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Adsorption Studies of Cd (II), and Cu (II) Metal Ions from Aqueous Solutions by Synthesized Co and Sn Co-doped TiO₂ Nanoparticles.

Gullipilli Sandhya, Y V S Sai Krishna, and R Ravichandra Babu*.

Department of chemistry, GITAM Institute of Science, GITAM (Deemed to be University) Visakhapatnam, Andhra Pradesh-530045, India

ABSTRACT

Copper and Tin co-doped Titania nano particles has been prepared by Sol gel method and characterized by XRD, FE-SEM, EDX, FT-IR, HR-TEM and Point Zero charge. The elemental data of copper, tin, titanium and oxygen were confirmed by Energy Dispersed Spectroscopy (EDAX). From TEM images size is found to be $\approx 10\text{nm}$ which confirms that the dopants co and Sn reduces the size of nanoparticles. Batch sorption studies were carried out to investigate the adsorption Cd(II) and Cu(II) on Co-Sn/TiO₂ for various concentrations of 0.1 mg/L to 10 mg/L. The maximum adsorption capacity were found to be 2.41 mg/g for Cd(II), 2.08mg/g for Cu (II) for 0.1ppm concentration at 303 K. Langmuir, DR-isotherms and Kinetic models such as Pseudo second order and Reichenberg film diffusion was also found to be well fit to experimental data. Thermodynamic parameters including ΔH° , ΔS° and ΔG were calculated from the results of adsorption thermodynamics. The value of the thermodynamic parameter ΔH° indicated an exothermic adsorption process. A negative value of ΔG shows the feasibility and spontaneity of material-anion interaction. The results suggested that the simple and cost effective method and shows excellent adsorption removal properties on heavy metals for industrial applications.

Keywords: Cobalt and Tin co-doped TiO₂, Sol-gel, isotherms, and Kinetic studies.

*Corresponding author

INTRODUCTION

Due to the vast industrialization environment is getting polluted and since few decades water pollution has become the important consideration. Proper monitoring and control of contaminants discharge should be there for the effective development of industries [1–3] Considerable release of threatful metals, chemicals and dyes into water bodies by various activities of industries create water pollution [4–6] Heavy metals compared to other contaminants create numerous environmental issues and induce health and price cutting complications [7-8]. Cadmium causes a number of life threatening disorders such as renal damage, bone deformations in embryos, hypertension etc [9-10]. Copper containing fertilizer usage cause pollution it enters the food chain thereby causing carcinogenic effects to human beings [11] For the extraction of an required analyte for its estimation several methods are proposed. [12–16] Solid phase extraction (SPE) is low cost and low time consumption technique that is been widely used due to its selectivity and sensitivity.[17-18] As SPE is popular for extracting analytes adsorbents like activated carbon, silica gel carbon nanotubes are used [19-22]. Certain factors such as adsorption capacity, selectivity and binding constants limit the use of above materials as sorbents for metal removal. As the above mentioned methods have several drawbacks, nano materials have been developed to improve their selectivity and binding capacities for certain heavy metals. Nano particles have some unique properties like high surface activity and high active surface to volume ratio so they can adsorb metal ions effectively which are not shown by other materials. [23-24]. Nanomaterials have vast applications with regard to environmental and health problems which is useful considerably in medicine and environmental remediation.[25-26].

Titanium dioxide as a photocatalyst shows several potential advantages in the removal of organic and inorganic pollutants. By doping the titanium dioxide with transition metal ions, photoactivity enhancement and the visible region absorption spectrum shift could be obtained [27-28]. Dopants have the ability to improve the surface area, cause a decrease in size and change the morphologies of the nanomaterials, which result in enhancing various properties of nanomaterials.[25-26] Literature survey ,reveals that some of the heavy metals can be removed by using different types of metal oxides such as, TiO₂, Ag₂O,ZnO, Fe- TiO₂, Co₃O₄ - TiO₂, Nd-TiO₂, Sn- TiO₂, Cu- TiO₂, Ag- TiO₂, Au-Cu/ TiO₂, Ag-Mg/ TiO₂ [29-40]

In this investigation, we synthesized Co-Sn co-doped TiO₂nanoparticles by a sol-gel method and characterized it by XRD, FESEM, TEM FT-IR, and PZC. Co-Sn co-doped TiO₂ nanoparticles were applied to investigate their utility and analytical efficiency as an adsorbent on the selectivity and adsorption capacity for Cu(II) & Cd(II).

EXPERIMENTAL

The Reagents, Tetra butyl titanate (TBOT) were purchased from Sigma Aldrich Chemical Co Ltd., USA. Cobalt nitrate, Stannous Chloride, Copper Sulphate, Cadmium chloride, Ammonia solution, isopropyl alcohol and anhydrous ethanol, were obtained from Merck (India) Ltd.

Sample preparation:

Stock solutions were prepared from the reagent grade chemicals using Millipore ultrapure water. Cadmium chloride was used as a source for Cd(II) ions, Copper sulphate for Cu(II). 0.1M HNO₃ and 0.1M NaOH aqueous solutions were employed to maintain the pH during the reaction.

Method of synthesis:

Appropriate amounts of stannous chloride and Cobalt Nitrate were weighed in a 250 ml beaker and dissolved in 40ml of anhydrous ethanol by stirring for 1hr.The above solution is turned into alkali by addition of 4.5mL of concentrated ammonium hydroxide. Stirring is continued for another 12 hours and washed with ethanol three times. The residue is dispersed in 40ml ethanol. Subsequently, 5m of TBOT dissolved in isopropyl alcohol was introduced to the system drop wise, followed by heating the solution at about 70°C. The whole process was kept under vigorous stirring for 12hrs, and the formed precipitate is washed ethanol for five times and dried in a vacuum oven followed by calcinations in muffle furnace at 500 °C for 2hrs.

Batch Experiment:

The effect of some parameters on the adsorption of Cd (II), Cu (II) ions on Co-Sn co-doped TiO₂ was investigated by using batch experiments. The following independent variables were evaluated. Effect of different parameters such as the contact time, pH, initial concentration & temperature. Experiments have been carried out by taking 0.1 mg of adsorbent in sample bottles containing 20 ml of Cd(II) and Cu(II) solution with concentration 0.1 mg/L to 10 mg/L on thermoregulatory orbital shaker. The pH of solutions is adjusted with 0.1 N NaOH or HCl solutions. The stirring time is maintained between 10 to 24hrs at a temperature range of 20 – 50°C. After each experiment run, the removal capacity for each metal was evaluated by using Inductively Coupled Plasma Mass Spectrometer (ICP – MS), make Agilent Technologies (Model No. 7700). The metal ion concentration retained by sorbent (mg/g) sorption capacity (q_e) can be determined by using the formula:

$$q_e = \frac{(C_0 - C_e)V}{m}$$

Where, C_0 and C_e are the initial and final concentrations of Cu(II) & Cd(II) in aqueous solution (mg/L), q_e is the equilibrium adsorption capacity (mg/g) respectively. V is the liquid volume (L) and m is the mass of Co-Sn/TiO₂ used (g).

Characterization of Co and Sn co doped TiO₂ nanoparticles:

XRD data were identified by X-ray diffraction (XRD, DX2700, and China). The FE-SEM micrographs and EDAX were characterized by using a JEOL 6335F FE-SEM microscope. Fourier transform infrared (FT-IR) spectra for Co and Sn doped TiO₂ nanoparticles was carried out with IR-Prestige-21 Shimadzu FT-IR spectrophotometer, by KBr pellet method. The particle size and morphology of the sample was examined by high resolution transmission electron microscopy HR-TEM by instrument JEOL/JEM 2100 respectively

RESULTS AND DISCUSSION**X-ray Diffraction Studies:**

Fig. 1a.shows the XRD patterns of 0.20 mmol Co-Sn/TiO₂ powders. It is found that the anatase crystal phase is observed for all of the samples [41]. By comparing with undoped TiO₂ the doped oxide shows peak shifting due to incorporation of metals by doping. No extra peaks other than TiO₂ were obtained corresponding to metals before and after adsorption. Only increase in the intensity of anatase TiO₂ peaks and peaks broadening is observed. It can be ascribed to the uniform distribution of doped metals and also the adsorbed metals. The well-defined diffraction peaks with 2θ are at about 25°, 38°, 48°, 54°, 54°, 62°, 68°, 70°, 74°, and 82° which are assigned to the (101), (004), (200), (105), (211), (204) (116), (220), (215) and (224) crystal planes, respectively. it is consistent with the standard JCPDS values of anatase TiO₂ (JCPDS Card No. 21-1272) [42-43].

Fourier Transform Infrared Spectroscopy Study:

The FTIR spectra of the samples before and after treatment are shown in Fig. 1b, The broad adsorption peaks 450–700 cm⁻¹, 3400 cm⁻¹ and 1417 cm⁻¹ observed corresponds to Ti-O-Ti [44-48]. H–O–H stretching and bending vibrations were observed at peaks 1,620 cm⁻¹. No additional peaks are present upon Co and Sn doping, supporting the efficient dispersion of Co and Sn. Shifting of peaks from 1693.5, 3666.679, 2362.8 to 1666.497, 3664.75 and 2360.871 is observed due to adsorption Cu(II). Shifting of peaks from 1693.5, 3896.2, 2362.8 to 1666.497, 3849.9 and 2360.8 is observed due to adsorption Cd (II).

Field Emission-Scanning Electron Microscopic study:

Field Emission Scanning Electron Microscopy was used to identify the surface morphology and size of the particles. Fig 1c,d & e shows the FE-SEM micrographs before and after treatment. The surface morphology of the sample pertains to a mixture of nano particles. The average particle size was found to be ~10 nm. Co and Sn ions on doping on TiO₂ control the growth of particles and agglomerated spherical shaped nanoparticles

can be seen. It can be observed that adsorption of metals Cu(II) and Cd(II) caused some structural changes on the surface of adsorbent.

Energy Dispersive X-ray (EDX) spectra:

The energy dispersive X-ray (EDX) spectra of Co and Sn co-doped TiO₂ before adsorption are shown in Fig. Fig 1c, d & e respectively. In Fig 1c the peaks corresponding to titanium, oxygen and the respective doped metals cobalt and Tin can be clearly seen in these spectra. Fig 1d & e shows the additional peaks which confirms the adsorption of Cu (II) and Cd(II) after treatment .

Transmission Electron Microscopy:

Transmission electron microscopy was used to examine the particle size, crystalline and morphology of the samples. Fig. 1f shows that the nano crystallites show spherical shape. Due to doping cobalt and tin particles are seen as dark patches on the surface of transparent TiO₂ nanoparticles. Close observation suggests that spherical shaped particles, with average particle size of ≈ 10nm are formed.

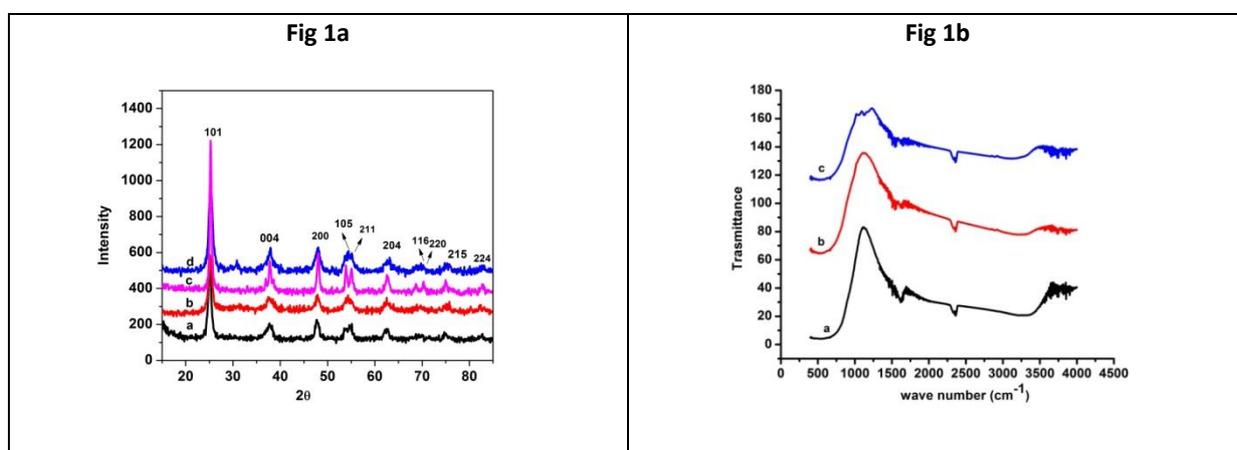


Fig 1a: XRD patterns of a) Undoped TiO₂ b) Co-Sn/ TiO₂ c) after adsorption of Cu(II) d) after adsorption of Cd(II) **1b:** FT-IR spectra of (curve a) Co-Sn/TiO₂ nanoparticles (Curve b) after adsorption of Cu(II) (curve d) after adsorption of Cd(II)

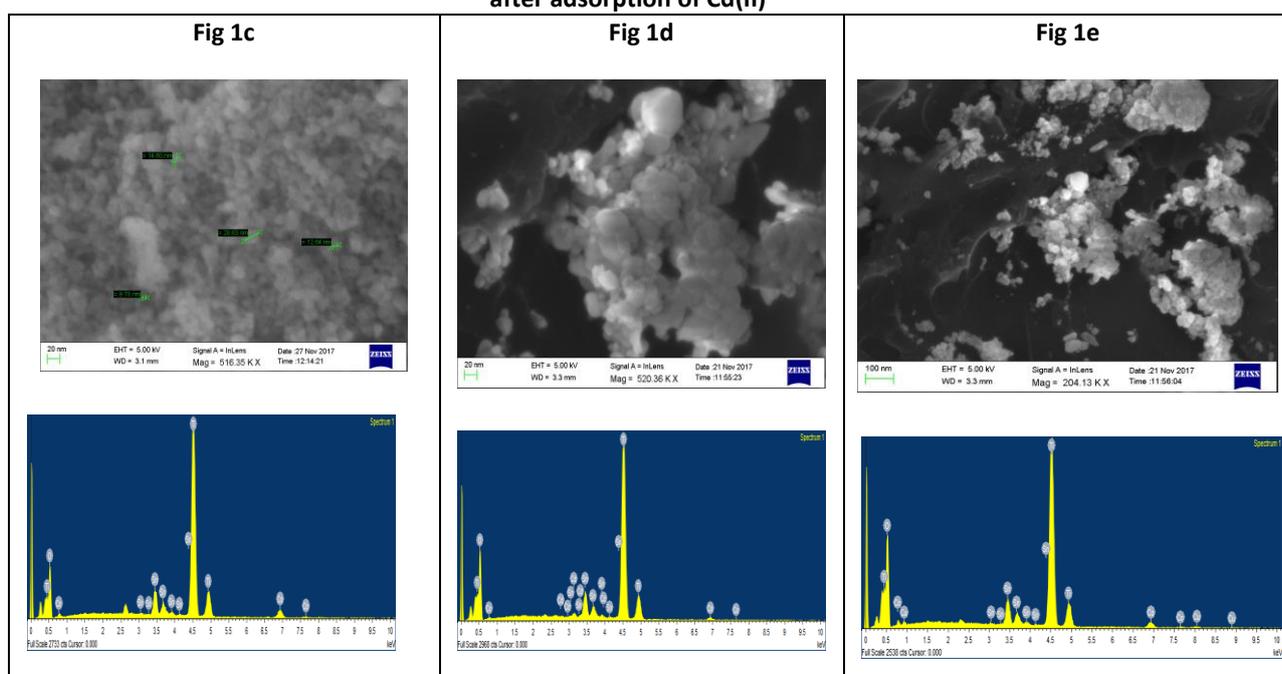


Fig 1: FE-SEM image and EDS spectra of Co-Sn /TiO₂ nanoparticles (c) after adsorption of Cd(II) (d) after adsorption of Cu(II) (e)

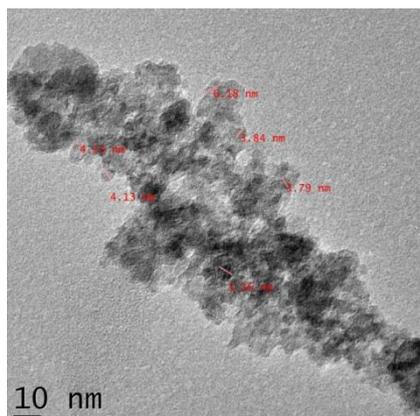


Fig 1f: HR-TEM of Co-Sn/TiO₂ nanoparticles

Effect of initial concentration:

The effect of initial concentration as shown in Fig. 2a, b on the adsorption of heavy metals such as Cu(II) and Cd(II) onto Co-Sn/TiO₂ nano particles was studied for various concentrations of 0.1mg/L to 10mg/L. Appropriate amount of doped oxide (1.0mg) was taken for all the studies by maintaining the pH at 7 and 8 for Cu(II) and Cd(II) respectively. The contact time is maintained at 50min for Cd(II) and 40min for Cu(II) and no prominent uptake was noticed after 24 h. The absorption capacities are found to be 2.41 mg g⁻¹ and 2.08 mg g⁻¹ for Cd(II) and Cu(II) for 0.1ppm concentration.

Effect of Contact Time:

The effect of contact time of adsorption of heavy metals Cu (II) and Cd (II) onto Cu-Sn/TiO₂ nano particles was studied starting from 10 min to 24hrs stirring time. The results are shown in Fig 2a, b. The optimum contact time was found to be 50min for Cd(II) and 40min for Cu (II) respectively and no noticeable uptake was observed after 24 hrs. The adsorption efficiency is about 99.27% for Cd (II) and 98.82 % for Cu(II) under optimum experimental conditions for all the given concentrations.

Initially rapid adsorption is noticed which can be attributed to availability of large no of active sites on metal oxide surface. But gradually it decreases until the equilibrium is reached due to slow pore diffusion of solute molecules on to the adsorbent and also the active sites become fewer due to high concentration of solution.

Effect of pH:

The effect of pH on the adsorption of heavy metals Cu(II) and Cd(II) onto Co-Sn/TiO₂ nano particles was studied by varying the pH of solution from 2 to 10 . The batch experiments were carried out for 20ml solution of heavy metals Cu(II) and Cd(II) with concentration 0.1 mg L⁻¹ to 10 mg L⁻¹ and 1.0 mg of adsorbent for 40 min and 50min contact time respectively. The results were shown in Fig 2c. It was noticed that the pH 7 & 8 holds good for the maximum sorption of Cu (II) and Cd (II) respectively. Removal of metals is influenced by the initial pH of solution as it affects the charge of the adsorbent and also speciation of metals in solution. [49] Free Metal ions Cu (II) and Cd (II) are present only below pH 7 and hydroxides are formed if pH increased further. Experimental determination of Point zero charge of Co-Sn/TiO₂ is found to be 6.1. The charge of adsorbent below PZC is positive resulting in less removal of metal ions due to competition between metal ions and H⁺ ions: As the pH increased it leads to decrease in H⁺ ions which enable the adsorption of Cu (II) and Cd (II) on to Cu-Sn/TiO₂ nano particles. Cationic adsorption is favorable at pH values higher than PZC [50]. So, Sorption of Cu (II) and Cd (II) was propitious at pH conditions greater than 6.1. Experimental results also suggest that the maximum adsorption occurs at pH 7 for Cu(II) and pH 8 for Cd(II) and beyond that no further uptake is observed with increase in pH and a plateau is obtained. Hence, further experiments are carried out at optimum pH. The equilibrium sorption amount of Ag(I) and Pb(II) ions sorbed (Q_e) for an initial concentration

of 0.1 ppm was found to be 2.41 mg/g for Cd (II) and 2.08 mg/g for Cu (II) under the experimental conditions which clearly shows that the sorption efficiency of Cd (II) is superior to Cu (II) towards Co-Sn/TiO₂.

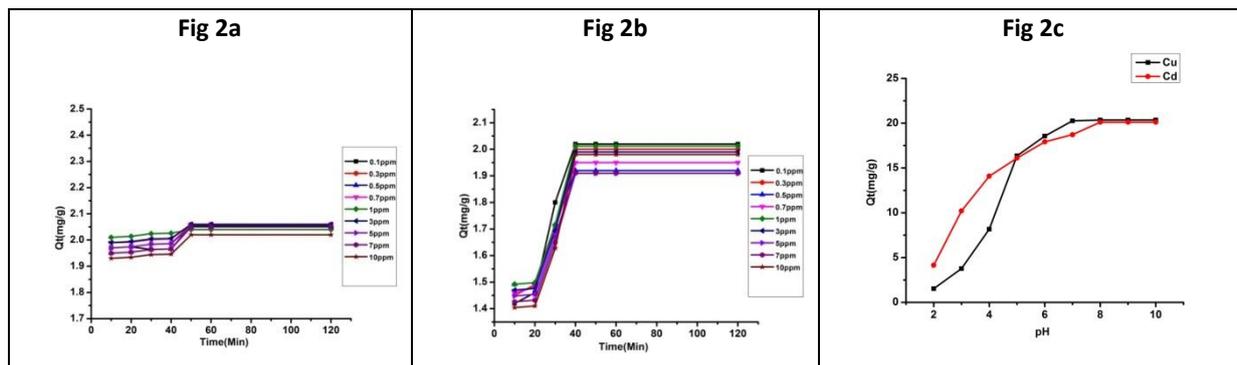


Fig 2: Effect of initial concentrations on (a), Cu (II) ions (b) Cd (II) ions and effect of pH (c) on Cu(II) and Cd(II) ions sorption on Co-Sn/ TiO₂

Equilibrium modeling

The adsorption isotherm models such as Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin were applied to data of Cu (II) and Cd(II) adsorption. The correlation coefficients of the above stated isotherms were found as 0.914, 0.999, 0.978, and 0.804, for Cd(II) and 0.922, 0.999, 0.979, 0.798 for Cu(II) respectively. From the (R²) values it can be concluded that Freundlich and Dubinin Radushkevich isotherms models are better fitted for both Cu (II) and Cd(II). The Freundlich adsorption isotherm as shown in Fig. 3a. The value of K_f is related to the degree of adsorption. As per the K_f values given in Table 1, Cd (II) have greater K_f value i.e 0.1341 mg/g when compared to Cu (II) of K_f value 0.1338 mg/g. This can be attributed that Cd(II) has greater affinity towards the sorbent than Cu(II) which can also be correlated with their adsorption capacities. The D-R adsorption isotherm Plot between ln Q_e versus ε² gave straight lines as shown in Fig. 3b The sorption free energies (E) of Cd(II) is 16.9 kJ/mol and Pb (II) is 16.9 kJ/mol depicts that the processes is chemisorptions [51]. We can also observe that Q_{max} value for Cd(II) 2.57 and Cu(II) is 2.57 which are in correlation with the experimental values.

Table 1: Isotherm Models of Cd(II) and Cu(II) by Co-Sn/TiO₂ particles

Isotherm model	Parameters	Cd(II)	Cu(II)
Freundlich model	1/n	0.966	0.972
	n	1.035	1.029
	K _F (mg/g)	0.1341	0.1338
	R ²	0.999	0.999
D-R model	Q _m (mg/g)	2.57	2.57
	β (mol ² /KJ ²)	0.175	0.176
	E(KJmol ⁻¹)	16.9	16.9
	R ²	0.978	0.979

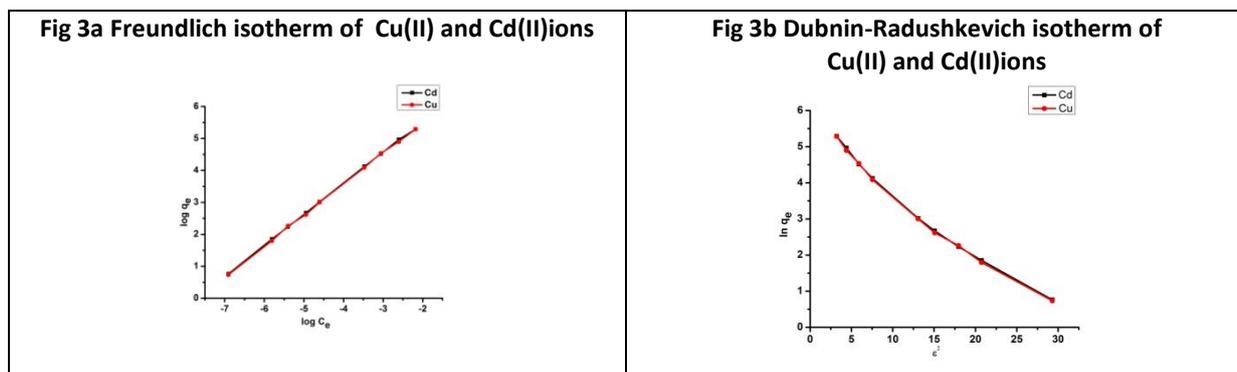


Fig 3- Adsorption isotherm models of Copper & Cadmium sorption on Co-Sn/TiO₂

Adsorption kinetics:

The adsorption kinetics such as pseudo first order, pseudo Second order, Weber-morris intraparticle diffusion, Reichenberg film diffusion models have been applied to the data of Cd(II) & Cu(II) sorption on to Co-Sn/TiO₂. The correlation coefficients of the above kinetic models reveals that pseudo Second order & Reichenberg film diffusion models are better fit for the data of Cd(II) & Cu(II) sorption on to Co-Sn/TiO₂. Fig 4a, b shows that the corresponding R² values for the pseudo-second-order kinetic model were in the range of 0.98 to 0.99 for all Cu(II) and Cd(II) ions on Co-Sn/TiO₂, a good agreement between the experimental and the calculated q_e values indicating the applicability of the pseudo-second-order kinetic model to describe the adsorption process of Cd(II) & Cu(II) ions on Co-Sn/TiO₂ as shown in Table 2. It is suggested that the adsorption process was controlled by chemisorptions. This Reichenberg plot as shown in Fig 4c gave a straight line with R² values for this diffusion model are 0.974 and 0.986 for Cu(II) and Cd(II) ions on Co-Sn/TiO₂ respectively confirming the film diffusion.

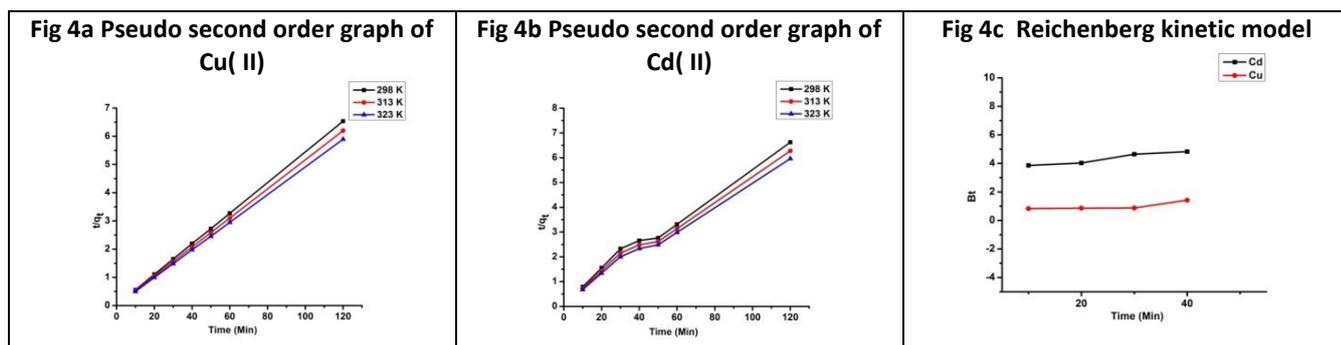


Fig 4: Kinetic parameters study of Cadmium and Copper ions sorption on Co-Sn/ TiO₂

Table 2: Pseudo Second order Kinetic parameters Cd(II) and Cu(II) by Co-Sn/TiO₂ particles

Temperature (K)	Pseudo Second order							
	Q _e (mg/g) Experimental		Q _e (mg/g) Calculated		K ₂ (g/mg min)		R ²	
	Cd(II)	Cu(II)	Cd(II)	Cu(II)	Cd(II)	Cu(II)	Cd(II)	Cu(II)
298	1.84	1.8	1.85	2.0	4.95	186	1	0.986
313	1.94	1.9	1.96	2.0	3.78	175	1	0.988
323	2.04	2.0	2.04	2.1	3.74	169	1	0.990

Effect of temperature

Temperature variation studies of Cd(II) & Cu(II) ion sorption on Co-Sn/TiO₂ were studied. The sorption rate constants data obtained from the pseudo second order rate equation were further utilized to evaluate the activation energy. The Arrhenius plot as shown in Fig 5a of ln k₂ versus 1/T gave the activation energy for the sorption process of Cu(II) as 79.69 kJ/mol and on Cd(II) as 34.58 kJ/mol and hence follows chemisorptions process.[52]

Sorption Thermodynamics

Linear plots were obtained by plotting ln D versus 1/T as shown in Fig. 5b. R² values were found to be 0.960 and 0.974 in case of Cu (II) and Cd (II) respectively. Solution of 1 ppm of initial concentration (at 323 K) was used to calculate the thermodynamic parameters such as ΔH°, ΔS° and ΔG as shown in Table 3. Values were 0.279 kJ/mol, 0.033 kJ/K mol, and - 7.00 kJ/mol for Cd(II) and 0.272 kJ/mol, 0.033 and - 6.95 kJ/mol for Cu(II), respectively. High distribution coefficient value was observed in Cd(II) system in comparison with Cu(II) system. The value of the ΔG° is - 6.95 kJ/mol Cu(II) and -7.00 kJ/mol in Cd(II) indicating that the feasibility and spontaneity of the adsorption process were far superior in case Cd(II) than that of Cu(II); positive value of ΔH° indicates the endothermic nature, and positive value of ΔS° indicates the randomness at the solid and solution interface.

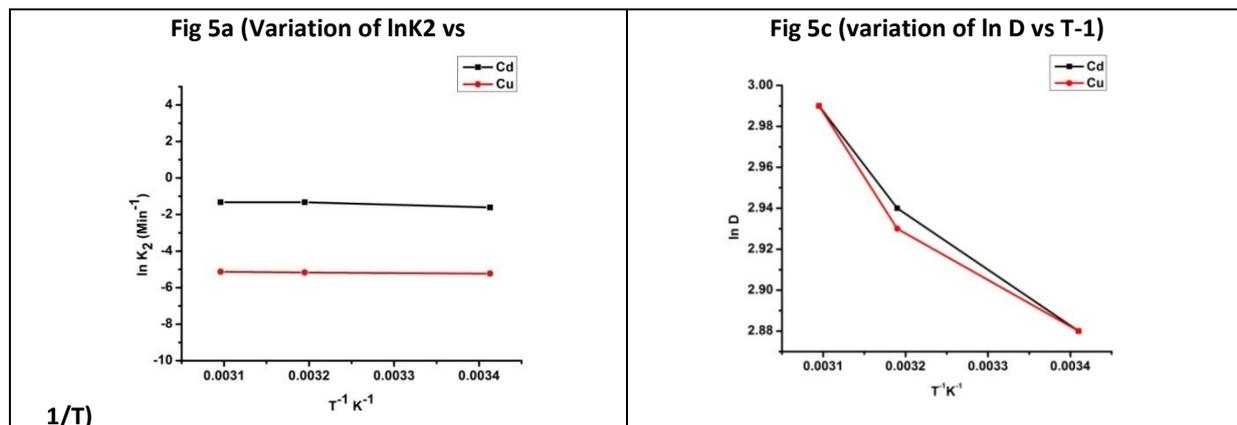


Fig 5: Thermodynamic study for sorption of Cadmium and Copper ions sorption on Co-Sn/ TiO₂

Table 3: Thermodynamic Parameters for the sorption of Cd(II) and Cu(II) by Co-Sn/TiO₂ particles at 323 K

Metal ions	Initial metal ion Concentration(mg/L)	ΔH° (kJ/mol)	ΔS° ($\text{Jk}^{-1} \text{mol}^{-1}$)	ΔG° (kJ/mol)
Cd (II)	1	0.279	0.033	-7.00
Cu (II)	1	0.272	0.033	-6.95

CONCLUSIONS

The experimental results indicate that Co-Sn/TiO₂ nano metal oxide synthesized by sol-gel method can be an effective adsorbent for the adsorption of Cu (II) and Cd (II) ions from aqueous solutions for various concentrations of 0.1 mg/L to 10 mg/L. The optimized conditions were found to be adsorbent dosage (1.0mg), pH 7 & 8 for Cu (II) and Cd (II) respectively. The optimum contact time is 40min and 50min respectively at for Cu (II) and Cd (II) respectively 323K. The adsorption isotherms for Cu (II) and Cd (II) were well fitted to Freundlich sorption isotherm and Dubinin Radushkevich isotherm. In the Reichenberg Kinetic model, the Plot of Bt vs t indicating that a thin film of Cu (II) and Cd (II) was formed on the surface of Co-Sn/TiO₂ nano metal oxide. All kinetic results suggest that sorption of Cu (II) and Cd (II) by adsorbent Cu-Sn/TiO₂ followed the pseudo second-order kinetics model. The values of ΔG° , ΔH° and ΔS° proved that the reactions were spontaneous and endothermic following chemisorptions mechanism in case of both Cu (II) and Cd (II). The Co-Sn/TiO₂ exhibited a good capability to be used in water and wastewater treatment for removal of Cu (II) and Cd (II) at trace level ranging from 0.1 to 10 ppm.

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