption [ $\text{mol}^2 (\text{kJ}^2)^{-1}$ ];  $\varepsilon$ : the surface potential energy;  $R$ : gas constant ( $\text{kJ mol}^{-1} \text{K}^{-1}$ );  $T$ : absolute temperature.

The free energy ( $E$ ), of transfer of 1 mol of adsorbate from infinity to surface of adsorbent [46,47] can be given from constant  $B$  and calculated using the next equation:

$$E = 1/\sqrt{2B} \quad (21)$$

Linear form of D-R equation is expressed as:

$$\ln q_e = \ln q_0 - B\varepsilon^2 \quad (22)$$

A diagram of  $\ln q_e$  vs.  $\varepsilon^2$  gives a straight line. The values of  $q_0$ ,  $B$  and  $E$  were calculated and listed in Table-4. The value

TABLE-4  
CONSTANTS OF LANGMUIR, FREUNDLICH AND DUBININ-RADUSHKEVICH MODELS FOR THE ADSORPTION OF COBALT USING Si-Cl-RHA AT DIFFERENT TEMPERATURES

Temp. (°C)	Langmuir			Freundlich			Dubinin-Radushkevich			
	$q^0$ (mg/g)	$b$ (L/g)	$R^2$	$K$	$n$ (mg/g)	$R^2$	$q_0$ (mg/g)	$B$ ( $\text{mol}^2/\text{KJ}^2$ )	$E$ (KJ/mol)	$R^2$
25	75.7	0.154	0.994	21.4	4.45	0.989	123	$2.6 \times 10^{-3}$	13.8	0.977
45	117	0.085	0.992	27.4	4.07	0.974	214	$2.7 \times 10^{-3}$	13.5	0.962
65	151	0.109	0.993	41.7	4.02	0.954	256	$2.0 \times 10^{-3}$	15.7	0.980



of E can determine the type of the adsorption as an ion exchange ( $E = 8-16 \text{ kJ mol}^{-1}$ ), or physical ( $E < 8 \text{ kJ mol}^{-1}$ ) [48]. In our study, the adsorption free energy is more than  $8 \text{ kJ mol}^{-1}$  at three different temperatures, which indicates that, the adsorption of Co(II) ion onto (Si-Cl-RHA) is classified as a chemical adsorption (ion exchange) process. The value of correlation factor  $R^2$  of D-R equation is fairly good for the adsorption of cobalt (0.977) *i.e.* Co(II) ions adsorption obey D-R equation. The  $q_0$  amounts computed from D-R equation are greater than  $q^0$  computed from Langmuir model. This difference indicates that the Langmuir hypothesis of monolayer coverage of the surface may result in disesteem of the adsorption capacity. The adsorption energies are recorded in Table-4 and Si-Cl-RHA has energy of  $13.8 \text{ kJ mol}^{-1}$  for adsorption of Co(II).

**Effect of the temperature:** It was proven that the quantity of adsorbed cobalt onto Si-Cl-RHA increases as the solution temperature increases from 25 to 65 °C. Langmuir, Freundlich and Dubinin–Radushkevich isotherm parameters were obtained at various temperatures and the obtained results are listed in Table-4.

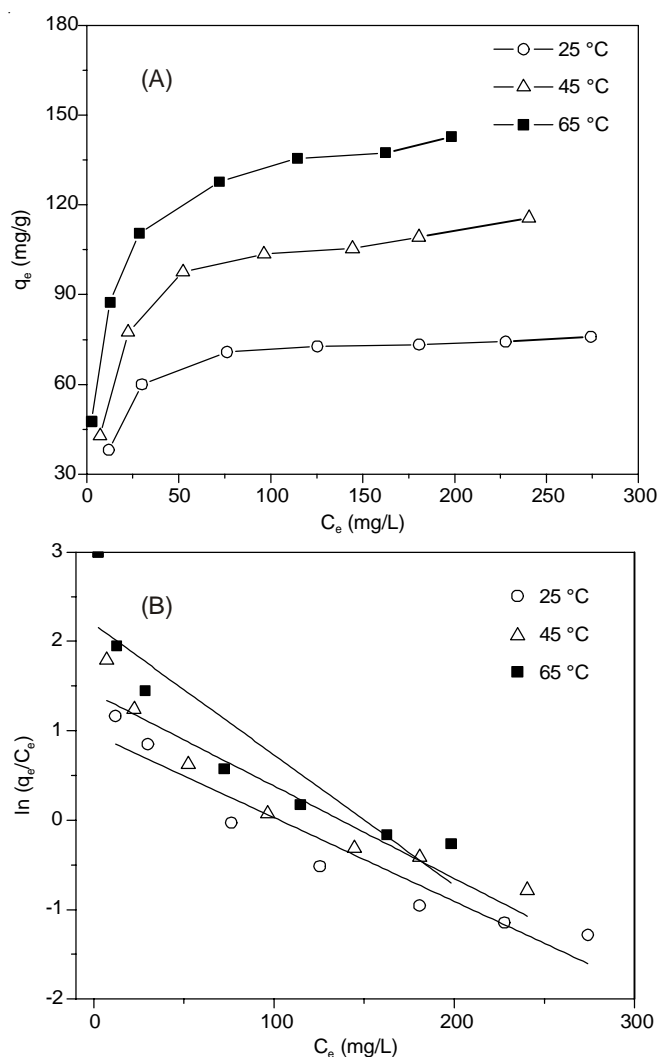


Fig. 10. (A) The influence of different temperatures on Co(II) adsorption, (B) Khan and Singh diagram for cobalt adsorption onto Si-Cl-RHA

Increase of Si-Cl-RHA capacity for adsorption of cobalt in relation to temperature is a direct result of: (1) pore size

improvement or adsorbent surface activation by creation of some new active sites [49]. (2) high temperature leads to fast kinetics because of enhanced mobility of cobalt ions towards the adsorbent surface from the bulk solution. (3) increase of the amount of diffusion inside Si-Cl-RHA structure [50]. (4) it may also due to the overcoming of the barrier of activation energy and speeding up of the intra-particle diffusion rate given the short time duration of the kinetic experiments [51]. (5) cobalt hydrolysis enhancement with increasing temperature as reported by Abbas *et al.* [52]. The  $1/n$  value is generally based on the type and intensity of sorption process in addition to the distribution of surface active sites [53].

**Thermodynamic parameters:** Standard free energy ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were evaluated using the next equations [52] to get an approaching about the mechanism concerned in cobalt adsorption process:

$$\ln K_d = \Delta S^\circ/R - \Delta H^\circ/RT \quad (23)$$

$$\Delta G^\circ = -RT \ln K_d \quad (24)$$

R is a universal gas constant and T is absolute temperature in Kelvin (K).  $K_d$  is the thermodynamic equilibrium constant and can be determined by the method of Khan and Singh [54].  $\Delta H^\circ$  and  $\Delta S^\circ$  were obtained from vant's Hoff plot of  $\ln K_d$  vs.  $1/T$ .  $\Delta G^\circ$  may be deduced using eqn. 24. Calculated values of  $K_d$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta G^\circ$  are summarized in Table-5. Endothermic nature of cobalt adsorption onto prepared Si-Cl-RHA is indicated by an increase in  $K_d$  with temperature increase. This is confirmed by the positive enthalpy changes ( $\Delta H^\circ$ ) for Co(II).

Temp. (K)	$K_d$ ( $\text{L g}^{-1}$ )	$\Delta G^\circ$ ( $\text{kJ mol}^{-1}$ )	$\Delta H^\circ$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )	$\Delta S^\circ$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )
298	2.4	2.229		
318	4.0	3.701	24.942	89.514
338	8.1	5.900		

Values of  $\Delta G^\circ$  listed in Table-5 are positive for cobalt. This supposes that the cobalt adsorption is non spontaneous and indicates the formation of thermodynamically unstable adsorbed species [55]. The positive value of entropy changes  $\Delta S^\circ$  in case of cobalt-Si-Cl-RHA systems indicates the increased entropy at the adsorbent/adsorbate boundary during the cobalt ion adsorption onto Si-Cl-RHA [56]. Furthermore, the enthalpy changes  $\Delta H^\circ$  for Co(II) ions is more than  $10 \text{ kJ mol}^{-1}$  which suggests that Co(II) sorption onto the Si-Cl-RHA is chemical adsorption in nature [57].

**Effect of diverging ions:** In this study, equal volume of the same concentration of cobalt and interfering ions were mixed and shaken with known weight of Si-Cl-RHA. Adsorbed amount of cobalt in presence of others ions was calculated and obtained results were listed in Table-6.

Due to the presence of  $\text{Ca}^{2+}$ ,  $\text{Na}^+$  and  $\text{K}^+$  ions, the % removal of Co(II) was decreased by 21.8, 1.25 and 11.38 %, individually. Also, the of presence of  $\text{CO}_3^{2-}$ ,  $\text{HCO}_3^-$  and  $\text{Cl}^-$  decreases the sorption capacity by 12, 13.03 and 14.13 %, sequentially. Based on these results we can deduce that the existence of cations or anions decreases the remediation of Co(II) using Si-Cl-RHA. In contrast to the above results, the existence of

TABLE-6  
EFFECT OF INTERFERING IONS ON Co(II) ADSORPTION USING (Si-Cl-RHA)

Type of cations (100 mg/L)	Uptake $q_e$ (mg/g)	Removal (%)	Type of anions (100 mg/L)	Uptake $q_e$ (mg/g)	Removal (%)
Co <sup>2+</sup>	72.0	72.0	PO <sub>4</sub> <sup>3-</sup>	72.83	72.83
Ca <sup>2+</sup>	50.5	50.5	CO <sub>3</sub> <sup>2-</sup>	60	60
Na <sup>+</sup>	70.75	70.75	HCO <sub>3</sub> <sup>-</sup>	58.97	58.97
K <sup>+</sup>	60.62	60.62	Cl <sup>-</sup>	57.87	57.87
–	–	–	SO <sub>4</sub> <sup>2-</sup>	86.9	86.9

TABLE-7  
DESORPTION OF Co(II) USING DIFFERENT DESORBING AGENTS

Effect of type of reagent on % desorption		Effect of [H <sub>2</sub> SO <sub>4</sub> ] (M)		Effect of [HCl] (M)	
Reagents (0.5 M)	Desorption (%)	Concentration (M)	Desorption (%)	Concentration (M)	Desorption (%)
H <sub>2</sub> O	5.0	–	–	–	–
Sulphuric acid	99.5	0.1	90.5	0.1	75
Hydrochloric acid	95.0	0.2	95	0.2	83
Nitric acid	88.0	0.3	96	0.3	89
Sodium carbonate	80.0	0.4	98	0.4	92
Sodium bicarbonate	74.0	0.5	99.5	0.5	95

PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> increases the sorption capability of Si-Cl-RHA by 0.83 % and 14.09 %, respectively. Therefore, the PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> have to be added during the treatment of Co(II) using Si-Cl-RHA to increase its sorption capacity.

**Desorption of Co(II) ions:** In the desorption investigation, two important parameters are concerned: (a) restoring the adsorbent close to its original form for reuse effectively and no loss or change in physical properties [58]. (b) yielding the adsorbate in a concentrated form. Recovery of the biosorbed Co(II) from loaded Si-Cl-RHA was performed using different eluting reagents including some salt solution (NaHCO<sub>3</sub>, Na<sub>2</sub>CO<sub>3</sub>) and some mineral acids (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl). As seen from Table-7, H<sub>2</sub>SO<sub>4</sub> was the best eluting agent in case of Co(II): Si-Cl-RHA study. Chemical form of the Co(II) species could be changed by using these reagents and in addition to that the bond between the Co(II) and the Si-Cl-RHA could be destroyed and consequently, adsorbed Co(II) ion is liberated from the Si-Cl-RHA. In this study, using of 0.5 H<sub>2</sub>SO<sub>4</sub> is sufficient to reach maximum desorption effectiveness of Co(II) from the Si-Cl-RHA.

**Potential use of Si-Cl-RHA to treat low level radioactive liquid waste (LLLW):** The main objective in our study, based on the establishing the applicability of the concerned method, was to investigate the efficiency of the process for treatment of radioactive liquid wastes. For this purpose, removal of cobalt from simulates of low level radioactive liquid waste (LLRLW) produced in Nuclear Research Center at Inshas, in Egypt [59] and process wastewater (PWW) that might originate in investigation laboratories in the same Center, was carried out using optimal experimental parameters. The LLLW stimulant was prepared from reagent grade chemicals dissolved in double distilled water. Tap water polluted with small amounts of radio nuclides is the process wastewater.

The simulated wastewater used in the present work was prepared by adding low concentration of cobalt to tap water. The chemical composition of LLLW and PWW simulates used in the experiments as well as the obtained data are listed in Tables 8 and 9, respectively.

TABLE-8  
CHEMICAL COMPOSITION AND REMOVAL RESULTS OBTAINED FOR SIMULATED LLLW<sup>a</sup>

Ca:Mg		1:1	
Total hardness (g/L)		0.003	
SO <sub>4</sub> <sup>2-</sup> (g/L)		0.03	
Cl <sup>-</sup> (g/L)		0.02	
NO <sub>3</sub> <sup>-</sup> (g/L)		0.06	
PO <sub>4</sub> <sup>3-</sup> (g/L)		0.001	
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup> (g/L)		0.001	
<sup>137</sup> Cs		<sup>60</sup> Co	
Added (mg/L)	Removal (%)	Added (mg/L)	Removal (%)
0.008	93	0.025	99.5

<sup>a</sup>pH adjusted at 6 with HCl or NaOH, an average of three experiments.

TABLE-9  
CHEMICAL COMPOSITION AND REMOVAL RESULTS OBTAINED FOR SIMULATED PWW<sup>a</sup>

Cl <sup>-</sup> (mg/L)	18	CN <sup>-</sup> (mg/L)	0.001
Fe <sup>-</sup> (mg/L)	0.3	Na <sup>+</sup> (mg/L)	70
SO <sub>4</sub> <sup>2-</sup> (mg/L)	17	k <sup>+</sup> (mg/L)	14
Fe <sup>3+</sup> (mg/L)	0.12	Ca <sup>+</sup> (mg/L)	24
NO <sub>3</sub> <sup>-</sup> (mg/L)	0.02	Mg <sup>+</sup> (mg/L)	10
<sup>60</sup> Co			
Added (mg/L)	25	Removal (%)	98.5

<sup>a</sup>pH adjusted at 6 with HCl or NaOH, average of three experiments.

## Conclusions

From this study, it is concluded that: (1) The rice husk ash can be utilized for extraction and precipitation of silica gel using different acid leading to sorbent with various characterizations. (2) The thermodynamic study indicates that the adsorption of Co(II) onto Si-Cl-RHA is a non spontaneous, endothermic process and the adsorbed quantity increased with increasing temperature. (3) The presence of anions or cations in solution reduces the capability of Si-Cl-RHA for sorption Co(II) whereas, the existence of PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> increases the capacity by 0.83 and 14.09 %, respectively. Therefore, the PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup> could be added during the treatment of Co(II) using (Si-Cl-RHA). (4) Recovery of Co(II) and consequently

regeneration of Si-Cl-RHA is achievable using 0.5 M H<sub>2</sub>SO<sub>4</sub> with desorption efficacies higher than 99.5 %. (5) Removal of cobalt and cesium from simulates of low level radioactive liquid waste was performed with % removal of <sup>60</sup>Co and <sup>137</sup>Cs of 99.5 and 93 % respectively and from process wastewater (PWW) with % removal for <sup>60</sup>Co of 98.5 %. (6) Finally, the Si-Cl-RHA is a promising alternative sorbent for adsorption and separation of Co(II) ions from aqueous solutions.

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