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Functionalized nano spheres for efficient sequestration of cadmium ions

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Abstract

This manuscript communicates the synthesis, characterization and its subsequent application in Cd(II) ions sequestration of thiosemicarbazide functionalized nano silica spheres. The spheres are developed by sol-gel method, activated with an organosilane precursor and later on conjugated with thiosemicarbazide through one step Manich reaction. The successful grafting is confirmed through FTIR, TGA, SEM and EDX analysis. The Cd(II) ions sequestration from aqueous solutions is studied exhaustively in competitive and non competitive environments in batch experiments using radiotracer technique. The sorption process is fast and attain equilibrium in 40 minutes time with 98% Cd(II) ions sequestration at pH 7 and follows first order kinetics (K = 0.0465 min^{-1}). The sorption data follow the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms and its characteristic constants: N = 10 mmole g^{-1} and b = (0.1) × 10^4 dm^3 $mole^{-1}$, 1/n = 0.64 and of C_m=0.04 mmole g^{-1} and D-R constants β= −0.00064 kJ^2 $mole^{-2}$, X_m=1.8 mmole g^{-1} and E_s=8.8 kJ $mole^{-1}$ have been computed. The sorption of Cd(II) ions onto nano spheres is spontaneous (ΔG= -1050.00 $Jmol^{-1}K^{-1}$) and endothermic in nature (ΔH=2.45 $Jmol^{-1}K^{-1}$). The Cd(II) ions sequestration is highly reduced in the presence of Cyanide, EDTA, Aluminum and Nickel ions. The sorbent is regenerable and can be used several times.

Keywords : Thiosemicarbazide; functionalized nano spheres; cadmium; wastewater treatment

1. Introduction

Heavy metals due to their technological importance have extensive applications in industries such as electroplating, tanneries, paints, metallurgy, chemical and pharmaceutical etc. The large scale production and disposal of these heavy metals poses serious health and environmental hazards because of their frequent appearance in wastewater. Many metal processing industries discharge their wastes, without prior purification which causes serious environmental problems. The concentration of these toxic heavy metals is often higher than the permissible limits. Trace metal determination and cleaning is essential in pharmaceutical, food, agricultural and chemical industries. Direct determination of metal ions at trace level is difficult due to their presence beyond the detection limit and matrix interferences. Classical methods such as co-precipitation, ion exchange, solvent extraction, cloud point extraction and biosorption etc. are used for pre-concentration/separation of trace level impurities [1] [2]. Due to their inherent limitations a promising material for pre-concentration/separation is always demanded.

Functionalized sol gel nano silica is a prospective candidate for cleaning of low level impurities from aqueous, petrochemicals and gaseous media. Silica tailored with organic functional groups is getting special attention and used in various areas like adsorption of radiotracers [3,4], ion exchange[5], biotechnology[6], catalysis[7] and green chemistry[8]. Silica surface can be tailored with desired functional groups, which selectively direct the chelation of target metal ion towards the sorbent surface[9] [10].

Cadmium is used in a variety of industrial applications and causes a variety of syndromes, renal dysfunction hypertension, lung and liver damage, and teratogenic effects[11]. Considering the toxicological effects of cadmium and its strategic importance there has always been a demand of preparing novel separating agents which could be effectively used for the sequestration of Cd(II) ions from aqueous media. Keeping this important purpose in mind we report the synthesis of novel nano sorbent through covalent grafting of organic ligand thiosemicarbazide (TSC) to nano silica spheres. Thiosemicarbazide is one of the key compounds having N-S donor atoms and capable of complexation with a number of metal ions in pharmacological and biological applications [12- 14], and never used as complexing agent on the surface of nano silica spheres for the sequestration of Cd(II) ions. It has a great potential and can be used for the sequestration of cadmium from aqueous and organic media.

2. Experimental

2.1. Reagents and chemicals

Tetraethylorthosilicate (TEOS) 97%, N-Cetyl-N, N, N–Trimethylammonium bromide (CTAB), thiosemicarbazide (TSC) and 3-aminopropyltrimethoxy silane (APMTS) 98% and all other analytical grade reagents were used without any purification.

^{115}Cd radiotracer was prepared by the irradiation of spec pure metal in PARR-1, the research reactor of PINSTECH at a neutron flux of 7×10^{13} Sec^{-1} and dissolved in concentrated HCl. The acid was removed by repeated evaporation with distilled water and finally 5.0 cm^3 stock solution was made for further experiments. Radiochemical purity of the tracer was checked by 25 Cm^3 Ge(Li) detector coupled with a 4k series of 85 Canberra, USA multichannel analyzer

The buffer solutions of pH 1-8 were prepared by using an appropriate volumes of potassium chloride and hydrochloric acid (pH 1-2), sodium acetate and acetic acid (pH 3-6) and boric acid and sodium hydroxide solutions (pH 7and 8).

2.2 Apparatus/ instruments

All pH measurements were made on a Metrohm-605 pH meter. The shaking was carried out in a 30 ml Pyrex glass vials lined with screw- type polythene cap. Gross gamma-ray detection was made on a Tennelec; USA counting assembly equipped with a 25 cm^3 NaI (Tl) crystal.

2.3 Synthesis of thiosemicarbazide functionalized nano silica spheres

Nano silica spheres were prepared using sol-gel method as described in the literature [15]. -NH_2 functional groups were immobilized onto nano silica as reported earlier[16]. For the synthesis of thiosemicarbazide functionalized nano spheres 5 g of TSC was dissolved in 50 ml of distilled water in a three neck flask placed on a hot plate fitted with a condenser and magnetic stirrer. 30 ml of 37 % formaldehyde was drop wise added to this solution, and the mixture was refluxed for 1 hour at 90°C**.** The resulting mixture was distilled to remove unreacted water and formaldehyde. 10 g of NH_2-silica (APTMS) and 50 ml methanol was added to this solution and refluxed for 30 min with vigorous stirring at 90°C. The resulting TSC functionalized silica spheres were filtered, washed repeatedly with deionized water, ethanol and methanol and dried in oven at 45 °C for 12 hours. The synthesis scheme is given in Fig. 1.

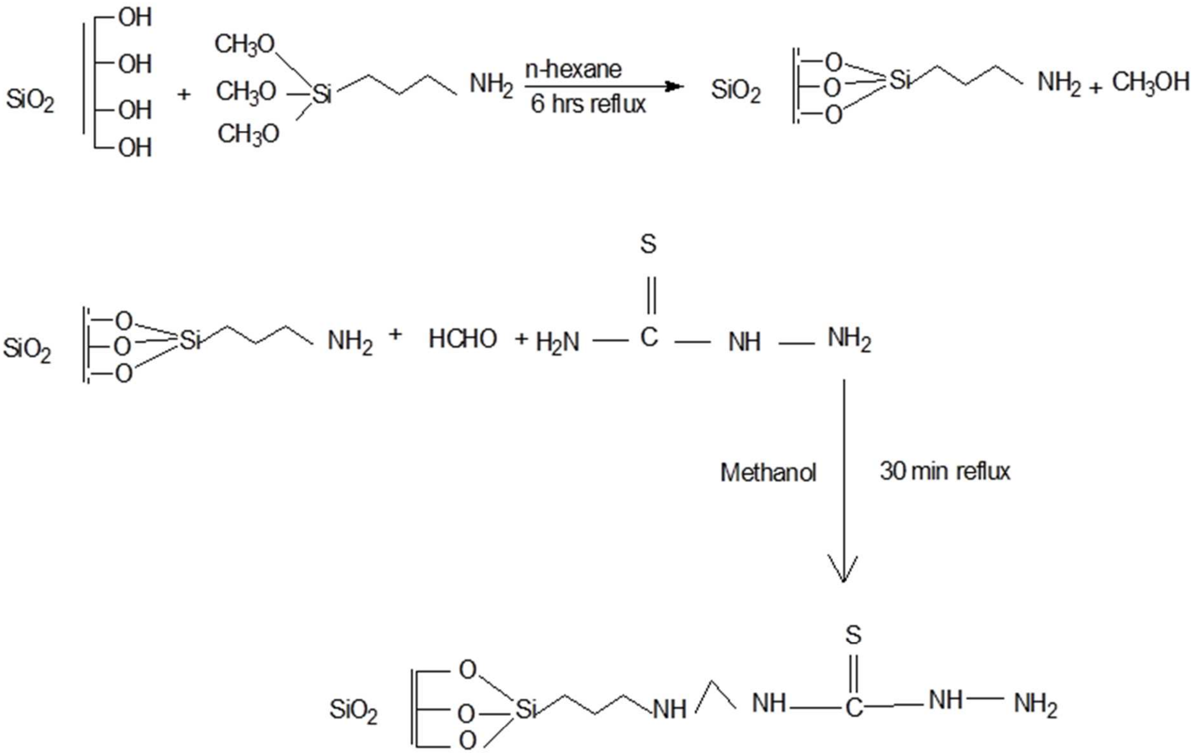

Fig.1 Synthetic scheme for the preparation of TSC functionalized nano spheres

2.4 Procedure for cadmium ions sequestration

Cadmium sequestration was investigated in batch experiments using radiotracer technique at room temperature (25± 1°C) unless described. A known amount of radiotracer was added to a 5 cm^3 solution of an electrolyte of specific pH, in 30 cm^3 glass vial and mixed uniformly. Then 1 cm^3 solution was taken out for gross gamma counts (A_0). A_0 is considered as initial concentration of Cd(II) solution. The remaining solution was equilibrated with a known quantity of nano spheres for a specific period of time in a Wrist action shaker (Griffin UK). After shaking, the solution was centrifuged for about 5 minutes and 1 cm^3 of the aliquot was taken out for radio assay (A_e). A_e is the equilibrium concentration of Cd(II) ions removed. Cadmium % sorption was calculated by using the relationship

$$\% \, Sorption = \frac{A_o - A_e}{A_e} \times 100 \qquad (1)$$

The distribution coefficient K_d is calculated as

$$K_d = \frac{Amount\ of\ metal\ ions\ sorbed}{Amount\ of\ metal\ ioin\ solution} \times \frac{Volume\ of\ solution\ (V)}{Weight\ of\ sorbnt\ (W)} = (cm^3/g) \qquad (2)$$

3. Results and Discussions

3.1. Characterization of the sorbent

Specific surface area, total pore volume and pore diameter of sol-gel silica nano spheres was calculated from Brunauer-Emmett-Teller (BET) equation. The nano spheres were porous in nature with a surface area of 920 m^2/g, pore volume of 0.96 cm^3/g and a pore diameter of 4.17 nm. The high surface area is an important factor for immobilization of organic molecules. Fig.2. presents the scanning electron microscope (SEM) images of virgin (left) and functionalized silica nano spheres (right). The similarity between the two images reveal that the particles preserve their spherical morphologies after functionalization, suggesting that anchoring is a chemical process. The surface is fine-tuned with desired function groups without disturbing the basic morphology of the parent nano spheres. The nano size of the spheres was confirmed from SEM images.

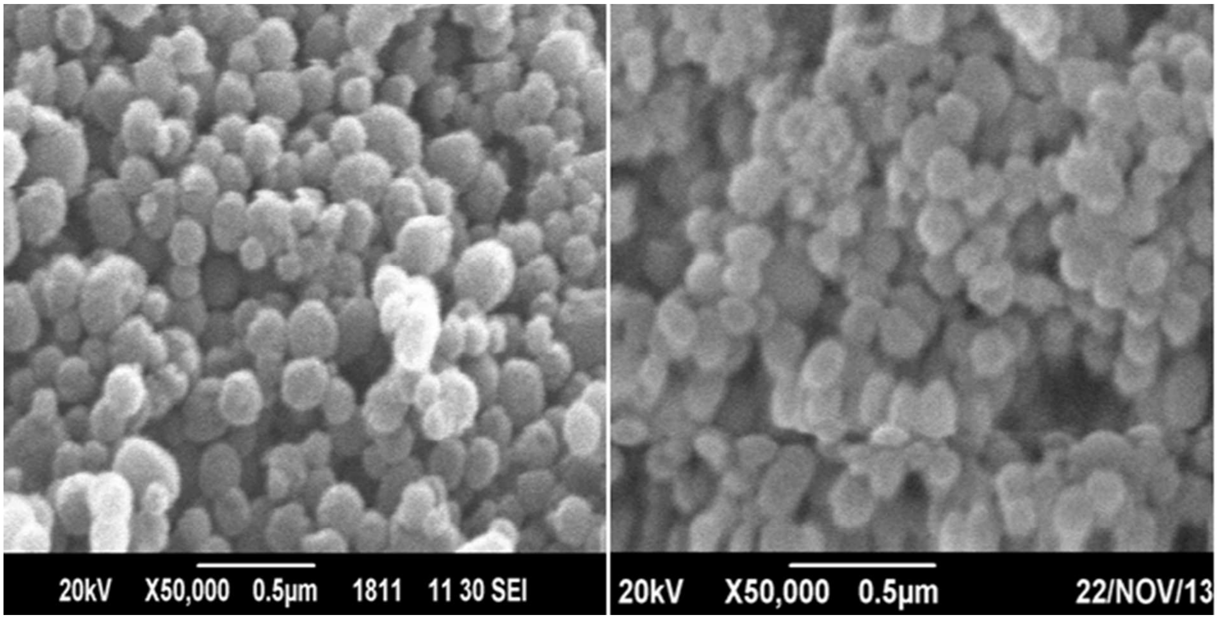

Fig. 2 SEM images of nano silica sphere (left) and thiosemicarbazide functionalized nano spheres (right)

Fig. 3 shows EDX analysis of functionalized nano silica spheres. The spectrum of fine silica show signals for the presence of oxygen, sulfur and nitrogen along with carbon and silicon which originate from organic moitities during anchoring of silica spheres. The EDX spectra further confirm successful immobilization of these organic groups on the surface. The adsorption processes are assumed to occur by the complex formation reaction between these hetero atoms and Cd(II) ions.

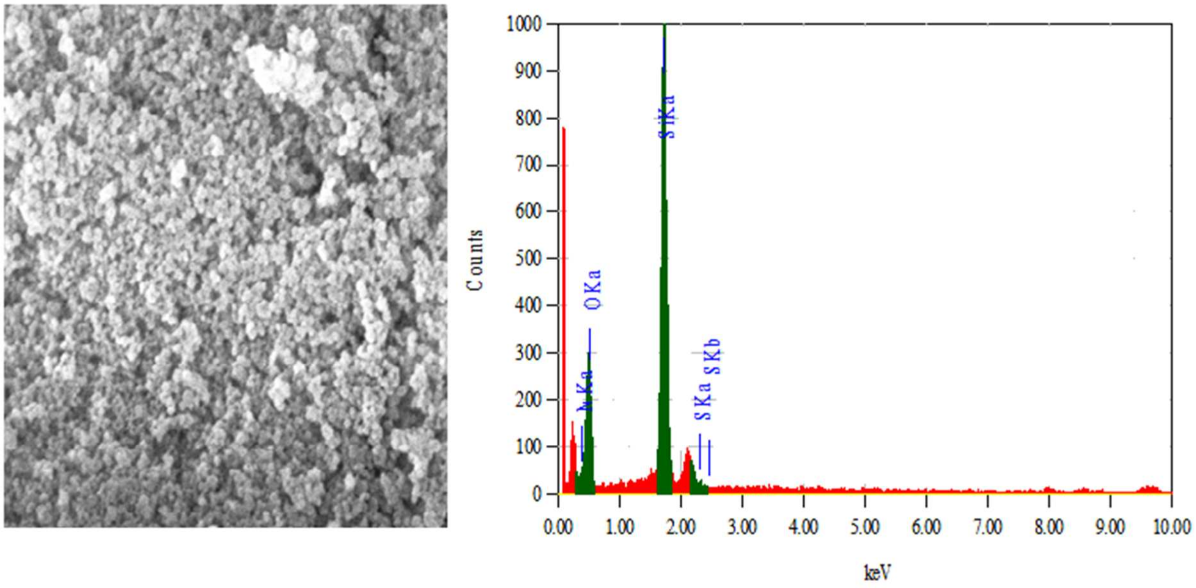

Fig. 3 EDX spectra of thiosemicarbazide functionalized nano spheres

The FT-IR spectra of the virgin (a) APTMS (b) and TSC (c) modified nano spheres is given in Fig. 4. The careful study of the figure shows that after functionalization with APTMS nano silica shows visible adsorption peaks at 1542 and 1637.37 cm^{-1} (Fig. 4.b) matching to the bending vibration of N-H group, N-H (3200-3500 cm^{-1}) and C-N(1030-1230 cm^{-1}) stretching vibration overlap with the broad absorption band of silanol group and Si-O-Si vibrations[17 18] (Fig.4.b). The bands at 2855.50 and 2927.1 cm^{-1} are assigned to symmetric and asymmetric vibrations of CH_2 groups. The appearance of these peaks is an excellent proof for the immobilization of the amine moitities. After immobilization of TSC ligand some new peaks appeared at 1344.93 and 1489.57 cm^{-1}, which are assigned to S =C-NH vibration of TSC immobilized silica [19 20] (Fig.4.c). The stretching vibration peaks of C=S (730 cm^{-1}- 1089 cm^{-1}) overlap with strong skeletal vibrations of silica. The appearance of some new peaks and disappearance/ modification of original peaks attest successful immobilization of the chelating ligand.

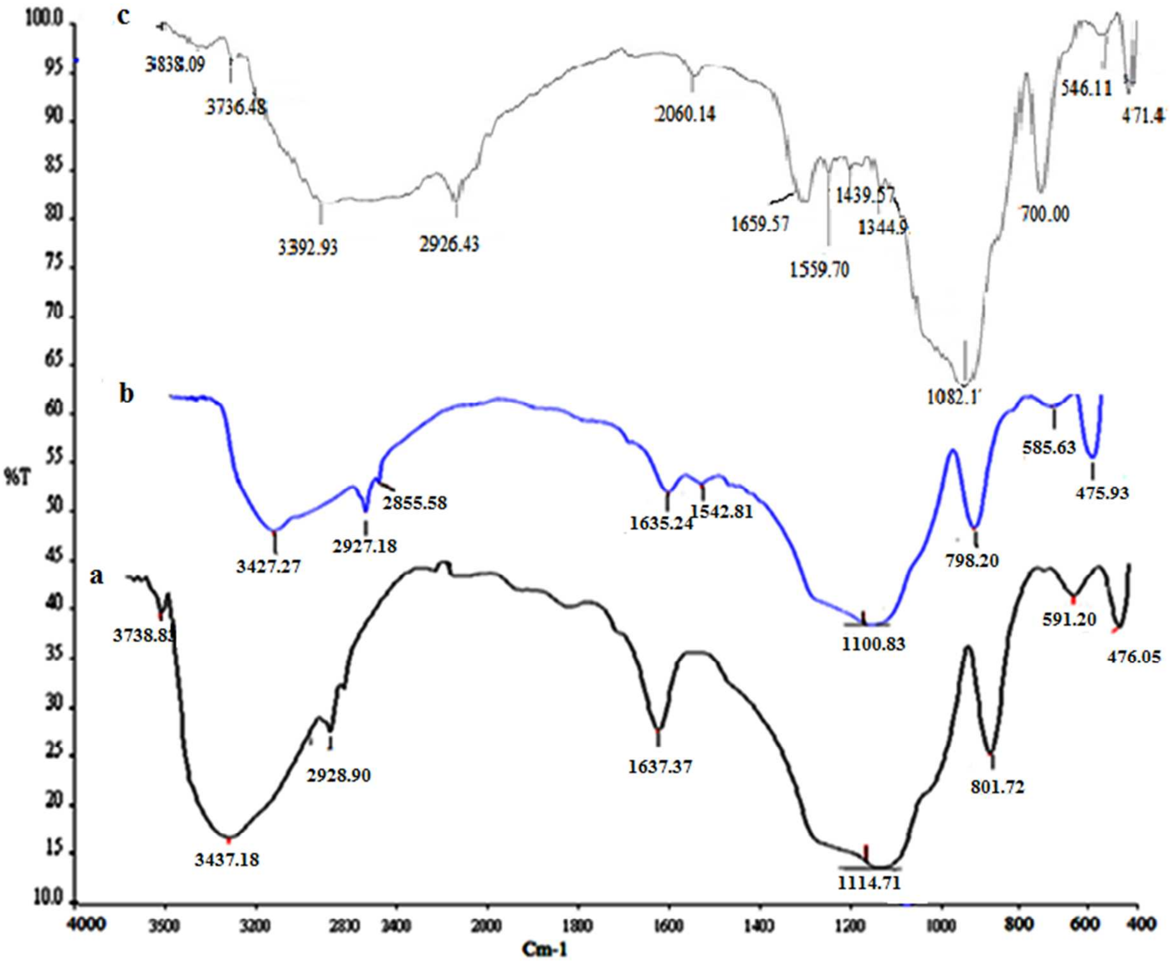

Fig. 4 FTIR analysis of virgin (a), NH_2 (b) and thiosemicarbazide (c) functionalized nano spheres

Thermograms for the plain and functionalized silicas are recorded over a temperature range of 30-700 ^{0}C at constant heating of 10 ^{0}C/min (Fig.5). Virgin spheres showed high stability, only physisorbed water and residual surfactant was removed. The 3-aminopropyl trimethoxy silane (APTMS) modified silica spheres loses its weight from 30-200 ^{0}C (5%), 200-

500 ^{0}C (4%) and 500-700 ^{0}C (6%) correspond to physically adsorbed water, the decomposition of organic groups[21] and condensation of silanol groups to yield siloxane groups respectively. The thiosemicarbazide modified nano spheres loses its mass in temperature range 30-250 ^{0}C (3%), 250-500 ^{0}C (3%) and 500 - 700 ^{0}C (6%), attributed to the loss of water molecules [22] [23], decomposition of -NH-C=S organic molecule and condensation of surface silanol to produce siloxane groups [24] [25]. The differences in thermal behavior of the materials show that they have different chemical compositions owing to the attachment of organic functional groups.

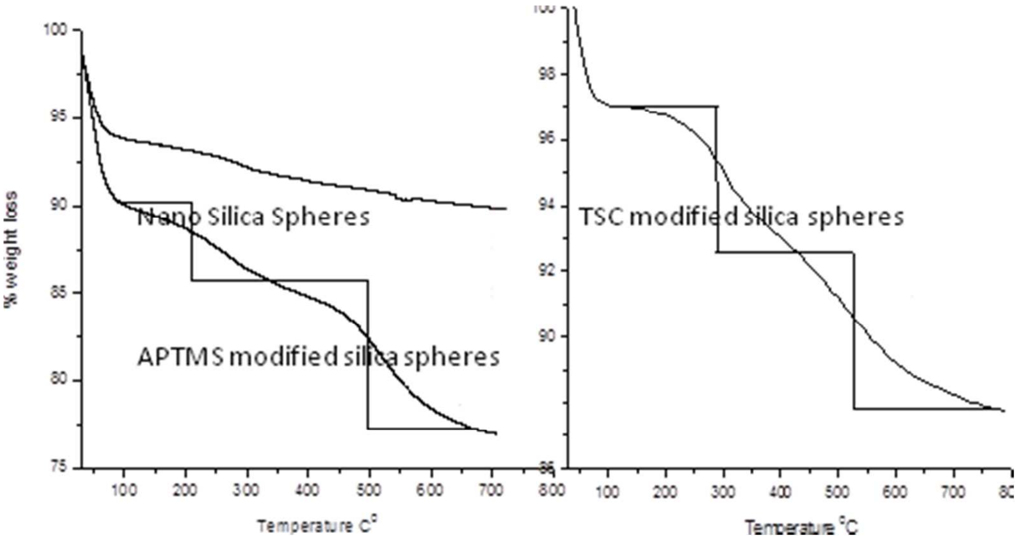

Fig. 5 Thermogravimetric analysis of virgin, APTMS and TSC functionalized nano spheres

3.2 Evaluation of nano spheres for metal ions sequestration

3.2.1 Effect of pH on Cd(II) sequestration

pH affects the sequestration process in several ways such as solubility of metal ions, counter ion concentration and the extent of ionization of the adsorbate [26]. It also provides additional selectivity to the sorbent. Keeping this in mind we examined the role of pH in the removal of Cd(II) ions from aqueous solution in a pH range of 1 to 8 and the results are depicted in Fig 6. Initially up to pH 4 no sorption occurred, might be due to the protonation of thiol and amine groups. The sorption of Cd(II) ions starts at pH 5 and attains maximum at pH 7 while at pH 8 it again decreases. In this pH range neither protonation of the ligand hetero atoms nor precipitation of the metal is expected[27 28]. Maximum sorption capacity of Cd(II) has been reported for pyrocatechol functionalized XAD in the pH range of 5-8 [29], at PH 4-5, tiron[30], aminophenol[31] and between 5 and 6 dithizone[32]. Above pH 5, the ligand coordination sites are deprotonated and more lewis bases such as –OH, -NH and =S- present on the surface of the sorbent are available to positively charged metal ions for chelation[33]. Up to pH 8 the dominant species of the Cd(II) is Cd^{+2} (100%)[28]. Above pH 8 the metal is prone to precipitation and hydrolysis[34] and yields $Cd(OH)_2$. Further sorption tests were not conducted and pH 7 is selected as an optimum sorptive media for further experiments.

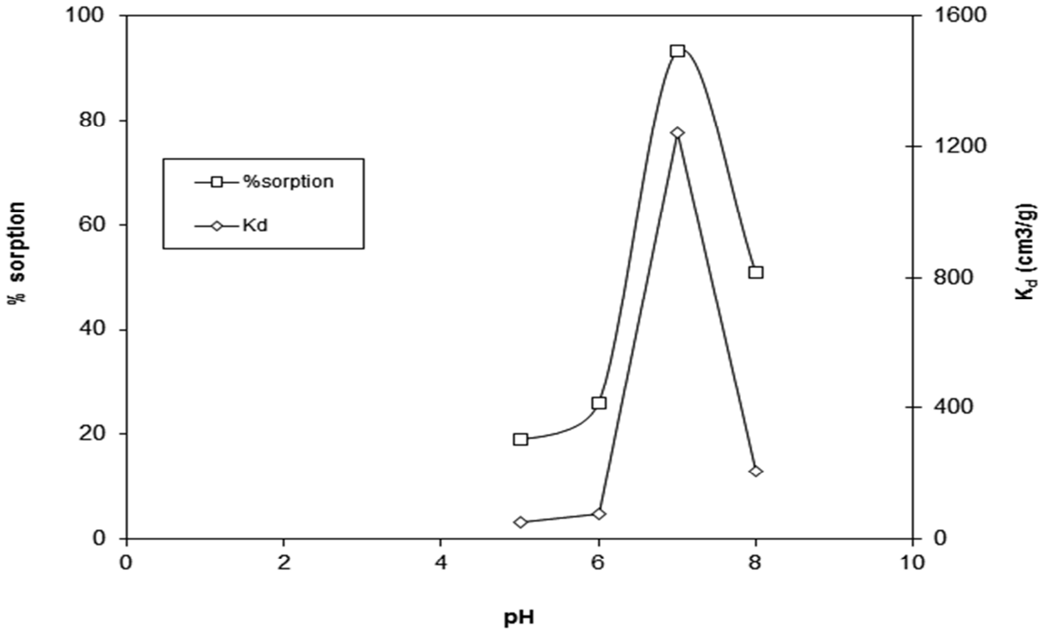

Fig. 6 Effect of pH on Cd(II) ion sequestration by TSC functionalized nano spheres

3.2.2 Kinetics of Cd(II) ions removal

The influence of equilibration time on the rate of sequestration of Cd(II) ions onto TSC functionalized nano spheres is studied in the range 5-60 minutes and the results are presented in Fig. 7. It can be seen that the sorption kinetics was fast and about 85% of cadmium is removed within first 10 minutes of agitation. The fast equilibration reflects the strong affinity of the material for binding metal ions which broadens its scope for application on large scale. The detailed kinetics evaluation of the process shows that the process is first order with a rate constant K (0.0465 min^{-1}). Further intra particle diffusion is not a predominant process initially and intra particle diffusion rate, R_D is 8.92μmolg^{-1} min$^{-1/2}$. The surface diffusion also plays a role in determining the kinetics.

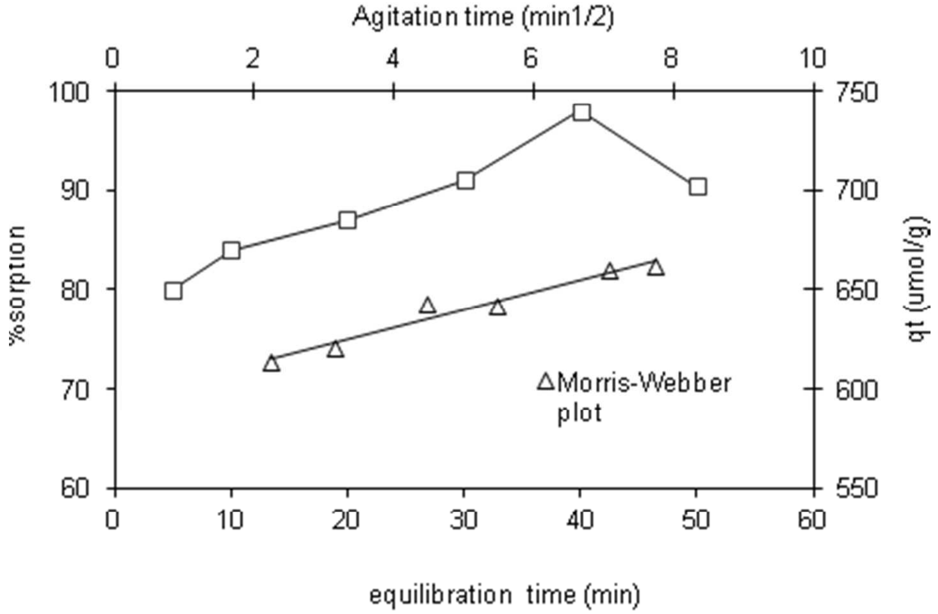

Fig. 7 Cd(II) ions sequestration as a function of equilibrium time

3.2.3 Effect of functionalized material quantity on sequestration of Cd(II) ions

Effect of gel quantity on the Cd(II) ion sequestration has been examined from 2-12 mg/ml of the TSC functionalized nano spheres at constant Cd(II) concentration ($7.39\text{x}10^{-5}$ M). The nano spheres offer its large surface area and vacant adsorption sites to the incoming metal ions. Initially increase in nano spheres dosage leads to increased sequestration. After some time when all the present sorbate ions are accommodated then increase in adsorbent dosage have no effect on sorption of metal ions and it remains constant. It shows that a small amount of the nano functionalized sorbent (4mg/ml) suffices to accommodate all the present heavy metal ions in a given volume which again shows the suitability of the sorbent on large scale.

3.2.4 Effect of Cd(II) ions concentration on its sequestration

The effect of initial concentration of Cd(II) ions on its removal from aqueous solution was examined over 8-fold increase in the concentration ($3\text{x}10^{-5}$- $24\text{x}10^{-5}$ M) of Cd(II) ions at pH 7.0 and 20 mg of functionalized nano spheres and the results are presented in Fig. 8. The initial metal ion concentration provides a driving force which helps to overcome the mass transfer resistance of the accumulating material in aqueous medium. This leads to increase in uptake capacity of the material[35]. At lower concentrations, the metal ions present in system experience lower inter-ionic repulsion, are capable of interacting with binding sites of the material. To explain the sequestration mechanism, the data were fitted to Freundlich, Langmuir and D-R isotherms models as shown in Equations 3-6 and the constants calculated from these equations are reported in Table. 1.

$$\frac{C_e}{q_e} = \frac{1}{Nb} + \frac{C_e}{N} \qquad (3)$$

where C_e is the equilibrium concentration (mmol) of Cd(II) ions in solution, q_e is the amount of cadmium adsorbed at equilibrium (mmol g^{-1}), N is the maximum sorption capacity (mmol g^{-1}) and b is Langmuir constant.

$$logC_{ads} = logC_m + \frac{1}{n}\log C_e \qquad (4)$$

where C_e and C_{ads} are the equilibrium concentration (mol L^{-1}) of Cd(II) ions in solution and sorbed on nano spheres (mol g^{-1}) respectively. C_m and 1/n are Freundlich constants shows maximum sorption capacity and sorption intensity respectively.

$$lnC_{ads} = lnX_m - \beta\varepsilon^2 \qquad (5)$$

where C_{ads} is the sorbed metal ion in mol g^{-1} per unit mass of the sorbent, X_m is the maximum sorption capacity in mol g^{-1} of the nano sheres, β is a constant in units of kJ^2 mol^{-2} and Ɛ is a polynomial potential. The mean sorption energy E_s is related to X_m and calculated by the equation

$$E_s = \frac{1}{\sqrt{-2\beta}} \qquad (6)$$

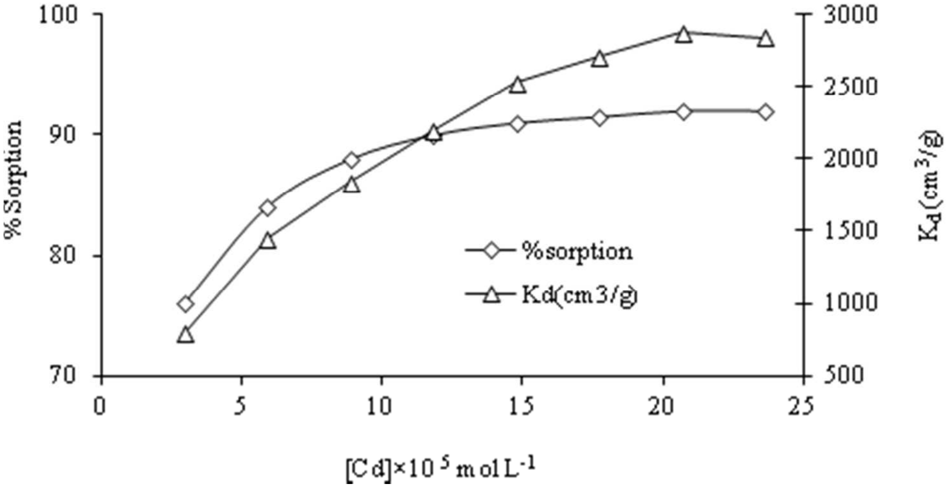

Fig. 8. Cd(II) ions sequestration as function of cadmium concentration

Table. 1 Langmuir, Freundlich and D-R isotherm constants of Cd(1I) ions uptake by TSC functionalized nano spheres

Isotherm model	**Constants**	**Values**
Langmuir isotherm	N (mmol g^{-1})	10
	b x 10^3 (Lmol^{-1})	0.1
	R^2	0.98
Freundlich isotherm	1/n	0.64
	C_m (mmol g^{-1})	0.04
	R^2	0.99
D-R isotherm	β (K J^2mol^{-2})	-0.0064
	X_m (mmol g^{-1})	1.89
	E_s (K J mol^{-1})	8.84
	R^2	0.98

3.2.5 Effect of temperature on Cd(II) ions sequestration

Temperature plays an important role in metal ions removal by a solid surface. It either increases or decreases the sorption of metal ions. If sorption increases with rise in temperature, it indicates chemisorption nature of the sorption process and the reverse is true for physiosorption. This increase is due to the creation of new sorption sites, acceleration of sorption steps or due to transport against an energy barrier [36]. The effect of temperature on Cd(II) ions sequestration by functionalized nano silica spheres is studied in a temperature range of 283-323 K under optimized conditions and the results are presented in Fig. 9. Thermodynamic parameters like enthalpy change (ΔH) Entropy change (ΔS) were calculated using the following relationships [37].

$$\log K_c = \frac{-\Delta H}{2.303\ RT} + \frac{\Delta S}{2.303R} \qquad (7)$$

where $K_c = \frac{F}{1-F}$ where F is the fraction of metal ion sorbed at equilibrium, T is Kelvin temperature and R is universal gas constant in units of KJ mol^{-1} K^{-1}. The plot of log Kc verses 1/T gives a straight line. The values of ΔH = 2.45 J mol^{-1}K^{-1} and ΔS = 16.96 Jmol^{-1}K^{-1}were computed from the slope and intercept of the plot. The positive value of enthalpy indicates the endothermic nature of process. The large increase in entropy favors the stability of Cd(II)—TSC complex on the surface of the nano spheres. The Gibbs free energy (ΔG) was calculated by using the relationship

$$\Delta G = -RTlnK_c \qquad (8)$$

The numerical value calculated for ΔG was found to be - 1050.00 J mol^{-1} at 293.16 K. The large negative value of ΔG reflects the spontaneous nature of the process.

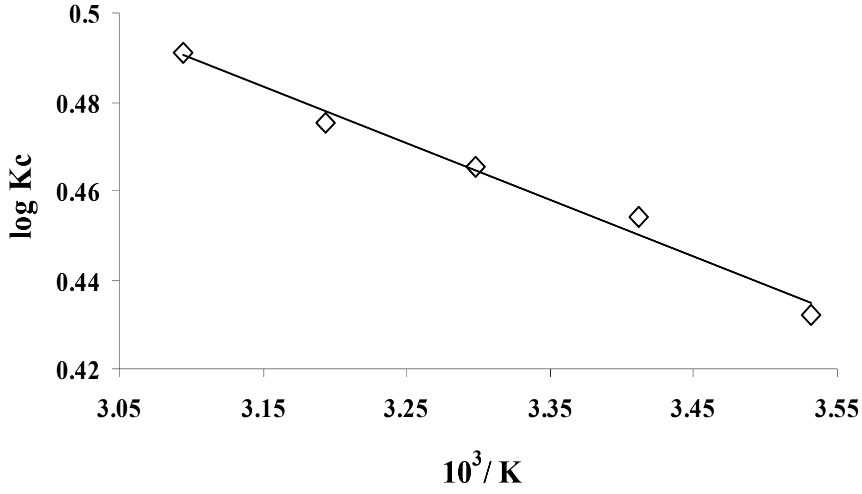

Fig. 9 Effect of temperature on Cd(II) ions sequestration by TSC functionalized nano spheres

3.2.6 Effect of interfering ions on cadmium sequestration

The common ions present in real life samples affect the sequestration of Cd(II) ions. This behavior is explained on the basis of nature of interacting ion and environment around the metal ion of interest. In this study we investigated the effect of various counter ions on the uptake of Cd(II) under optimized conditions. Each salt was taken in 10 mg quantity and its effect on Cd(II) ions sequestration was studied and the results are summarized in Table 2 and 3. The nil refers to the condition where no complexing ion except Cd(II) is present in solution. Although all the ions added affected the Cd(II) ions sequestration but the thiosulfate, cyanide, EDTA, Cu^{2+}, Ni^{2+} and Al^{+} drastically reduced it as shown in Table. 2 and 3.

Table. 2 Effect of anions on Cd(II) ions sequestration of by TCS functionalized nano spheres

Compounds	**Interfering ion**	**Sorption (%)**
Blank	Nil	98
KI	I^{-}	86
KF	F^{-1}	80
$Na_2B_4O_7$	$B_4O_7^{-2}$	76
Na_2SO_4	SO_4^{-2}	74
K_2CrO_4	CrO_4^{-2}	70
$C_6H_5O_7Na_3$	$C_6H_5O_7^{-3}$	67

$Na_2C_2O_4$	$C_2O_4^{-2}$	62
$Na_2S_2O_3$	$S_2O_3^{-2}$	45
KCN	CN^{-1}	20
EDTA	EDTA	02

Table. 3 Effect of cations on Cd(II) ions sequestration of by TCS functionalized nano spheres

Compound	**Interfering ion**	**Sorption (%)**
Blank	Nil	98
Fe(III)	Fe^{+3}	86
$SnCl_2$	Sn^{+2}	85
$MnCl_2$	Mn^{+2}	82
LiCl	Li^{+1}	80
$AgNO_3$	Ag^{+2}	79
Cu SO_4	Cu^{+2}	49
$NiNO_3$	Ni^{+2}	15
Al NO_3	Al^{+2}	02

3.2.6 Regeneration of the spheres

The Cd(II) ions were fully desorbed from the surface of the sorbent by treating with 1M HCl solution. After regeneration the nano spheres were conditioned in pH solution and reused for the removal of cadmium. The material was stable enough after three sorption-desorption cycles and no significant change was observed in the sorption capacity of the thiosemicarbazide functionalized silica.

4. CONCLUSION

The functionalized nano silica sorbent having nitrogen and sulphur functional groups is effectively employed as Cd(II) scavenger from spiked cadmium samples in batch experiments. The nano spheres can adsorb 98% Cd(II) ions in 40 minutes time at pH 7. The sorption processes follow first order kinetics and characterized by surface and intra-particle diffusions mechanism.

The sorption process follow the Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherms with a maximum sorption capacity of 10 mmol g^{-1}. The positive value of entropy (16.96 $Jmol^{-1}K^{-1}$) shows the formation of stable Cd-TSC complex and suggests the chemisorption nature of the process confirmed by E_s=8.8 kJ mol^{-1} computed from D-R isotherm. The Cd(II) ions sequestration is highly reduced in the presence of Cyanide, EDTA, Aluminum and Nickel ions. The sorbent is regenerable and can be used several times. These functionalized nano spheres are promising tools for the removal of trace amount of cadmium from drinking and industrial water.

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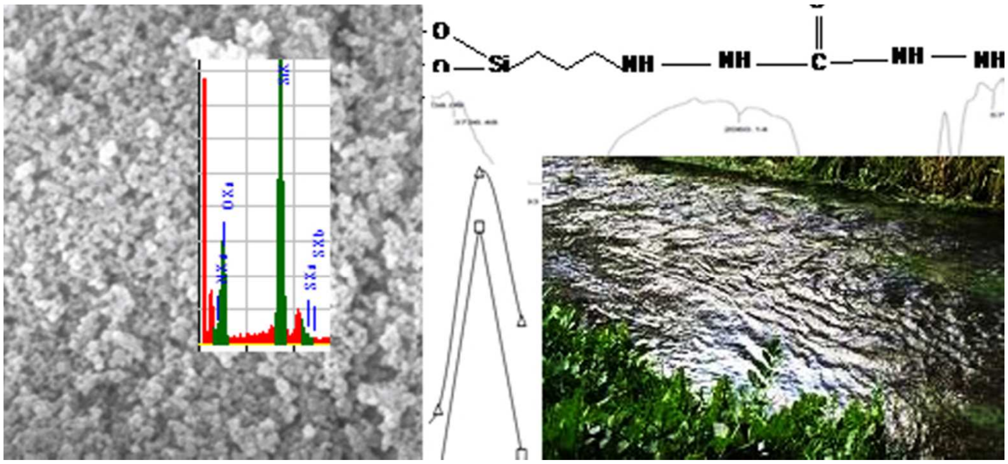

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