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Application of ZnO Nano Rods for the Batch Adsorption of Cr(VI): A Study of Kinetics and Isotherms

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Abstract: The present study reports the synthesis of nano Zinc Oxide (ZnO) and its adsorption behaviour. The ZnO obtained by precipitation method were found to be well-defined nano rods arranged like flower. The shape, size and structure of ZnO were characterized from X-Ray Diffraction (XRD), Energy Dispersive X-ray (EDX) and Scanning Electron Microscope (SEM) analysis. These nano rods were utilized for the adsorption of hexavalent chromium ions [Cr(VI)] from their aqueous solution by using batch adsorption technique. Different physico-chemical parameters such as metal ion concentration, pH, dosage level and equilibrium contact time were studied during adsorption. The amount of chromium adsorption increases with increase in adsorbent dosage, whereas the adsorption was maximum in the first 40 min with optimum value of pH 3. The kinetic of adsorption was best fitted by the pseudo-second-order rate equation. Similarly, the equilibrium adsorption data were fitted well by both Temkin and Freundlich adsorption isotherm models in comparison to Langmuir adsorption model. The adsorption of chromium was supported by EDX and SEM analysis. Moreover, the change in the SEM morphology of ZnO nano rods into nano sheets after adsorption is an interesting observation of the present investigation.

Keywords: Nano Rods, Nano Sheets, Adsorbent, Hexavalent Chromium Ions, Adsorption Isotherm, Pseudo-Second-Order Kinetics

Introduction

Rapid urbanization as well as industrialization adversely affects the environment by polluting both the atmosphere and the aquatic systems. Different industries require different types of materials for their operation and the heavy metals are found to be the most essential commodities. Industries such as mining, pharmaceuticals, tanneries, electro-plating, chemical-manufacturing units etc., generates huge amount of wastes and effluents. Again the inadequately treated effluents consist of various toxic metals such as chromium, cadmium, arsenic, nickel, lead, mercury, copper etc,. The toxicities of these metals were well documented by different researchers (Förstner and Wittmann, 1985; Mukherjee, 1986; Nriago, 1988). Most of these metals were reported to be accumulated into the living tissues (Madoni *et al*., 1996; Oehme, 1979; Carson *et al*., 1986). Not only for human beings, these metals also affect in the growth of plants and animals too.

The present study is based on the separation of chromium metal from aqueous solutions. The major sources of chromium metal into the natural water systems are from tanneries, textile dyeing, metal finishing, pharmaceutics and electroplating industries. Both hexavalent and trivalent chromium are stable and exist in aqueous systems. However, hexavalent chromium is more toxic and known to be carcinogenic and mutagenic to living organisms.

There are various techniques such as ion exchange, membrane filtration, electro-chemical technologies, chemical precipitations, adsorption etc, for the effective removal of heavy metals from water (O'Connell *et al*., 2008; Wang *et al*., 2003; Sahu *et al*., 2009; Hashim *et al*., 2011). Amongst all, adsorption technique is the most preferred one due to its flexibility in designing and operation. Similarly, different types of materials were reported as effective adsorbents (Chu, 2002; Sharma and Forster, 1996; Yabe and de Oliveira, 2003; Tewari and Vivekananda, 2013). However, in the present scenario, nano based adsorbents are more convenient for the adsorption of heavy metal from aqueous solutions (Zhang and Fang, 2010; Hua *et al*., 2012; Mahdavi *et al*., 2017; Taman *et al*., 2015). These smart materials can separate the metals due to their increased surface to

volume ratio. Nano metal oxides such as of titanium, iron, magnesium, aluminium, copper, zinc etc, were used by many researchers for the removal of toxic metals (Recillas *et al.*, 2011; Agrawal and Sahu, 2006; Mahdavi *et al.*, 2012; Sheela *et al.*, 2012). Beside these, certain doped nano and micro-based metal adsorbents were also studied for the separation of different metals (Shenashen *et al.*, 2017; Zolfaghari *et al.*, 203). These materials are promising adsorbents for their high selectivity and activities towards the target components (Henglein, 1989; El-Sayed, 2001). Metal oxides along with carbon based nano adsorbents show efficiency due to their increased surface area and optimal magnetic properties (Aillon *et al.*, 2009). Certain low cost mesoporous adsorbents (Warkocki *et al.*, 2015; El-Safty and Shenashen, 2013), along with sensor-based adsorbents were also reported for the adsorption of various toxic metals (El-Safty *et al.*, 2013; 2012). Review of literature showed that ZnO nano particles are effective for the removal of hazardous metals and contaminants from waste water (Gupta *et al.*, 2015; Wang *et al.*, 2010; Alswata *et al.*, 2017; Hosseini *et al.*, 2016). Moreover, this oxide is an eco-friendly, economical and easily synthesized nano adsorbent to be employed as an adsorbent. Apart from toxic metals, these adsorbents were also found to remove various dye-based contaminants from wastes (Zafar *et al.*, 2018; Dehghani and Mahdavi, 2015; Konicki *et al.*, 2018). In addition to these, certain nano ZnO doped with other metals have also been reported as adsorbents (Ghiloufi *et al.*, 2016; Meng *et al.*, 2015). Similarly, investigations involving ZnO nano rods were also carried out for the removal of toxic metals (Ghaedi *et al.*, 2015; Yuvaraja *et al.*, 2018). But, however, study related to ZnO with similar morphology as in the present study for chromium adsorption is found to be scarce in literature. Moreover, ZnO nano rods in flower arrangement are also a rare phenomenon to study. The objective of the present investigation involved with such ZnO nano rods with sufficient porosity for the adsorption of Cr(VI) from its aqueous solutions. As an extension work of our previous studies with the synthesis of ZnO nano particles by various methods (VenuGopal and Kamila, 2017), here we report the utilization of the nano ZnO obtained from only one synthesis method for its uniqueness.

Materials and Methods

Analytical grade zinc sulphate, sodium hydroxide, potassium dichromate were used in the experiment and were of AR grade with more than 99% purity. Concentrated nitric acid is obtained from Merck India. The chemicals were used as received without any further purification. Deionized double distilled water was used throughout the experiment.

Synthesis of ZnO Nano Particles

Zinc oxide nano particles were synthesized by precipitation method using zinc sulphate and sodium hydroxide (VenuGopal and Kamila, 2017). To the aqueous solutions of zinc sulphate (0.1 M), 0.2 M sodium hydroxide solution was added drop wise with constant stirring till the pH becomes 11. This stirring was then continued for around seven hours to get a white colour dense precipitation. The precipitates were centrifuged and dried at 100°C for 4 h. These samples were kept for overnight to dry and then it is ground to make fine powders of zinc oxide. This was then characterized for the shape, size and arrangement from XRD, EDX and SEM analysis. The X-ray diffraction spectra were taken by RIGAKU smart lab X-ray Diffractometer using CuKα radiation λ = 1.5405 Å and X-rays generator operating at 40 kv. The scanning range was maintained within 20-100 deg with the scanning speed of $5°$ min^{-1}. The elemental composition, shape and structures of the particles have been carried out from EDX and SEM analysis by using GEMINI ULTRA 55 instruments.

Batch Adsorption Studies

A synthetic stock solution of hexavalent chromium (1000 mg/L) was prepared from potassium dichromate by dissolving 2.829 mg in 1L deionized water (Mekonnen *et al.*, 2015; Bhattacharya *et al.*, 2006). From this stock solution, required concentrations of chromium solutions were prepared for adsorption study.

In the batch adsorption process, the metal ions were added to the calculated amount of adsorbents in 250 mL Erlenmeyer flasks and were shaken under constant condition using rotary shaker to allow sufficient time for reaching adsorption equilibrium. The pH of the solution was adjusted by using 0.01 M HNO_3 and 0.01 M NaOH solutions. The initial metal ion concentration (C_0) has been varied in the range 100-500 mg/L with pH 3 and 0.05 g adsorbent dose. The shaking time was for 60 min at 30°C. The effect of initial pH on adsorption was studied in the range of 2.5-4.5 keeping the chromium ion concentration as 100mg/L and adsorbent dose as 0.05 g at 30°C for 60 min shaking. Similarly, the effect of contact time (30, 40, 50, 60,70 min) has been carried out for 100 mg/L chromium with 0.05g of adsorbent at pH 3. Besides, the variation of adsorbent dosage has also been carried out in the range 0.02-0.1 g keeping the chromium concentration as 100 mg/L with 60 min shaking at 30°C.

After adsorption, the solution contents were centrifuged and the supernatant liquid was taken for absorption study from UV-visible spectrophotometer (ELICO made SL-159 UV-visible spectrophotometer)

using Di-Phenyl Carbazide complex technique (DPC). The adsorbents were separated by using Whatman 41 filter paper [CAT No 1441-070]. These spent adsorbents were used for SEM, EDX analysis to know the morphology and elements. Similarly, Fourier Transform Infrared Analysis (FTIR) of ZnO nano particles has been done for both before and after adsorption. This analysis determines the vibrational frequency changes of the functional groups in the adsorbent.

The amounts of adsorption [q_e (mg/g)] at equilibrium and adsorption efficiency or percentage of removal (%) were calculated by using the following expressions (Alswata *et al.*, 2017):

$$q_e\left(mg/g\right) = \frac{\left(C_o - C_e\right)V}{m} \tag{1}$$

$$\% = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

where, C_o is the initial metal ion concentration and C_e is the final metal ion concentration, q_e is the amount of adsorbate adsorbed on the surface of the adsorbent, V is the volume of solution (L), m is the mass of adsorbent (g) (Oliveria *et al.*, 2005). This removal percentage and amount of adsorption were investigated for different parameters such as metal ion concentration, effect of pH, adsorbent amount and mixing time. Besides, the experimental data obtained were fitted into different adsorption isotherm models such as Langmuir, Freundlich and Temkin isotherm models in order to determine the sorption performance and capacity of the adsorbent.

Results and Discussion

Characterization of Nano Particles

The XRD pattern of zinc oxide nanoparticles shows (Fig. 1) well defined peaks located at Bragg angles, (2θ) = 31.75, 34.35 and 36.23. All these characteristic peaks are in high intensity corresponding to planes having miller indices (100), (002) and (101). These peaks indicate that the products obtained are pure and good in crystalline nature. Besides, these data also provide the information about the formation of hexagonal wurtzite structure for ZnO nanoparticles [Ref:JCPDS file no. 36-1451]. The

average crystallite size, D was calculated by using Debye-Scherrer equation as below (He *et al.*, 2008):

$$D = \frac{K\lambda}{\beta\cos\theta} \tag{3}$$

where, K is Scherrer constant and the crystallite shape factor, λ represents the wavelength of X-ray source 1.5405 Å used in XRD, β is full width at half maximum of diffraction peak and θ is the Bragg angle of intense peak. The calculated average crystallite size was found to be 37nm. Similarly, EDX analysis gives details of elemental composition of zinc and oxygen. The SEM morphology provides (Fig. 2) well-defined rod shaped structures of ZnO nanoparticles in the range of 49-140nm. The surface morphology plays an important role of an adsorbent for its capacity to adsorb. This depends on the surface structure of the adsorbent. In the present study the structure of nano particles obtained were of well-defined nano rods arranged in flower type. It has been observed that after adsorption, there is a significant change of the surface in presence of Cr(VI). Besides, there is increase in particle size from nano to micro after adsorption (1.49 μm). The presence of chromium is supported by EDX analysis (Fig. 3 and Table 1).

The FTIR for ZnO nano powder as well as with chromium after adsorption have been carried out in the range 400-4000cm^{-1}(using KBr pellet method with 0.4 cm^{-1}resolution in Perkin Elmer make instrument). This technique is a direct method for the identification of functional groups on the surface of the adsorbent where the adsorption depends on the porosity and the surface area of the adsorbent. The FTIR spectra of ZnO show several significant adsorption peaks (Fig. 4). Before adsorption, the vibration band at 485 cm^{-1} was related to ZnO (Zaka *et al.*, 2011; Hong *et al.*, 2009). Similarly the band shown at 1508 cm^{-1} was assigned to be of O-H bending vibrations and this has been shifted to 1514 cm^{-1} after adsorption. As per the literature, hydroxyl groups were identified by the characteristic broad peak in the range 3750-3250 cm^{-1}. This is due to the stretching vibrations of OH bonds (Jamhour *et al.*, 2016). Presently, the same has been observed at 3357 cm^{-1} before adsorption and there is shifting of peak (3337cm^{-1}) for ZnO-Cr after adsorption.

Table 1: Elemental compositions of zinc oxide nano particles before and after adsorption

| SL No.	ZnO	C		O		Zn		Cr	
		Wt %	At%	Wt %	At%	Wt %	At%	Wt %	At%
1	Nano particles before adsorption	18.85	46.65	11.87	22.01	69.28	31.43	----	----
2	Nano particles after adsorption	**11.50**	**24.68**	**32.77**	**52.82**	**50.07**	**19.99**	**5.07**	**2.51**

Adsorption Mechanisms

Effect of Metal Ion Concentration

The initial metal ion concentration (C_0) was varied in the range between 100-500 (mg/L) at pH 3 and at 30°C using 0.05 g adsorbent. There was decrease in metal removal with increase in initial metal ion concentration. It may be due to limited number of active sites of the adsorbent that become saturated with increasing metal concentration (Alswata *et al.*, 2017).

Effect of pH

The pH of the system controls the adsorption capacity, because this influences the surface properties of the adsorbent and ionic forms of the chromium metal in solution. Presently, the initial pH on adsorption was studied in the range 2.5-4.5 keeping the initial chromium ion concentration as 100 mg/L and adsorbent dose as 0.05 g at temperature 30°C. The optimal pH for chromium removal is found to be 3. At higher pH the separation is less probably due to formation of metal hydroxide. Similarly at low pH, the metal binding sites become positively charged due to H^+ ions concentration and thus there is repulsion effect towards chromium ions (Singanan, 2011). Alswata *et al.* (2011) reported the similar observation for the removal of metal ions at acidic range. It is because of the H^+ ions in the solution that compete with metal ions for acidic sites on the adsorbents surface (Mahdavi *et al.*, 2012). Similarly, according to Attia *et al.* (2010), the adsorption of chromium was maximum at less pH whereas it decreases at higher pH.
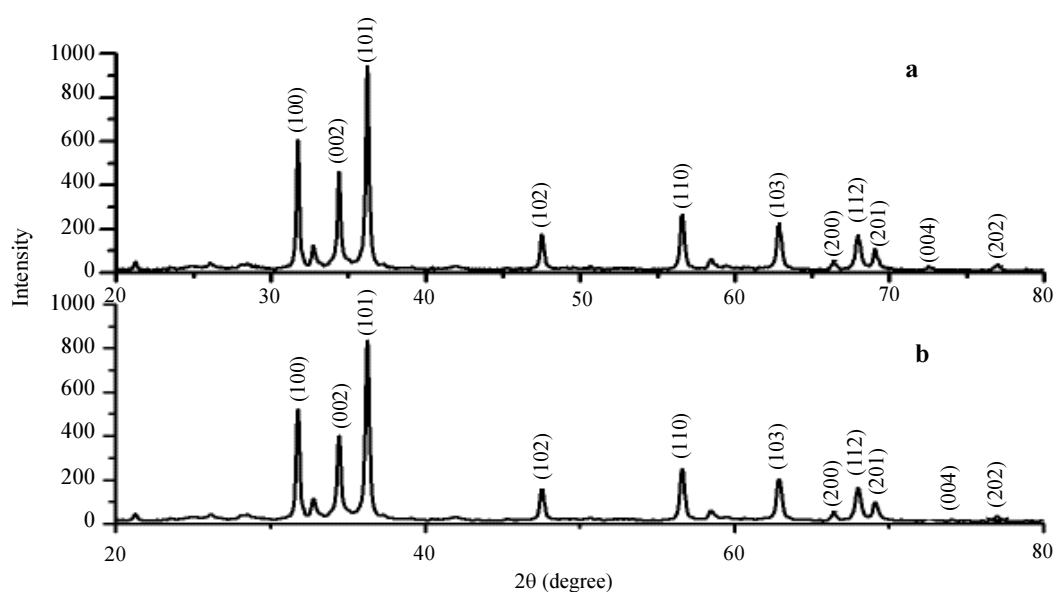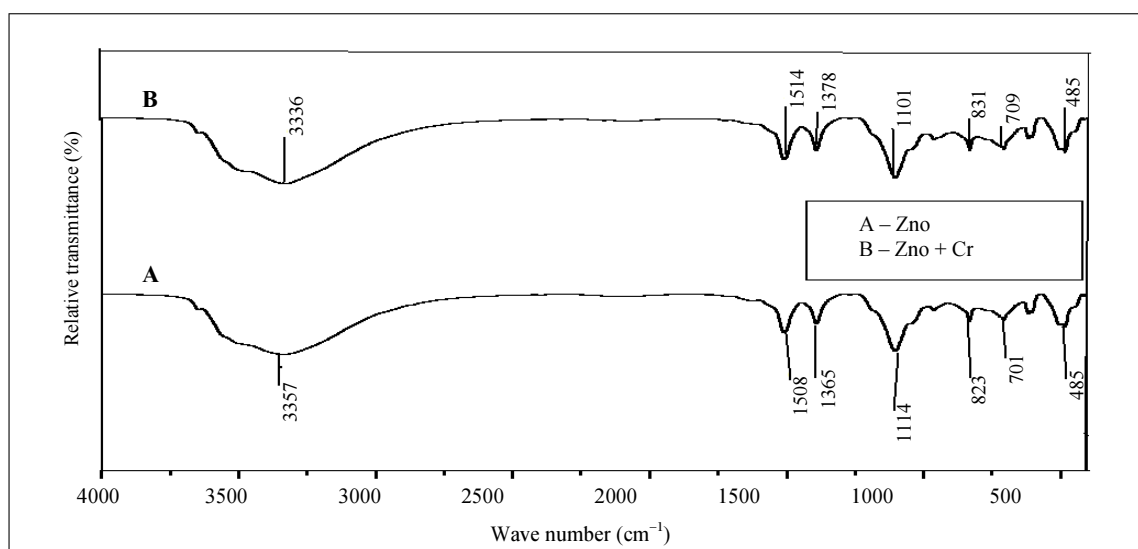

Fig. 1: X-Ray diffractogram of ZnO nano particles: (a) Sample XRD pattern and (b) standard XRD pattern
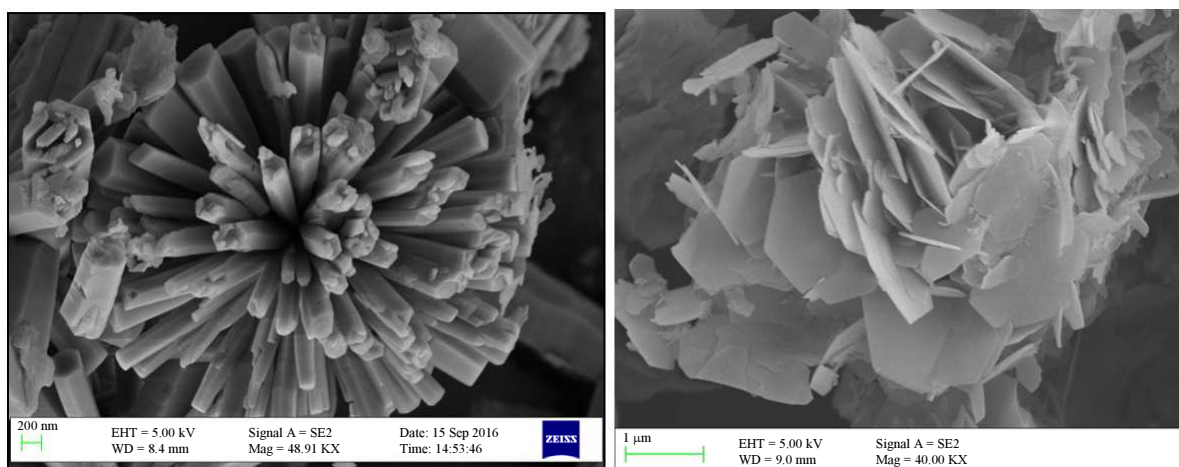
Fig. 2: (A) SEM morphology of ZnO Nano particles before adsorption (B) SEM morphology of ZnO Nano particles after adsorption
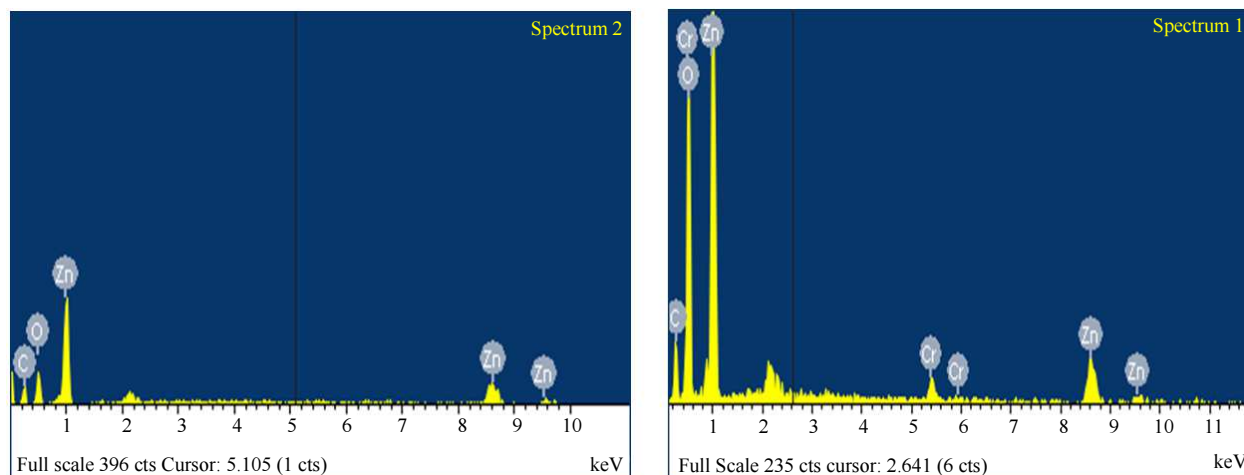
Fig. 3: (A) EDXA image of ZnO Nano particles before adsorption (B): EDXA image of ZnO Nano particles after adsorption

Fig. 4: FTIR of ZnO Nano particles and Cr(VI) ions adsorbed with ZnO Nano particles

Effect of Mixing Time

Contact time is an important factor in batch adsorption process. The extent of chromium removal was found to be increased first up to 40 min. of mixing and then the adsorption decreases. Initially the vacant surface sites are available for adsorption but they become saturated with the metal adsorption with the time. More over it would be difficult to be occupied due to repulsive forces between the bulk phases and the solute molecules on the solid (Alswata *et al.*, 2017; Kumar *et al.*, 2011; Alothman *et al.*, 2013).

Effect of Adsorbent Doses

The effect of adsorbent dosage on the adsorption was studied in the range 0.02-0.1 g. It has been found that the removal of Cr(VI) increases with the increase in adsorbent dosage. This increment might be due to the larger surface area and availability of more adsorption sites, whereas the adsorption amount decreases with the adsorbent. This is because of the adsorptive capacity of adsorbent available was not fully utilized at a higher adsorbent dosage in comparison to lower adsorbent dosage. The percentage of removal of Cr(VI) with respect to all parameters and adsorption at equilibrium, q_e are presented in Fig. 5 and 6, respectively.

Adsorption Isotherm Models

Adsorption isotherms are important to describe the adsorption behaviour of solute on the specific adsorbents. The equilibrium of adsorption is one of

the physico-chemical aspects that is used for the evaluation of adsorption process as a unit operation. These models help in studying the nature of the adsorbent, surface area of the adsorbent, adsorbate-adsorbent interactions and moreover the adsorption capacity of the adsorbent (Alswata *et al.*, 2017). They also indicate the distribution of adsorbable solute between the liquid and solid phases at various equilibrium (Oliveria *et al.*, 2005).

Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform strategies without transmigration of adsorbate in the plane surface (Hameed *et al.*, 2007). Once a site is filled, no further adsorption can take place at that site. This is indicative of the saturation point or the achievement of maximum adsorption by the surface. The linear form of this isotherm is presented as (Okoli and Ezuma, 2014; Anah and Astrini, 2018; Langmuir, 1918):

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \tag{4}$$

where, q_e is amount of metal adsorbed(mg/g) C_e is concentration after adsorption(mg/L), q_m is maximum monolayer coverage capacity (mg/g), K_L is Langmuir

constant (L/mg). A linear plot of $(1/q_e)$ against $(1/C_e)$ with slope $(1/K_L q_m)$ and intercept of $(1/q_m)$ shows the satisfaction of the Langmuir model for adsorption. The constants K_L and q_m relate to the energy of adsorption and maximum adsorption capacity, respectively.
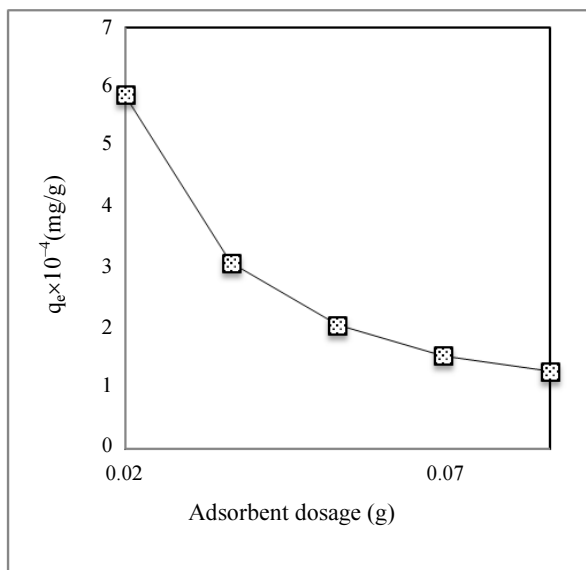
The Freundlich model is based on the adsorption behaviour of a heterogeneous surface in multilayer coverage. It is considered to be the most popular adsorption model for a single solute system of monolayer adsorption (Freundlich, 1928). As per Freundlich model the degree of site occupation increases with the decrease in the binding strength. So the stronger binding sites are occupied first followed by the weaker binding sites. The linear form of Freundlich isotherm model is given as (Freundlich, 1907):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{5}$$

where, K_f is the Freundlich constant and the indicator of adsorption capacity whereas $\frac{1}{n}$ is the strength of adsorption process or adsorption intensity. These constants were determined from the slope and intercept from the plot of $\log q_e$ (mg/g) against $\log C_e$ (mg/L).
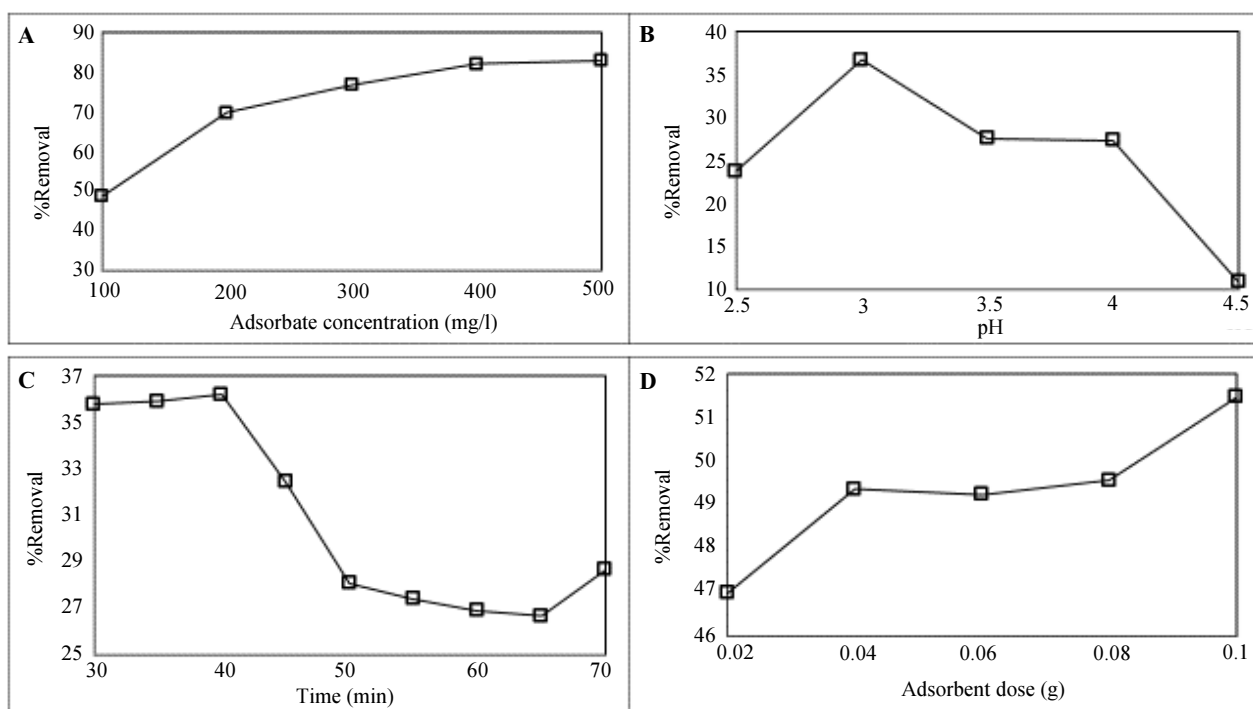
Fig. 5: (A) Effect of adsorbate concentration (mg/l) on adsorption of Cr(VI) ion. (B) Effect of P^H on adsorption of Cr(VI) ion. (C) Effect of contact time (min) on adsorption of Cr(VI) ion. (D) Effect of adsorbent dose (g) on adsorption of Cr(VI) ion

Fig. 6: Effect of adsorbent dose (g) on adsorption capacity of ZnO NPs

Similarly, Temkin isotherm model is based on the heat of adsorption of adsorbate molecules, which would decrease linearly with the increase in coverage of the adsorbent surface due to adsorbate-adsorbent interactions. This isotherm is used for heterogeneous surface energy systems (Mohamed *et al.*, 2008; Atar *et al.*, 2012) and the linear form of this isotherm model is given as (Temkin and Pyzhev, 1940; Akpomie *et al.*, 2015):

$$q_e = B \ln A + B \ln Ce \qquad (6)$$

where, $B = RT/b$, b is the Tempkin constant related to heat of sorption (J/mol), A is the Temkin isotherm constant (L/g), R is the gas constant (8.314 J/mol K) and T is the absolute temperature (K). The constants A and B are calculated from the intercept and slope of the linear plot of q_e (mg/g) against ln C_e. All the isotherms are shown in Fig. 7 and the constants are presented in Table 2.

The applicability of each model is determined by comparing the correlation coefficient, R^2. The higher the value of R^2, the better is the goodness of the fit (Adeogun *et al.*, 2012). In the present study, R^2 values of Temkin and Freundlich isotherm models are found to be more than that of Langmuir isotherm model. Furthermore, one of the adsorption constants for Langmuir isotherm is negative, which indicates the unsuitability of this isotherm for the present study. This also reveals that heterogeneous adsorption is the preferred technique than homogeneous adsorption. The value 'n' from the Freundlich model indicates the degree of non-linearity between solution concentration and adsorption. According to literature, when n = 1, the adsorption is supposed to be of linear type and if it is more than 1, the adsorption is considered to be a physical process whereas it becomes chemical process when the value is less than 1 (Alswata *et al.*, 2017).

Kinetics of Adsorption

Kinetics of adsorption is one of the most important characteristics that is responsible for the efficiency of adsorbents. The adsorbate can be transferred from the solution phase to the surface of the adsorbent in several steps. In order to study the mechanism of the process and potential rate controlling steps, the kinetics of adsorption onto adsorbent were analyzed by using different kinetic models. For such analysis, two kinetic models were applied in the present investigation. The kinetics of chromium adsorption on ZnO nano particles were analyzed by fitting the data into the Lagergrens first order model and pseudo second order equation to know the correlation coefficients (R^2). Pseudo-first order kinetics that generally describes the initial stage of the adsorption process is given as Equation 7 (Lagergren, 1898). Similarly, the pseudo-second order kinetics, which provides better description of the whole adsorption process and based on the adsorption capacity, is expressed as Equation 8 (Ho and McKay, 1999; Anbia and Parvin, 2011):

$$Log\left(q_e - q_t\right) = \log q_e - \frac{k_1}{2.303}t \qquad (7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_t}\right)t \qquad (8)$$

where, q_e is the amount of Cr(VI) adsorbed (mg.g^{-1}) at equilibrium time and q_t is the amount of Cr(VI) adsorbed (mg.g^{-1}) at time t(min). k_1 and k_2 are the first order rate constant (min^{-1}) and second order rate constant (g.mg^{-1}.min^{-1}), respectively.

For first order kinetics, the value k_1 is obtained from the slope of the linear plot of log ($q_e = q_t$) against time where the linear plot indicates the applicability of Lagergrens model. Similarly, for second order kinetics, the values of q_e and k_2 can be determined by the slope and intercept of the linear plot of t/q_t against time (Fig. 8).

In the present study, for pseudo first order rate kinetics, the q_e and the rate constant, k_1 values were found to be 18.96 mg.g^{-1} and 0.002 min^{-1}, respectively. The regression coefficient, R^2 for this model was determined as 0.694. Similarly, for pseudo second order, the q_e and rate constant, k_2 were 21.5

mg.g^{-1} and 0.004 g.mg^{-1}.min^{-1}, respectively. The regression coefficient, R^2 was found to be 0.999. The plot for pseudo first order model was not linear and the R^2 value is much less in comparison to that of pseudo second order kinetic model. This indicates that the pseudo second order kinetic model provided good correlation for the adsorption of chromium onto nano ZnO in the present study. Review of literature reveals that the second order rate kinetic is indicative of chemical adsorption involving valency forces through sharing the exchange of electrons between the adsorbent and the metal ions (Idris *et al.*, 2013).

Table 2: Adsorption constants of Langmuir, Freundlich and Temkin isotherms for Cr (VI) adsorption

Langmuir isotherm			Freundlich isotherm			Tempkin isotherm		
q_m (mg/g)	K_L (L/mg)	R^2	$1/n$	K_f (mg/g)	R^2	b	A (L/mg)	R^2
0.00165	-76.313	0.9381	5.597	$6.824 \times 10^{\alpha 6}$	0.992	85.106	3.162	0.998
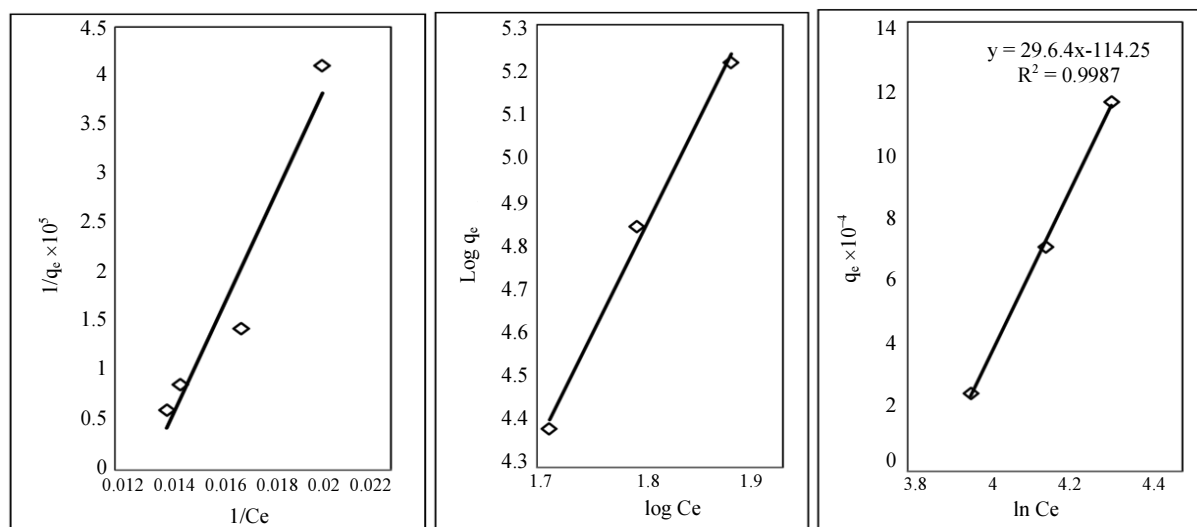
Fig. 7: (A) Langmuir adsorption isotherm for adsorption of Cr(VI) (B) Freundlich adsorption isotherm for adsorption of Cr(VI) (C) Tempkin adsorption isotherm for adsorption of Cr(VI)
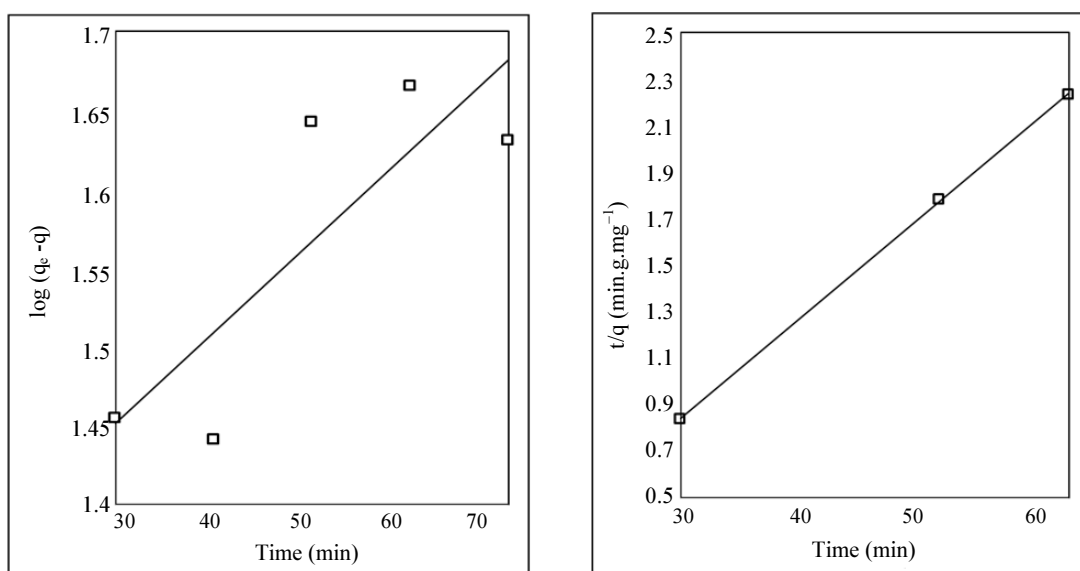
Fig. 8: (A) First order kinetics of Cr(VI) adsorption (B): Pseudo second order kinetics of Cr(VI) adsorption

Conclusion

In this investigation, ZnO nano rods were prepared and characterized for their shape, size and purity successfully. The prepared nano particles were studied for the removal of Cr(VI) from aqueous solution in batch adsorption technique. The optimum parameters for the removal of Cr(VI) from 100 mg/L aqua solutions were found to be at pH 3, 0.1 gm of adsorbent dose and 40 minutes of agitation, respectively. The SEM morphology of adsorbent before and after adsorption indicates the adsorption of chromium metals over the adsorbents by changing their shape from nano rods to nano sheets. Freundlich and Temkin isotherm models have provided better fit for this metal ion to the experimental data rather than Langmuir model indicating heterogeneous adsorption as the preferred technique over homogenous adsorption. The value of n in Freundlich isotherm again reveals the adsorption to be chemical rather than physical process. In addition, the adsorption kinetics shows that the mechanism followed the pseudo-second-order kinetic model indicating chemical adsorption to be the preferred one. This is an added supplement to the findings from isotherms. Moreover, the present investigation revealed that the nano rods could be used as an adsorbent for the removal of toxic metal like Cr(VI) from aqueous solutions/effluents. Furthermore, these nano materials are non-toxic, eco friendly and can easily be synthesized from very basic precursors. However, extensions of the present investigations are to be carried out further to make these nano adsorbents for actual applicability for the industrial effluents.

Acknowledgement

Author's Contributions

Sushma Kamath: Sushma is the first author and she did all the experimental work along with data collection.

Venu Gopal Vishwakarma Ramanjaneyalu: Venu Gopal's contribution includes coordination of data analysis and supporting the experimental work.

Susmita Kamila: Susmita is the supervisor and the corresponding author. Her contribution includes Research planning, organisational design and framework of the manuscript.

Ethics

No ethical issue/conflict is involved related to this work.

References

Adeogun, A.I., S.O. Kareem, J.B. Durosanya and E.S. Balogun, 2012. Kinetics and equilibrium parameters of biosorption and bioaccumulation of lead ions from aqueous solutions by *Trichoderma longibrachiatum*. J. Microbiol. Biotechnol. Food Sci., 1: 1221-1234.

Agrawal, A. and K.K. Sahu, 2006. Kinetic and isotherm studies of cadmium adsorption on manganese nodule residue. J. Hazardous Mater., 137: 915-924. DOI: 10.1016/j.jhazmat.2006.03.039

Aillon, K.L., Y. Xie, N. Ei-Gendy, C.J. Berkland and M.L. Forrest, 2009. Effect of nanomaterial physicochemical properties on in vivotoxicity. Adv. Drug Deliv. Rev., 61: 457-466. DOI: 10.1016/j.addr.2009.03.010

Akpomie, K.G. F.A. Dawodu and K.O. Adebowale, 2015. Mechanism on the sorption of heavy metals from binary-solution by a low cost montmorillonite and its desorption potential. Alexandria Eng. J., 54: 757-767.

Alothman, Z.A., M. Naushad and R. Ali, 2013. Kinetic, equilibrium isotherm and thermodynamic studies of Cr(VI) adsorption onto low-cost adsorbent developed from peanut shell activated with phosphoric acid. Environ. Sci. Pollut. Res., 20: 3351-3365. DOI: 10.1007/s11356-012-1259-4

Alswata, A.A., M.B. Ahmad, N.M. Al-Hada, H.M. Kumari and M.Z.B. Hussain *et al.*, 2017. Preparation of Zeolite/Zinc oxide nano composites for toxic metals removal from water. Results Phys., 7: 723-731. DOI: 10.1016/j.rinp.2017.01.036

Anah, L. and N. Astrini, 2018. Isotherm adsorption studies of Ni(II) ion removal from aqueous solutions by modified carboxymethyl cellulose hydrogel. IOP Conf. Ser.: Earth Environ. Sci., 160: 012-017. DOI: 10.1088/1755-1315/160/1/012017

Anbia, M. and Z. Parvin, 2011. Desulfurization of fuels by means of a nanoporous carbon adsorbent. Chem. Eng. Res. Des., 89: 641-647. DOI: 10.1016/j.cherd.2010.09.014

Atar, N., A. Olgun and S. Wangb, 2012. Adsorption of Cadmium (II) and Zinc (II) on boron enrichment process waste in aqueous solutions: Batch and fixed-bed system studies. Chem. Eng. J., 192: 1-7. DOI: 10.1016/j.cej.2012.03.067

Attia, A.A., S.A. Khedr and S.A. Elkholy, 2010. Adsorption of chromium ion (VI) by acid activated carbon. Braz. J. Chem. Eng., 27: 183-193. DOI: 10.1590/S0104-66322010000100016

Bhattacharya, A.K., S.N. Mandal, S.K. Das, 2006. Removal of Cr (VI) from aqueous solution by adsorption onto low cost non-conventional adsorbents. Ind. J. Chem. Technol., 13: 576-583.

Carson, B.L., H.V. Ellis and J.L. McCann, 1986. Toxicology and Biological Monitoring of Metals in Humans, Including Feasibility and Need. 1st Edn., Lewis Publishers, Chelsea, MI, ISBN-10: 087371072X, pp: 328.

Chu, K.H., 2002. Removal of copper from aqueous solution by chitosan in prawn shell: Adsorption equilibrium and kinetics. J. Hazardous Mater., B90: 77-95. DOI: 10.1016/S0304-3894(01)00332-6

Dehghani, M.H. and P. Mahdavi, 2015. Removal of acid 4092 dye from aqueous solution by zinc oxide nanoparticles and ultraviolet irradiation. Desalinat. Water Treatment, 54: 3464-3469. DOI: 10.1080/19443994.2014.913267

El-Safty, S.A. and M.A. Shenashen, 2013. Optical mesosensor for capturing of Fe(III) and Hg(II) ions from water and physiological fluids. Sensors Actuators B: Chem., 183: 58-70. DOI: 10.1016/j.snb.2013.03.041

El-Safty, S.A., M.A. Shenashen and A. Shahat, 2013. Tailor-made micro-object optical sensor based on mesoporous pellets for visual monitoring and removal of toxic metal ions from aqueous media. Small, 9: 2288-2296. DOI: 10.1002/smll.201202407

El-Safty, S.A., M.A. Shenashen and A.A. Ismail, 2012. A multi-pH-dependent, single optical mesosensor/captor design for toxic metals. Chem. Commun., 48: 9652-9654. DOI: 10.1039/c2cc34788a

El-Sayed, M.A., 2001. Some interesting properties of metals confined in time and nanometer space of different shapes. Acc Chem. Res., 34: 257-264. DOI: 10.1021/ar960016n

Förstner, U. and G.T.W. Wittmann, 1985. Metals in the Aquatic Environment. 1st Edn., Springer, New York.

Freundlich, H., 1907. Über die Adsorption in Lösungen. Zeitschrift für Physikalische Chemie - Stöchiometrie und Verwandschaftslehre, 57: 385-470.

Freundlich, H., 1928. Colloid and Cpillary Chemistry. EP Dutton and Co., New York.

Ghaedi, M., A.G. Nasab, S. Khodadoust, R. Sahrael and A. Daneshfar, 2015. Characterization of zinc oxide nanorods loaded on activated carbon as cheap and efficient adsorbent for removal of methylene blue. J. Indus. Eng. Chem., 21: 986-993. DOI: 10.1016/j.jiec.2014.05.006

Ghiloufi, I., J. El-Ghoul, A. Modwi and L. El-Mir, 2016. Ga-doped ZnO for adsorpsion of heavy metals from aqueous solution. Mater. Sci. Semi Conductor Process., 42: 102-106. DOI: 10.1016/j.mssp.2015.08.047

Gupta, V.K., I. Tyagi, H. Sadegh, R. Shahryari-Ghoshekandi and A.S.H. Makhlouf *et al.*, 2015. Nanoparticles as Adsorbent: A positive approach for removal of noxious metal ions: A review. Sci. Technol. Dev., 34: 195-214.

Hameed, B.H., A.T.M. Din and A.L. Ahmad, 2007. Adsorption of methylene blue onto bamboo-based activated carbon kinetics and equilibrium studies. J. Hazardous Mater., 141: 819-825. DOI: 10.1016/j.jhazmat.2006.07.049

Hashim, M.A., S. Mukhopadhyay, J.N. Sahu and B. Sengupta, 2011. Remediation technologies for heavy metal contaminated groundwater. J. Environ. Manage., 92: 2355-2388. DOI: 10.1016/j.jenvman.2011.06.009

He, C., T. Sasaki, Y. Shimizu and N. Koshizaki, 2008. Synthesis of ZnO nanoparticles using nanosecond pulsed laser ablation in aqueous media and their self-assembly towards spindle-like ZnO aggregates. Applied Surface Sci., 254: 2196-2202. DOI: 10.1016/j.apsusc.2007.09.007

Henglein, A., 1989. Small-particle research: Physicochemical properties of extremely small colloidal metal and semiconductor particles. Chem. Rev., 89: 1861-1873. DOI: 10.1021/cr00098a010

Ho, Y.S. and G. McKay, 1999. Pseudo-second order model for sorption processes. G Process Biochem., 34: 451-465. DOI: 10.1016/S0032-9592(98)00112-5

Hong, R.Y., J.H. Li, L.L. Chen, D.Q. Liu and H.Z. Li *et al.*, 2009. Synthesis, surface modification and photocatalytic property of ZnO nanoparticles. Powder Technol., 189: 426-432. DOI: 10.1016/j.powtec.2008.07.004

Hosseini, S.A., S. Mashaykhi and S. Babaei, 2016. Graphene oxide/zinc oxide nanocomposite: A superior adsorbent for removal of methylene blue - statistical analysis by Response Surface Methodology (RSM). South African J. Chem., 69: 105-112. DOI: 10.17159/0379-4350/2016/v69a13

Hua, M., S. Zhang, B. Pan, W. Zhang and L. Lv *et al.*, 2012. Heavy metal removal from water/wastewater by nanosized metal oxides: A review. J. Hazardous Mater., 211-212: 317-331.

Idris, S.A., K.M. Alotaibi, T.A. Peshkur, P. Anderson and M. Morris *et al.*, 2013. Adsorption kinetic study: Effect of adsorbent pore size distribution on the rate of Cr (VI) uptake. Microporous Mesoporous Mater., 165: 99-105. DOI: 10.1016/j.micromeso.2012.08.001

Jamhour, R.M.A.Q., T.S. Ababneh, A.I. Al-Rawashdeh, G.M. Al-Mazaideh and T.M.A. Al Shboul *et al.*, 2016. Adsorption isotherms and kinetics of Ni(II) and Pb(II) ions on new layered double hydroxides-nitrilotriacetate composite in aqueous media. Adv. Analytical Chem., 6: 17-33.

Konicki, W., D. Sibera and U. Narkiewicz, 2018. Adsorptive removal of cationic dye from aqueous solutions by $ZnO/ZnMn_2O_4$ nanocomposite. Separat. Sci. Tech., 53: 1295-1306. DOI: 10.1080/01496395.2018.1444054

Kumar, S., V.C. Srivastava and R. Badoni, 2011. Studies on adsorptive desulfurization by zirconia based adsorbents. Fuel, 90: 3209-3216. DOI: 10.1016/j.fuel.2011.06.029

Lagergren, 1898. About the theory of so-called adsorption of soluble substances. Kungliga Svenska Vetenskapsakademiens Handlingar, 24: 1-39.

Langmuir, I., 1918. Adsorption of gases on plane surfaces of glass, mica and platinum. J. Am. Chem. Soc., 40: 1361-1403. DOI: 10.1021/ja02242a004

Madoni, P., D. Davoli, G. Gorbi and L. Vescovi, 1996. Toxic effect of heavy metals on the activated sludge protozoan community. Water Res., 30: 135-142. DOI: 10.1016/0043-1354(95)00124-4

Mahdavi, S., M. Jalali and A. Afkhami, 2012. Removal of heavy metals from aqueous solutions using Fe_3O_4, ZnO and CuO nanoparticles. J. Nanoparticle Res., 14: 846-846. DOI: 10.1007/s11051-012-0846-0

Mahdavi, S., M. Jalali and A. Afkhami, 2013. Heavy metals removal from aqueous solutions using TiO_2, MgO and Al_2O_3 nanoparticles. Chem. Eng. Comm., 200: 448-470. DOI: 10.1080/00986445.2012.686939

Mekonnen, E., M. Yitbarek and T.R. Soreta, 2015. Kinetic and thermodynamics studies of the adsorption of Cr(VI) onto some selected local adsorbents. S. Af. J. Chem., 68: 45-52.

Meng, A., J. Xing, Z. Ei and Q. Li, 2015. Chromium doped ZnO nanoparticles: Synthesis, characterization adsorption property and reclycability. ACS Applied Mater. Interfaces, 7: 27449-27457. DOI: 10.1021/acsami.5b09366

Mohamed, A., G.I. Hesham and M.A. Mohamed, 2008. Equilibrium and kinetics of chromium adsorption on cement kiln dust. Proceedings of the World Congress on Engineering and Computer Science, Oct. 22-24, San Francisco, pp: 54-62.

Mukherjee, A.G., 1986. Environmental pollution and health hazards: Causes and control. Galgotia Publication, New Delhi.

Nriago, J.O., 1988. A silent epidemic of metal poisoning. Environ. Pollut., 50: 139-161. DOI: 10.1016/0269-7491(88)90189-3

O'Connell, D.W., C. Birkinshaw and T.F. O'Dwyer, 2008. Heavy metal adsorbents pre-pared from the modification of cellulose: A review. Bioresour. Technol., 99: 6709-6724. DOI: 10.1016/j.biortech.2008.01.036

Oehme, F.W., 1979. Toxicity of Heavy Metals in the Environment. 1st Edn., Marcel Dekker, New York, ISBN-10: 0608064688, pp: 469.

Okoli, J.U. and I.B.E. Ezuma, 2014. Adsorption studies of heavy metals by low cost adsorbents. J. Applied Sci. Environ. Manage., 18: 443-448.

Oliveria, E.A., S.F. Montanher, A.D. Andrader, J.A. Nobrega and M.C. Rollemberg, 2005. Equilibrium studies for the sorption of chromium and nickel from aqueous solution using rice bran. Process Biochem., 40: 3485-3490. DOI: 10.1016/j.procbio.2005.02.026

Recillas, S., A. Garcia, E. Gonzalez, E. Casals and V. Puntes *et al.*, 2011. Use of CeO_2, TiO_2 and Fe_3O_4 nanoparticles for the removal of lead from water: Toxicity of nanoparticles and derived compounds. Desalination, 277: 213-220. DOI: 10.1016/j.desal.2011.04.036

Sahu, S.K., P. Meshrm, B.D. Pandey, V. Kumar and T.R. Mankhand, 2009. Removal of chromium(III) by cation exchange resin', Indion 790 for tannery waste treatment. Hydrometallurgy, 99: 170-174. DOI: 10.1016/j.hydromet.2009.08.002

Sharma, D.C. and C.F. Forster, 1996. Removal of hexavalent chromium from aqueous solutions by granular activated carbon. Water SA, 22: 153-160.

Sheela, T., Y.A. Nayaka, R. Viswanatha, S. Basavanna and T. Venkatesha, 2012. Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles. Powder Technol., 217: 163-170. DOI: 10.1016/j.powtec.2011.10.023

Shenashen, M.A., N. Akhtar, M.M. Selim, W.M. Morsy and H. Yamaguchi *et al.*, 2017. Effective, low□cost recovery of toxic arsenate anions from water by using hollow-sphere geode traps. Chemistry: Asian J., 12: 1952-1964. DOI: 10.1002/asia.201700666

Singanan, M., 2011. Removal of lead(II) and cadmium(II) ions from wastewater using activated biocarbon. ScienceAsia, 37: 115-119. DOI: 10.2306/scienceasia1513-1874.2011.37.115

Taman, R., M.E. Ossman, M.S. Mansour and H.A. Farag, 2015. Metal oxide nano-particles as an adsorbent for removal of heavy metals. Adv. Chem. Eng., 5: 1-125.

Temkin, M.I. and V. Pyzhev, 1940. Kinetics of ammonia synthesis on protonated iron catalyst. Acta Physicochem. USSR, 12: 217-222.

Tewari, H. and Vivekananda, 2013. Removal of heavy metals from industrial effluents using *Pinus roxburghii* leaves as biosorbent: Equilibrium modelling. Water Sci. Technol., 67: 1894-1900. DOI: 10.2166/wst.2013.034

VenuGopal, V.R. and S. Kamila, 2017. Effect of temperature on the morphology of ZnO nanoparticles: A comparative study. Applied Nanosci., 7: 75-82.

Wang, X., W. Cai, Y. Lin, G. Wang and C. Liang, 2010. Mass production of micro/nano structured porous ZnO plates and their strong structurally enhanced and selective adsorption performance for environmental remediation. J. Mater. Chem., 20: 8582-8590. DOI: 10.1039/c0jm01024c

Wang, Y.H., S.H. Lin and R.S. Juang, 2003. Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents. J. Hazard. Mater., 102: 291-302. DOI: 10.1016/S0304-3894(03)00218-8

Warkocki, W., S.A. El-Safty, M.A. Shenashen, E. Elshehy and H. Yamaguchi *et al.*, 2015. Photo-induced recovery, optical detection and separation of noxious SeO_3^{2-} using a mesoporous nanotube hybrid membrane. J. Mater. Chem. A, 3: 17578-17589. DOI: 10.1039/C5TA02827B

Yabe, M.J.S. and E. de Oliveira, 2003. Heavy metals removal in industrial effluents by sequential adsorbent treatment. Adv. Environ. Res., 7: 263-272. DOI: 10.1016/S1093-0191(01)00128-9

Yuvaraja, G., C. Prasad, Y. Vijaya and M.V. Subbaiah, 2018. Application of ZnO nanorods as an adsorbent material for the removal of As(III) from aqueous solution: Kinetics, isotherms and thermodynamic studies. Int. J. Ind. Chem., 9: 17-25. DOI: 10.1007/s40090-018-0136-5

Zafar, M.N., Q. Dar, F. Nawaz, M.N. Zafar and M. Iqbal *et al.*, 2018. Effective adsorptive removal of azo dyes over spherical ZnO nanoparticles. J. Mater. Res. Technol. DOI: 10.1016/j.jmrt.2018.06.002

Zaka, A.K., A.W.H. Majid, M. Darroudi and R. Yousefi, 2011. Synthesis and characterization of ZnO nanoparticles prepared in gelatin media. Mater. Lett., 65: 70-73.

Zhang, L. and M. Fang, 2010. Nanomaterials in pollution trace detection and environmental improvement. Nano Today, 5: 128-142. DOI: 10.1016/j.nantod.2010.03.002

Zolfaghari, G., A. Esmaili-Sari, M. Anbia, H. Younesi and M.B. Ghasemian, 2013. A zinc oxide-coating mesoporous carbon adsorbent for lead removal from water: Optimization, equilibrium, modelling and kineticss studies. Int. J. Environ. Sci., 10: 325-340.