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The removal of cadmium ions from aqueous solutions using silica support immobilized with 2-hydroxyacetophenone-3-thiosemicarbazone

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***Abstract*— A 2-hydroxyacetophenone-3-thiosemicarbazone functionalized silica was prepared and investigated. The functionalized silica showed a powerful removal behavior towards Cd(II) in aqueous solutions. The different factors affecting Cd(II) ions adsorption on this substrate such as contact time, pH, initial cadmium (II) ions concentration and chelating capacity were studied in detail. The FT-IR analysis was done to characterize the functionalization of 2-hydroxyacetophenone-3-thiosemicarbazone onto 3-aminopropyl silica. The adsorption was described by the Langmuir and Freundlich adsorption isotherms. The maximum adsorption capacity was 313 µg/g from the Langmuir isotherm at initial concentration of 1000 µg/g. The kinetic results shows that the adsorption describes well with the pseudo-second order kinetic model. Functionalized silica can be used as good adsorbent for the removal of the heavy metal pollutants according to results.**

Keywords- Heavy metal removal, cadmium, isotherms, 2-hydroxyacetophenone-3-thiosemicarbazone, functionalized Silica

I. INTRODUCTION

It is well known that toxic metal ions remain a serious environmental problem facing the world for water pollution, as a result of their numerous industrial applications viz electroplating, Nickel-cadmium battery production and disposal, fuels and pigments [1]. In addition many of them are known to be highly toxic at low concentration, not biodegradable and tend to accumulated in living organisms causing a serious disease and disorder such as Cd^{+2}, Hg^{+2}, Cr^{+6} and Pb^{+2} etc. [2]. Cadmium is a toxin of environmental concern. The impact for non-cancer causes includes kidney, liver and lung damage [3]. The association of cadmium with hormone related cancer such as prostate and breast cancer has being actively investigated since the initial implication [4-6]. Different techniques such as chemical precipitation, ion exchange, evaporation and adsorption are used for the removal of cadmium ions from aqueous waste solutions. Adsorption technique has become one of most commonly used treatment methods for the removal of cadmium ions. The use of activated carbon, metal oxides and silica with various reagents utilized for removal cadmium has also been frequently practiced [7-9].

Among the different adsorbents, silica gel especially immobilized with various organic compounds with metal chelating ability has received great attention [10, 11]. Because this support offers pronounced advantages over other organic/inorganic supports as listed below: (a) immobilization on silica results in great variety of silylating agents, allowing pendant functional groups in the inorganic framework [12, 13]; (b) attachment is easier on silica surface than on organic polymeric supports, which have a high number of cross-linking bonds, requiring hours to reach equilibrium for surface activation [13]; (c) silica gel being the most popular substrate for surface studies because it is the first commercially available high specific surface area substrate with constant composition, enabling easy analysis and interpretation of results [13]; (d) silica gel has high mass exchange characteristics and no swelling [14]; (e) silica support has great resistance to organic solvents [15];(f) silica has very high thermal resistance [16].

The adsorption capacity of silica can be enhance by modification of its surface through chemical functionalization. In this study, a chelating agent (2-hydroxyacetophenone-3-thiosemicarbazone), which has a selective reactivity for the target metal ion, was immobilized in 3-aminopropyl silica. The functionalized silica was then used as an adsorbent for the removal for Cd(II) from polluted water. To our best knowledge the use of such material for the water purification was not reported. The adsorption kinetics and isotherms of this novel material for the Cd(II) adsorption has been carried out.

II. MATERIALS AND METHODS

2.1. Instrumentation

All atomic absorption spectrometer (Analytik-Jena-Nova-400) measurements were carried out on flame mode with single beam. AAS equipped with 100 mm burner, a cross flow nebulizer 5.0 ml/min and 1.2 mm slit were used throughout the experiments. Each experiment was duplicated under identical conditions using this instrument for concentration determination. IR spectra were recorded on Jasco FT-IR spectrometer model 610 by using KBr pellets. The pH measurements were made on a digital pH meter (HACH, sension 1, model 51935-00) equipped with a gel-filled pH electrode. The meter was calibrated with the buffers of 4, 7 and 10.

2.2. Chemicals and solutions

Laboratory wares used for analytical determination were cleaned first by trace metal grade nitric acid and hydrochloric acid, followed by repeated rinsing with de-ionized water. All of the reagents used were of analytical-grade. All the solutions were prepared with ultrapure water (resistivity: 18.2 MΩ.cm,) from a Elix analytical reagent-grade water

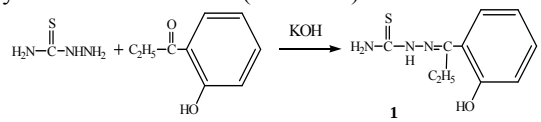
purification system. 3-Aminopropyl silica purchased from Aldrich with following characteristic particle platform irregular, functionalized 9%, Surface area 550 m^2/g, Mean pore size 60 A^o.

Calibration standard solutions and internal standards were prepared from commercial metal standard solutions. Analytic grade nitric acid (Fisher) was used as acid for the preparation of all the calibration standard solutions and analytical solutions.

Standard working solutions of cadmium were prepared from 1000 mg/L standard solution (Merck, Germny) and solutions of varying initial concentrations were prepared from a 1000 mg/L by serial dilution using distilled deionized water.

2.3 Synthesis of 2-hydroxyacetophenone-3-thiosemi-carbazone

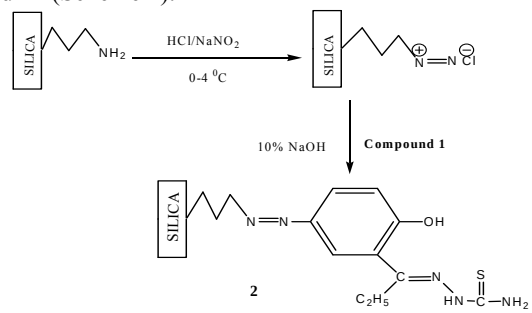
2-Hydroxy acetaphenone (0.3 mol dissolved in 50 mL of methanol), thiosemicarbazide (0.3 mol dissolved in 200 mL of water) and potassium hydroxide (3 g dissolved in 25 mL of water) were mixed in a round bottomed flask and refluxed for 3 h and after cooling , was poured in ice water. The yellow crystals obtained were washed repeatedly two or three times with ethanol and then purified by recrystallization in ethanol (Scheme 1).



SCHEME 1

2.4 Functionalization of 3-aminopropyl silica with 2-hydroxyacetophenone-3-thiosemicarbazone

3-Aminopropyl silica (10 gm) and 20 mL HCl solution (conc. HCl : H_2O ; 1:1 v/v) were stirred in conical flask at 0-4 ^0C, then added drop wise solution of 10 mL $NaNO_2$ (5 M solution of $NaNO_2$ in water) until the reaction mixture showed a permanent dark blue color with starch-iodine paper with continuous stirring. The diazotized silica was washed with ice cold water and reacted with 2-hydroxyacetophenone-3-thiosemicarbazone (2 gm dissolved in 50 mL of 10% NaOH solution) at 0-4 0C for 10 h. The resulting brown silica was filtered, washed with water and air dried (Scheme 2).



SCHEME 2

2.5. Removal studies with Batch method

Adsorption experiments were carried out in glass bottles containing functionalized silica (50 mg) with 10 mL of the cadmium ions concentration 1000 µg/L at solution pH (2.7) at 30±1 ^oC. Five milliliters of the solution from each glass bottle was taken at different time interval (5, 10, 20, 30, 60 and 120 min.) to determine the optimum contact time where the maximum adsorption was accomplished for cadmium (II) ions. The residual concentration of cadmium ions was determined using AAS. The amount of metal ion adsorbed by silica (q_e mmol/g) was calculated according to the following equation:

$$Qe = (Ci - Ce) \times V/m \qquad (1)$$

where *Ci* and *Ce* are initial and equilibrium concentration (µg/L),respectively. *V* (L) and *m* (g) are volume of the sample solution and mass of the functionalized silica, respectively.

The optimum contact time was determined as 10 min and used throughout all adsorption experiments. Uptake experiments of metal ions at different pHs (2.7, 7, 9 and 10) were carried out by placing 50 mg silica containing 10 mL solution of cadmium with an initial concentration of 1000 µg/L.the pH was adjusted using 0.1 M NaOH and 0.1 M HCl. The residual concentration of lead ions was determined using AAS. The amount of metal ion adsorbed by silica (q_e mmol/g) was calculated according to the equation (1). The results showed that qe maximum observed at pH 2.7 (Solution pH).

Cadmium ions concentration 500,600,900, 1000, 1100 and 1200 µg/L were prepared and used to obtain the adsorption isotherm data on the adsorption process. 50 mg silica was placed in a series of glass bottles containing 10 mL of cadmium ions solution with above said concentration at pH 2.7 for 10 minutes. After equilibration, 5 mL of the solution was taken for the determination of residual concentration of metal ions by AAS. The amount of metal ion adsorbed by silica (q_e mmol/g) was calculated according to the equation (1).

2.6 Kinetic adsorption experiment

The kinetic study uses two concentrations (500 and 1000 µg/L) at pH of 2.7. Data acquisition protocol includes the treatment of a series of 50 mg of the functionalized silica with 10 mL of cadmium solution. These series of samples are quenched at time interval by filtration. The concentrations of the filtrate were analyzed by AAS. These results were also used to obtain the adsorption kinetic.

III. RESULTS AND DISCUSSION

3.1. Characterization of Material

A schematic representation of synthesis of 2-hydroxyacetophenone-3-thiosemicarbazone (1) is shown in **scheme 1.** The FT-IR spectrum of 2-hydroxyacetophenone-3-thiosemicarbazone (Fig. 1) showed absorption bands at 3420, 3250,1623,1376, 1240 and 1106 cm^{-1} due to NH_2 stretching , O-H stretching, C=N stretching, C=S stretching, O-H bending and C-N stretching, respectively. The appearance of the characteristic IR absorption bands of these groups as a proof for the compound 1. The synthesized compound was used to functionalize 3-aminopropyl silica as shown as shown in scheme 2.

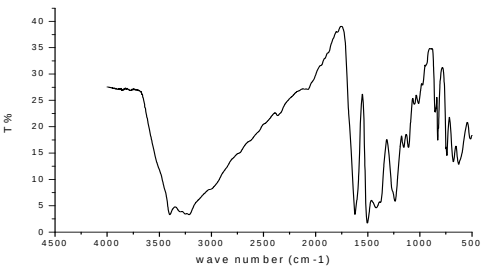


Fig. 1. FT-IR spectra of 2-hydroxy acetaphenone-3-thiosemicarbazone

In the FT-IR of 3- aminopropyl silica shows absorption band (Fig. 2a) at 1150 cm^{-1} for the Si-O-Si group and O-H stretching of silanol group at 3450 cm^{-1}.After functionalization new absorption bands (Fig. 2b) appear at 3436, 1670, 1525, 1390, 1230 and 1105 cm^{-1} which may be assigned to NH_2 stretching, C=N stretching, N=N stretching, O-H bending, C=S stretching and C-N stretching, respectively, and the presence of Si-O-Si group absorption band at 1150 cm^{-1} . The presence of absorption band of these groups confirmed that 3- aminopropyl silica functionalized with 2-hydroxyacetophenone-3-thiosemicarbazone.

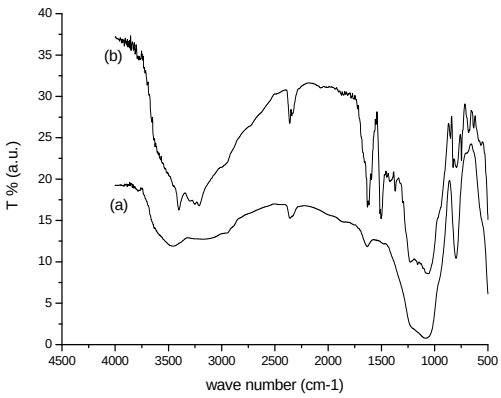


Fig. 2. Comparative FT-IR spectra of (a) 3-aminopropyl silica (b) functionalized silica with 2-hydroxy acetaphenone-3-thiosemicarbazone

3.2. Adsorption isotherms

The initial cadmium (II) concentrations (500-1100 µg/L) have been used for investigation of the adsorption isotherm. The equilibrium concentrations are obtained after 10 minutes of contact time. The amount of Cd (II) adsorbed on the functionalized silica was found to increase as the initial metal ion concentration increased and continued up to 1000 µg/L and level off there after (*C*e in Fig. 3). Two models, both Langmuir [17] and Freundlich [18], are applied to analyze the data. The Langmuir isotherm (Fig. 4) model is based on the equation of $Ce/Qe = 1/(Qmb) + Ce/Qm$, where *C*e is the equilibrium concentration obtained from the initial concentration upon a certain period of contact time with the chelating polymer, *Q*e is the amount of Cd(II) ions adsorbed per gram of functionalized silica (µg/g) at equilibrium, and *Q*m is the maximum adsorption capacity (µg/g). *b* is the Langmuir parameter related to energy of adsorption. *Q*e is derived from the equation 1. The linear plot of *C*e/*Q*e vs *C*e gives the intercept and slope corresponding to 1/(*Q*m*b*) and 1/*Q*m, respectively, from which both *Q*m and *b* are derived. A plot of *C*e/*Q*e vs *C*e should yield a straight line if the Langmuir equation is obeyed by the adsorption equilibrium [19].

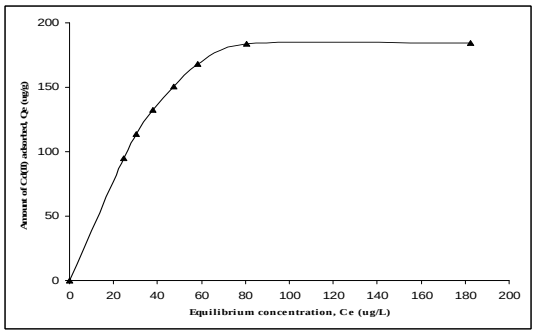


Fig. 3. Effect of the initial concentration on Cd(II) adsorption determined through equilibrium concentration and adsorption capacity

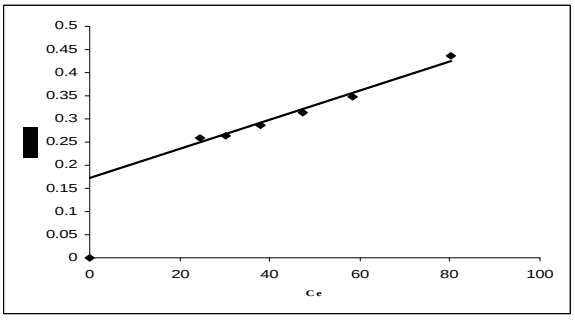


Fig. 4. Langmuir isotherm

On the other hand, the Freundlich isotherm (Fig. 5) is analyzed based on the equation of $\log Qe = 1/n \log Ce + \log K$, where *K* and 1/*n* are Freundlich constants, indicating the sorption capacity and sorption intensity, respectively. *C*e is the equilibrium concentration of cadmium (II) in aqueous solution and *Q*e is the sorption capacity. The plot of log*Q*e against log *C*e gives the intercept and slope corresponding to log *K* and 1/*n*, respectively, from which both *K* and *n* are obtained.

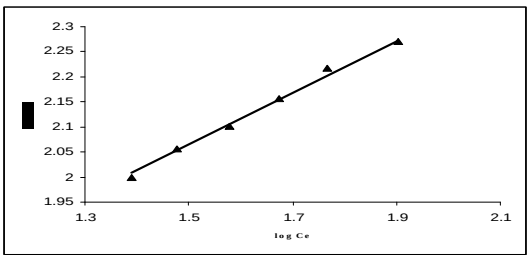


Fig. 5. Freundlich isotherm

Langmuir Model		
Qm(µg/g	b(L/µg)	R^2
313	0. 0185	0.8825
	Freundlich Model	
K	1/n	R^2
20.5	0.5109	0.9931

TABLE 1:LANGMUIR AND FREUNDLICH PARAMETERS OF CD(II)

3.3 Adsorption kinetics

The kinetic property of cadmium (II) adsorbed on the functionalized silica was assessed (Fig. 6). The adsorption rates were determined at pH of 2.7 in the range of Cd (II) concentrations 500 and 1000 µg/L in aqueous media. The adsorption kinetics exhibits the following characters: (1) the adsorption is fast, and (2) the adsorption increases with increased concentration of the metal ion. At any given concentration, the Pb (II) adsorption quickly rose, and then reached the plateau, which is the equilibrium capacity. In all two cases, the adsorption reached the equilibrium capacity in 10 minutes. This fast kinetics results from a high complexation process between the metal and the chelating units. At higher concentrations, more Cd(II) ions in liquid phase facilitate mass transfer to the solid surface as a result of great concentration gradient between the two phases. The noticeably short time to reach the equilibrium for present kinetic study complements those reported from various systems for the heavy metal removal. The equilibrium time is an important factor for cost-effective application in practical systems.

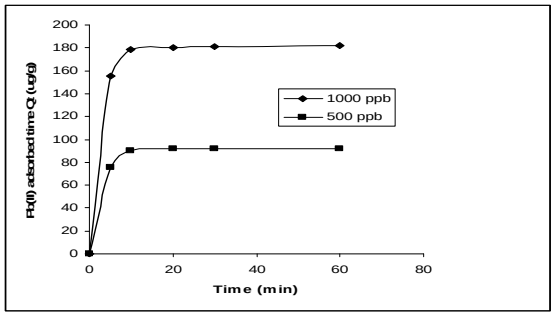


Fig. 6. The adsorbed amounts of Cd(II) at varying initial concentration with time

The adsorption kinetic mechanism was evaluated using one conventional model, namely the pseudo-second-order equations [19] In this case of pseudo-first-order, very low correlation coefficient values were obtained, so that this model was not reported for absorption kinetic studies.

A pseudo-second-order reaction is guided by the expression of $t/Qt = 1/(k_2Qe)^2 + t/Qe$ [20,21], where Qe (µg/g) is the amount of metal ion sorbed at equilibrium, Qt (µg/g) is the amount of metal ion on the surface of the sorbent at time t and k_2 [g/(µg min))] is the rate constant of pseudo-second-order adsorption. The values of $1/(k_2Qe)^2$ and 1/Qe are derived experimentally from the intercept and slope of the linear plots of t/Qt versus t, which eventually leads to values of k_2 and Qe (Fig. 7).

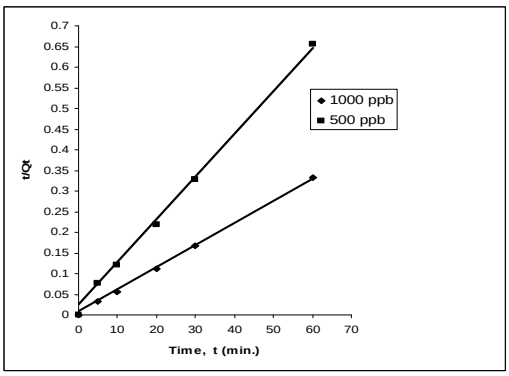


Fig. 7. Second order kinetic plot for the adsorption of Cd(II)

It is found that this pseudo-second-order approach gives high correlation coefficient values, indicating that the pseudo-second-order is the model applicable to the present adsorption kinetics. The kinetic data for second-order assessment are listed in Table 2.

Table 2: Kinetic parameters for Cd(II) adsorption onto the functionalized silica

C_0 (µg/L)	Second order		
	K_2 [g/(min µg)	Qe (µg/g)	R^2
500	0.2763	39.327	0.984
1000	0.0695	193.532	0.997

It is apparent that the high adsorption rate is corresponding to the fast equilibrium. This coupled with the Langmuir monolayer adsorption coverage suggests that the chelating silica has most of their chelating groups on or near the surface for easy access. As pointed out earlier, the complexation is very fast between Cd (II) ions with the chelating groups. All these factors indicate the potential high efficiency of the adsorption process, in particular as far as the rate is concerned.

This general tendency prompts us to speculate that different types of coordination mode would take place during the interaction of metal and functionalized silica. They are based on number of chelating units involved (Fig. 8) to cover two scenarios: when only one unit is available, an anion has to participate either in inner or outer coordination sphere to balance the charge (Fig. 8a-c); if two chelating units in the close proximity from the same chain and adjacent chains are available, they would complete six coordination (Fig. 8d).

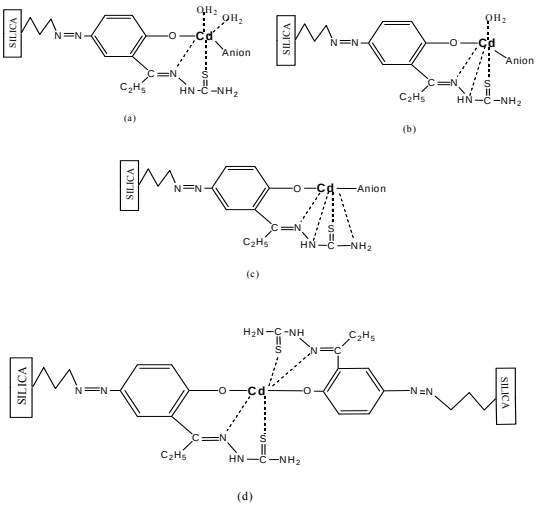


Fig. 8. Plausible coordination modes of metal and helating units

IV. CONCLUSION

The present research establishes the ability of silica support immobilized with 2-hydroxyacetophenone-3-thiosemi-carbazone to adsorb cadmium of low concentration with fast equilibrium rate. The investigation of it's for the removal has found the fast complexation capability for the lead of the ppb concentrations studied. The adsorption is best described with the Langmuir model, indicating the monolayer coverage of the metal ion on the surface of functionalized silica. The kinetic study has revealed a very fast adsorption process, which is in 10 minutes to reach the equilibrium capacity. The adsorption rate follows the pseudo-second-order according to reaction constants.

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