Adsorption of Pb(II) on Nano Sized SnO_2 Derived from Sol-Gel Method

P. Rejani, Asha Radhakrishnan, and B. Beena

***Abstract*—This study investigates the applicability of SnO_2 nanoparticles for the removal of Pb(II) from waste water . SnO_2nano particles of 15 nm size were synthesized using a sol-gel method and characterized by X-ray diffraction (XRD), FTIR, SEM and transmission electron microscope (TEM). Batch experiments were carried out to study the adsorption kinetics of Pb(II) on SnO_2. The effect of varying parameters such as contact time and P^H on the adsorption process were examined. The adsorption process was found to be highly P^H dependent. Experimental kinetic data were tested with pseudo-first –order and pseudo-second-order kinetic equations. The equilibrium data were modeled using general isotherm models. The experimental data agreed well with Langmuir isotherm model.**

***Index Terms*—Sol–gel method, adsorption, removal of lead.**

I. Introduction

An increasingly industrial global economy over the last century has led to many environmental problems. Heavy metals as water pollutants are a worldwide concern due their toxic effect on human [1]. Heavy metals are introduced into the environment from metallurgy mining, battery manufacturing industries etc. The presence of heavy metals in waste water and surface water is becoming a severe environmental and public health problem. Absorption is a conventional but efficient technique to remove heavy metals or organics from aqueous solutions. Many kinds of adsorbents for waste water treatment have been commercialized or are being developed [2].

In most cases, these adsorbents are highly porousmaterials, which provides adequate surface area for absorption. Thus, developing an adsorbent with large surface area and small diffusion resistance is of great significance in practical engineering applications [3].

Metal oxide materials prepared by sol-gel chemistry are high surface area and high porosity materials attractive in applications such as insulators and catalytic supports. The versatility of sol-gel chemistry provides a means of controlling the shape, morphology and textural properties of the final materials [4], [5]. Sol-gel chemistry also provides a means of preparing mixed oxide phases and can be controlled on both the molecular and nanoscales [6], [7].

In this study, SnO_2nano particle has been synthesized using a sol-gel method and applied for selective removal and recovery of heavy metals from waste water. SnO_2nano particles as a novel adsorbent is expected to offer an attractive and inexpensive option for the removal of heavy metals by considering its simple synthesizing method and high surface area. Heavy metal ion like Pb(II) was chosen as the metal ion adsorbate because it commonly exists in industrial waste water. Thus, the objective of this study is to assess the performance of SnO_2nano particle for the removal of heavy metal lead.

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II. Experimental

A. Materials and Methods

The chemicals used in the present study namely tin(IV) chloride, citric acid and sodiumhydroxide were of AR quality. Heavy metal ion solution of Pb(II) of 1000 ppm were prepared and used.

B. Preparationof Nano SnO_2

SnO_2 was synthesized using co-precipitation method. $SnCl_4$ was used as the starting material and NaOH as precipitant. 1M NaOH solution was added drop wise to the vigorously stirred solution of 0.1 M $SnCl_4$ & 0.01M citric acid (capping agent) and a large amount of white slurry was formed. The resulting slurry was continuously stirred for 2hrs,then filtered, washed with distilled water until all chloride ions were removed, dried and powdered.

C. Adsorptionstudy on Nano SnO_2 Surface

Adsorption studies were performed by batch process by taking 0.1 gm of synthesized SnO_2 in a 100 ml clean and dried stoppered bottle. Known concentration of 50 ml Pb^{2+} solution was added in the same stoppered flask. This flask was placed on a mechanical shaker at 160 rpm rate of adsorption of lead on SnO_2 particles. After desired time intervels [20, 40, 60, 80, 100 minetc], the solution was filtered using Whatman filter paper no. 41 and reserved for atomic absorption spectroscopy study. The experiments were repeated for different pH of the solution. The solid productie. adsorbent was washed with water and air dried. The solid was characterized by XRD.

The adsorption capacity q and removal percentage are expressed as follows:

$$q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

$$\text{Removal } (\%) = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

where q is the adsorption capacity of the adsorbate [mg.g^{-1}], w is the weight of adsorbent [g], v is the volume of solution [L], and Co [mgL^{-1}]and Ce [mgL^{-1}] are initial and equilibrium concentration of adsorbate in solution, respectively.

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D. Characterisation

X-ray diffractogram[2θ=10-90 °] was obtained on XPERT-PRO powder diffractometer with Cu-Kα radiation. The FTIR spectrum was recorded using KBr wafer on the Thermo Nicolet FTIR model AVATAR 370 DTGS. In the present study, SEM of the sample was recorded using a JED-2300 system. Adsorption studies were carried out using GBC-AAS spectrometer having lamb current 5milli ampere and wave length 270nm.HRTEM of the samples were taken using 300kv HRTEM (FEI-Model).

III. Results and Discussion

The structure identity and purity of the prepared nano particles were verified by XRD. Fig. 1a shows the X ray diffraction pattern of as-synthesized SnO_2nano particles. The observed peaks of the nano crystallite match well with standard JCPDS files, and no other crystalline phases were detected. The average crystallite size of the powders was determined by using Scherrer's formula,

$$D = 0.9\lambda/\beta\cos\theta$$

where D is the average crystallite size in nm, λ the wavelength of X-ray radiation, θ the Bragg's angle and β the full width at half maximum of the peak observed for the samples [8]. The average sizes of the particles were found to be 14nm which is in agreement with the data observed from TEM. The peak position fit well with the tetragonal structure of tin oxide with lattice parameters of a=4.7373Å and c=3.182Å, which is consistent with the standard data file (JCPDS file no. 88-0287). Fig. 1b presents X ray diffraction pattern of SnO_2nano particles after Pb(II) adsorption. This pattern shows some additional reflections corresponding to lead adsorption of the SnO_2. Presence of lead is clearly visible along with other less intensity peaks in the adsorbed pattern. This shows Pb(II) is adsorbed on SnO_2nano particles by some bonded interactions.

FTIR spectrum of nano SnO_2 (Fig. 2) shows the characteristic lines at 445 and550 cm^{-1} i.e. below 1000 cm^{-1}, which shows the metal–oxygen vibrational frequency range. Broad band in the region ~3240.87cm^{-1} is attributed to asymmetric and symmetric hydroxo –OH and aquo –OH stretches. A sharp medium band at ~1613.53 cm^{-1} is observed which is attributed to aquo H –OH bending.

The surface morphology of the synthesized tin dioxide is studied by scanning electron micrograph. Fig. 3 shows SEM image of the synthesized tin dioxide. This image shows the interconnected ultrafine SnO_2 particles with nano sized dimensions forming agglomerates. All the particles are irregular and some are spherical in nature. The TEM micrograph, Fig. 4, of the sample revealed that the SnO_2nano particle synthesized in this study are of 15 nm size.

A. Effect of P^H on Adsorption

The effect of solution P^H on the removal of Pb(II) during adsorption process is shown in Fig. 5.The adsorptivity at P^H 6 was higher than at any other P^H. The dependence of metal adsorption on P^H can be explained from the perspective of surface chemistry in an aqueous phase; the surface of metal oxide is generally covered with hydroxyl groups that vary in form at different P^H levels [9]. The fact that the adsorptivityvaries with P^H is explained by the behavior of hydrogen ion (H^+) and counter-ion activity in aqueous solution. The hydrogen ion activity predominates at lower P^H and decreases simultaneously at P^H6. Since Pb(II) activity is lower at lower value than P^H6, adsorptivity decreased. At values higher than P^H6, adsorptivity also decreased, since concentration of hydrogen ion was too low. Adsorption was not performed but precipitation occurred in strong basic P^H [10].

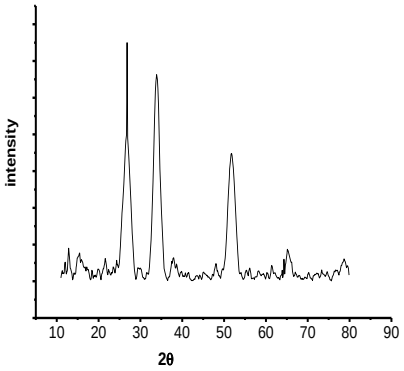

Fig. 1a. XRD spectrum of SnO_2

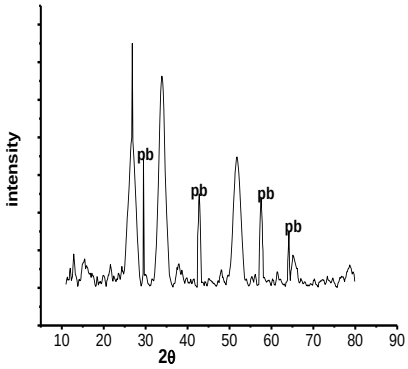

Fig. 1b. XRD spectrum of Pb(II) adsorbed SnO_2.

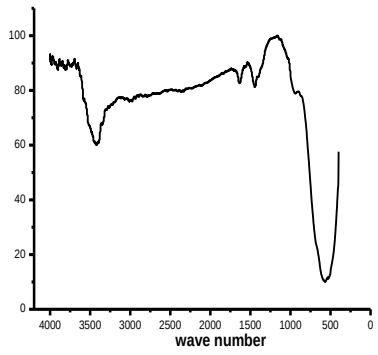

Fig. 2. FTIR spectrum of SnO_2 nano particle.

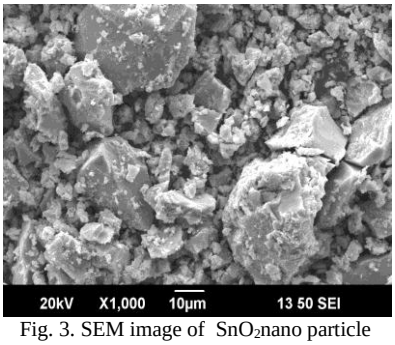

Fig. 3. SEM image of SnO_2nano particle

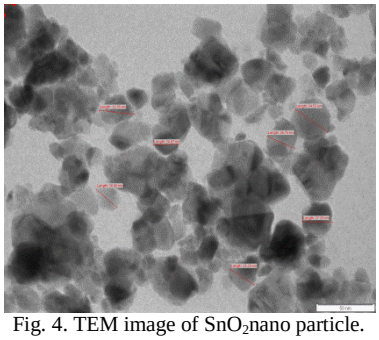

Fig. 4. TEM image of SnO_2nano particle.

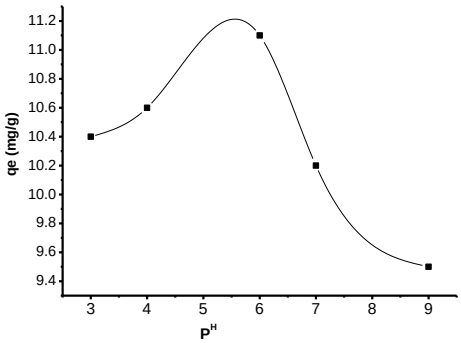

Fig. 5. The effect of solution P^Hon the removal of Pb(II) ions on 0.1gm SnO_2, SnO_2 was interacted with 30 ml (50ppm) of Pb(II) containing solution for 100 min .

B. Kinetic Study

The effect of contact time on adsorption of Pb (II) on SnO_2 was studied in the concentration range of 50 and 100 mg/L, and results are shown in Fig. 6. The adsorption is higher in the beginning due to a greater number of reaction sites available for adsorption. The equilibrium time was found to be 100 min. With the increase of initial Pb(II) concentration from 50 to 100 mg/L, the adsorption capacity also increased. On the basis of these kinetic data the shaking time was fixed at 100 min. for the rest of the batch experiments to make sure that equilibrium is reached. Kinetics of adsorption is one of the most attractive characterization to be responsible for the efficiency of adsorption. Adsorption kinetics of Pb(II) on SnO_2 was studied using pseudo-first-order and pseudo-second-order kinetic models. The kinetic equations may be written as

$$\text{Pseudo-first-order: } qt = qe\,(1 - e^{-k1t}) \quad (3)$$

$$\text{Pseudo-second-order: } qt = \frac{k_2 qe^2 t}{1 + k_2 q_e t} \quad (4)$$

where *qe* and *qt* are the amount of solute adsorbed per unit mass of the adsorbent at equilibrium and time *t*, respectively, k_1 and k_2 are the pseudo-first-order and pseudo-second-order rate constants respectively. Parameters of the pseudo-first-order and pseudo-second-order kinetic models were estimated from the experimental data using nonlinear curve fitting procedure. The results of kinetics were obtained by analyzing Fig. 7. Table I lists the kinetic parameters of the pseudo-first-order and pseudo-second-order kinetic models. The pseudo-second-order kinetic model provides much better R^2 value [0.992] than that of the pseudo-first-order kinetic model [0.9532]. The higher value of co-relation co-efficient (R^2) for pseudo-second-order kinetic model reveals that the pseudo-second-order model yields a better fit than the pseudo-first-order model.

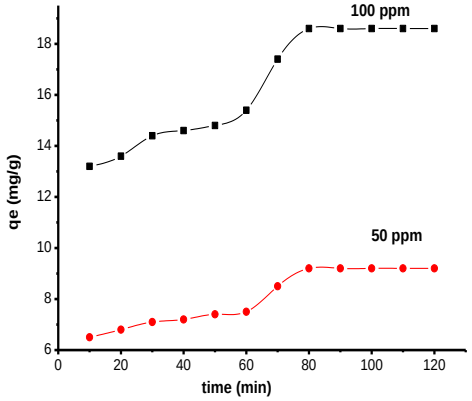

Fig. 6. Adsorption kinetics.

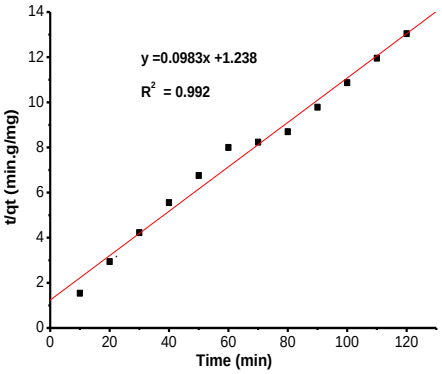

Fig. 7. Pseudo-second-order adsorption of Pb(II) on SnO_2kinetics of Pb(II) on SnO_2nano particle.

TABLE I: PSEUDO-FIRST-ORDER AND PSEUDO-SECOND-ORDER KINETICPARAMETER OR ADSORPTION OF PB(II)

Model	Parameter		
Pseudo-first-order	q_e[mg/g]	8.9	
		K_1 [g mg $^{-1}$ min^{-1}]	1.2 ×10^{-2}
		R^2	0.892
Pseudo-second-order	q_e[mg/g]	9.2	
		K_2[g mg $^{-1}$ min^{-1}]	1.83×10^{-3}
		R^2	0.992

C. Determination of Adsorption of Isotherms

Adsorption isotherms are important for the description of how adsorbates will interact with an adsorbent and are critical in optimizing the use of adsorbent. Thus, the co-relation of equilibrium data using either a theoretical or empirical equation is essential for adsorption data interpretation and prediction. Several mathematical models can be used to describe experimental data of adsorption isotherms [11] .In this respect , the experimental data for Pb(II) adsorption on nanoSnO_2 were compared using two isotherm models, Langmuir isotherm and Freundlich isotherm .

D. Langmuir Isotherm Model

The Langmuir isotherms describes monolayer coverage of adsorbate over specific homogenous sites, which are assumed to be identical, energetically equivalent and distant from each other and there are no interactions between molecules adsorbed on neighboring sites [12]. The Langmuir equation is

$$q_e = \frac{q_m\, b\, C_e}{1+bC_e} \quad (5)$$

where q_e and q_m[mg.g^{-1}] are the equilibrium and maximum adsorption amount of metal ion per unit weight of adsorbent, respectively, b represents the equilibrium constant of the adsorption reaction[L.mg^{-1}] and Ce [mg.L^{-1}] is the concentration of adsorbate at equilibrium.

E. Freundlich Adsorption Isotherm Model

Freundlich adsorption isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. This isotherm gives an expression encompassing the surface heterogeneity and the exponential distribution of active sites and their energies [13], [14]. The adsorption data were tested on the following linearized form of Freundlich adsorption isotherm by plotting q_e verses *Ce*

$$q_e = KC_e^{1/n} \quad (6)$$

where *Ce* is the amount adsorbed at equilibrium or the equilibrium concentration of adsorbate [mg.L^{-1}], and n and K are the Freundlich constants characteristics of the system indicating the extent of the adsorption and the degree of non-linearity between metal solution concentrates and adsorption, respectively. Fig. 8 and Fig. 9 represent the Langmuir and Freundlich adsorption isotherm models of Pb(II) adsorption on nanoSnO_2.

The experimental isotherm data fitted-well with the Langmuir equation based on the least squre fit, as shown in Fig. 8. The co-relation co-efficient (R^2) obtained from Langmuir model is found to be R^2= 0.993 for adsorption of Pb (II) on SnO_2nano particles.

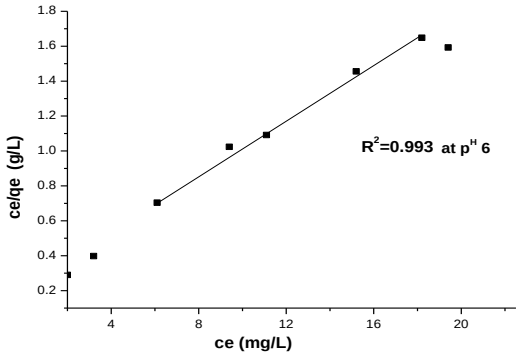

Fig. 8. Langmuir adsorption isotherm model.

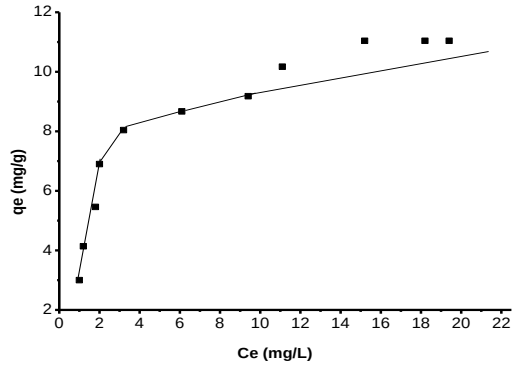

Fig. 9. Freundlich adsorption of Pb(II) adsorption on nanoSnO_2 model of Pb(II) adsorption on nanoSnO_2.

IV. Conclusion

The removal of Pb(II) from effluents is currently a major problem ; hence in this study nano SnO_2 is prepared as the adsorbent for the removal of Pb(II).Adsorption results show that SnO_2 can be efficiently used for adsorption of Pb(II) from aqueous solution .The adsorption rate was encouraging, and adsorption equilibrium were obtained within 100 min .The kinetics adsorption data were well fitted to the pseudo- second – order kinetic model. Under the influence of solution P^H , it was found that the amount adsorbed was maximum at P^H 6.The adsorption isotherms for Pb(II) on SnO_2 were also obtained The higher value of co-relation co-efficient (R^2) indicates that adsorption data of Pb(II) fit well with the Langmuir adsorption isotherm model. Thus, the method may show considerable promise for using nano SnO_2 as an effective adsorbent for separation of Pb(II) in complex matrices . The obtained SnO_2 is a promising candidate for potential application in heavy metal ion uptake from contaminated water sources.

References

[1] Y. M. Zhou, X. C. Hu, M. Zhang, X. F. Zhuo, and J. Y. Niu, *Ind. Eng. Chem.Res.*, vol. 52, pp. 876-884, 2013.

[2] N. Kannan and M. M. Sundaram, "Kinetics and mechanism of removal of methylene blue by adsorption on various carbon – a comparative study," *Dyes Pigm*, vol. 51, no. 1, pp. 25-40, 2001.

[3] J. Hu, G. Chen, and I. M. C. Lo, "Selective removal of heavy metals from industrial waste water using maghemite nanopartile: performance and mechanism," *Journal of Environmental Engineering*, vol. 132, no. 7, pp. 709-715, 2006.

[4] L. Arunkumar, "Synthesis and studies on some polymer-ceramic composites," Ph. D Thesis, Gulbarga University, Gulbarga, 2003.

[5] C. N. R. Rao, G. U. Kulkarni, P. J. Thomas, V. Agarwal, U. K. Goutham, and N. Ghosh, *CURR. Sci.*, vol. 85, pp. 1041, 2003.

[6] M. PannerSelvam, G. N. Subbanna, and K. J. Rao, *J. Mater. Res.*, vol. 16, pp. 2773, 2001.

[7] A. K. Lagshetty and Venkataraman, *Bull. Mater. Sci*, vol. 27, no. 6, December 2004, pp. 491-495.

[8] H. P. Klug and L. E. Alexander, *X-ray Powder Diffraction Procedure*, New York, John Wiley and Sons, 1954.

[9] J. Hu, G. Chen, and I. M. C. Lo, "Removal and recovery of Cr(IV) from waste water by maghemite nanopartile," *Water Research*, vol. 39, no. 18, pp. 4528-4536, 2005.

[10] M.-S. Kim, S. C. Hong, and J. G. Chung, *Environ. Eng. Res*., vol. 10, no. 2, pp. 45-53, 2005.

[11] Z. Shahryari, A. S. Goharriezi, and M. Azadi, *Int. J. Water Res. Environ. Eng.*, vol. 2, no. 2, pp. 016-028, March 2010.

[12] I. Langmuir, "The constitution and fundmental properties of solids and liquids," *J. Am. Chem. SOC*, vol. 38, pp. 2221-2295, 1916.

[13] R. Sips, "Combined form of Langmuir and Freundlich equations," *J. Chem. Phys.*, vol. 16, pp. 440, 1948.

[14] H. Freundlich and M. F. Umber, "Die Adsorption in lasugen," *Z. Phys. Chem.*, vol. 57, pp. 385-470, 1906.

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