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REMOVAL OF HEAVY METALS Pb(II), Cd(II) AND Cu(II) FROM WASTE WATERS USING SYNTHESIZED CHROMIUM DOPED NICKEL OXIDE NANO PARTICLES

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ABSTRACT. Adsorption of metal ions Pb(II), Cd(II) and Cu(II) are observed on chromium doped nickel nano metal oxide. Chromium doped nickel oxide was synthesized by combustion technique using glycine as a fuel. In this work, transmission electronic microscopy (TEM), scanning electronic microscopy (SEM), X-ray diffraction (XRD) and Brunauer–Emmett–Teller (BET) are applied to study the composition and structure of chromium doped nickel oxide. Batch equilibrium experiments were performed to study the removal efficiency of heavy metal ions. The effects of different parameters such as contact time, pH and adsorbent dose on the adsorption process were investigated. The adsorption kinetics and adsorption isotherms studies were also performed. The formation of hydroxide on the surface of chromium doped nickel oxide could be the main factor of cations removal due to its high adsorption affinity for aqueous solutes. Chromium doped nickel oxide may offer a potential remediation method for the removal of metals from water and environment.

KEY WORDS: Adsorption isotherms, BET, Adsorption efficiency, Batch equilibrium, Adsorption kinetics

INTRODUCTION

Exposure to heavy metals is one of the most severe global environment problems [1, 2]. Industrial waste may contain toxic and heavy metals such as Pd, Cr, Ni, Cu and Cd depending up on the type of the process and raw materials used. Heavy metals are non-biodegradable in nature [3]. Their presence even in low concentration in water is harmful to human health as well as aquatic life. Lead is a heavy metal and commonly used in households and many industries [4-6]. Thus industrial wastewater is considered to be a potential source of trace metal pollution [7, 8].

Recent approaches for the removal of heavy metals from wastewaters have mainly included chemical precipitation, adsorption, oxidation–reduction, evaporation, ionic exchange, electrochemical treatment, and membrane separation techniques [9-14]. Adsorption is most commonly used for heavy metals remediation from water [15, 16]. Activated carbons, clay minerals and chitosan/natural zeolites were used to remediate heavy metals from water and waste water [17, 18].

Metal oxides play a very important role in many areas of chemistry, physics and materials science. The metal elements are able to form a large diversity of oxide compounds. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts. There were several reports available in literature where in nano metal oxides and composites alone have been tried for the removal of heavy metals in waste water and ground waters [19-22].

Metal oxides of transition elements are well known to possess chemically active surfaces and large surface areas that can be employed to extract a range of ions from aqueous solutions. The properties of various metal oxides have been modified in order to change their electrical, optical, structural or thermal behaviors by doping in additional species. The aim of this study

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was to synthesize chromium doped nano nickel oxide by employing combustion technique using glycine as a fuel. During combustion process CO_2, H_2O and liberate heat in exothermic process and forms complexes with metal ions facilitating homogeneous mixing of the cations in solution [23, 24]. In this study the author has made an attempt to synthesize a metal doped nano oxide which can found to be a potential adsorbent for the removal of heavy metals such as Cd, Cu and Pb. Sorption studies were conducted at different initial pHs, equilibrium time, and adsorbent/adsorbate concentrations. Kinetic and isotherm adsorption models are performed in order to better understanding of the adsorption mechanism [25, 26]. Thermodynamic studies were also performed to determine the entropy, enthalpy and Gibb's free energy [27].

EXPERIMENTAL

Materials and reagents

All chemical stock solutions were prepared from reagent grade chemicals using Millipore ultrapure water. Nickel nitrate hexahydrate, chromium trioxide were purchased from Merck, India.

Method of preparation

For the synthesis of chromium doped nickel nano oxide, 0.02 M nickel nitrate hexa hydrate and 0.2 M glycine dissolved in a minimum amount of water. The contents were kept on a magnetic stirrer for 45 min until homogenous solution was obtained. After that 0.1 g of chromium trioxide as a source of chromium was added to the above solution and the stirring is continued for half an hour. The obtained solution was kept on a hot plate for one hour until gel type layer was formed and it is cooled. It is transferred into porcelain dish and placed in a pre-heated muffle furnace for 20 min at 500 ^{o}C. The obtained calcined powder was ground in a mortar for 15 min.

Powder XRD analysis

XRD characterization was performed to determine the crystalline structure of the synthesized adsorbent and the results are shown in Figure 1. The XRD scanning from 20-70^{o} shows the lines (111), (200), (116) and (220) at $2\Theta = 37.22^{o}$, 43.266^{o}, 51.725^{o}, and 62.965^{o} respectively for chromium doped Nickel nano oxide as shown in Figure 1. The diffraction peaks of the particles matched with the JCPDS file 87-0712 related to NiO peaks. The 2Θ value 51.725^{o} related to doped metal.

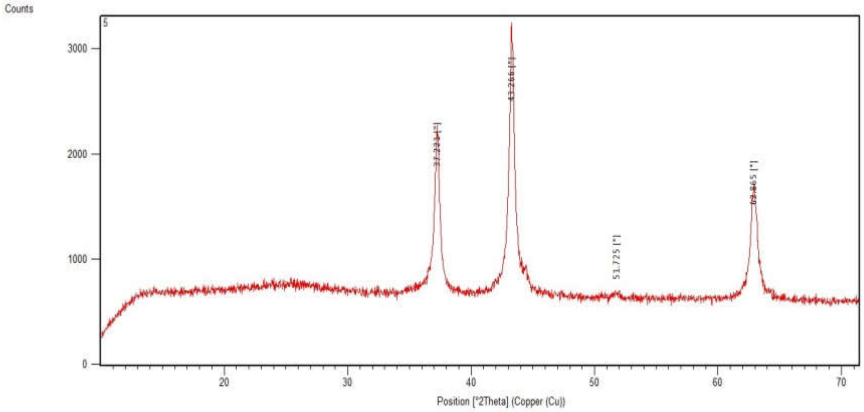

Figure 1. Powder XRD pattern of chromium doped NiO nanostructure.

$$D = K\lambda/\beta\ \mathrm{COS}\Theta \qquad (1)$$

where β is the line width at half maximum peak intensity, λ is the wave length of X-ray (0.154 nm), K is correction factor for particle shape (0.9 for spheres), D is the crystallite diameter, and Θ is the angle of incidence for the selected diffraction peak. The synthesized doped nano metal oxide was found to with an average size in between of 10 nm to 20 nm. No characteristic peak related to any other impurity was observed. "PANALYTICAL" Xpert-pro X-Ray diffractometer (P-XRD) was used for X-ray diffraction studies of NiO nano oxide with generator settings 40 kV and 30 mA at room temperature.

SEM analysis

In order to obtain insight information about surface morphology, particle size of the samples, SEM analysis were performed. The particles are agglomerated and this agglomeration was reduced by increase the grain growth. From the SEM micrograph, the prepared crystallites are nearly spherical in shape as shown in Figure 2.

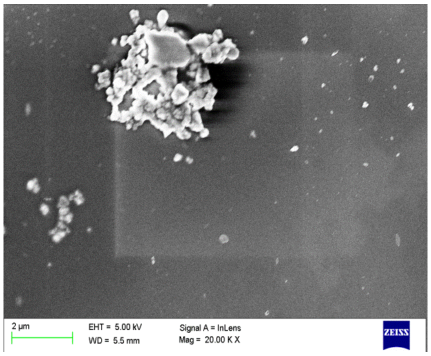

Figure 2. SEM micrograph of Cr doped NiO.

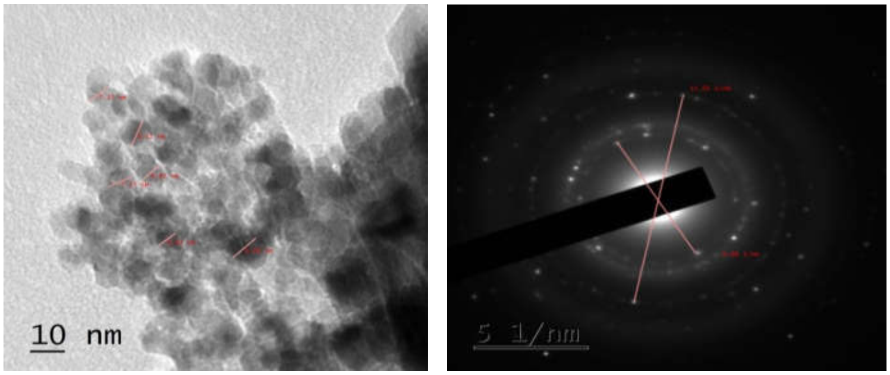

Figure 3. TEM micrograph of Cr doped NiO.

TEM micrograph analysis

The transmission electron microscope (TEM) has emerged as a powerful tool for probing the structure of metals and alloys. It can give morphological information of shape and size of particles in a microstructure. It can also reveal the nature of crystallographic defects. TEM use low wavelength electron which makes it possible to get a high resolution image. The average crystallite size of Cr doped NiO was found to be 10 nm as shown in Figure 3.

Brunauer-Emmett-Teller (BET) surface

The most common method used to measure the surface area of solid materials is the Brunauer-Emmett Teller (BET) method. The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. By using BET we can measure directly pore size distribution and surface area. The BET surface area of chromium doped nickel oxide was found to be 76 m^2/g with pore size 14 nm and pore volume of 0.33 cm^3/g.

Batch experiment

In order to study the effect of different parameters such as the contact time, pH, and adsorbent dosage, various experiments have been carried out by agitation of known amount of adsorbent (0.15 g) in 30 mL of solution containing Pb(II), Cd(II) and Cu(II) ions with concentrations ranging between 0.1 mg/L to 1 mg/L on rotary shaker at a constant speed of 180 rpm at room temperature (28 °C). The effect of pH was studied by adjusting the pH of solutions in the range of 2–10 with 0.1 N NaOH or HCl solutions.

The metal ions concentrations in the solution were determined 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 (Qe)] and distribution coefficient (D, mL/g) can be determined as follows:

$$Q_e = (C_0 - C_e)V/m \tag{2}$$

where Qe is the equilibrium adsorption capacity (mg/g), C_0 and C_e are the initial and equilibrium liquid-phase concentrations of solute in aqueous solution (mg/L), respectively. V is the liquid phase volume (L) and m is the mass of sorbent used (g).

RESULTS AND DISCUSSION

Effect of pH

In batch adsorption experiments pH is one of the major parameter and a great significance effect on rate of adsorption and the degree of ionization of adsorbate. The effect of pH on the chromium doped nickel oxide was carried out by varying pH from 2 to 10. While increasing the pH of the solution, the removal efficiency of cadmium(II), lead(II) and copper(II) metal ions considerably increased. The batch mode experiments were carried out by taking 30 mL of solution of trace metals (Pb, Cd and Cu) with a concentration of 1 mg/L and adsorbent dose 0.15 g and contact time of 45 min. It is noticed that the maximum percentage removal of trace metals were obtained in basic pH range, i.e. pH at 9.0. The results are reported in Figure 4.

Effect of contact time

The effect of contact time on adsorption of trace metals (Pb(II), Cd(II) and Cu(II)) onto chromium doped nickel oxide is shown in Figure 5. For chromium doped nickel oxide adsoprtion efficiency is about 99.6% for lead ions, 97.9% for cadmium ions and 97.8% for copper ions. The optimum condition of contact time is attanied at 45 min at constant adsorbent dose 0.15 g and it was still constant for remaining time period, i.e. 60, 80, 120 min, respectively. The concentration of metal ions in the batch mode process was 1 mg/L.

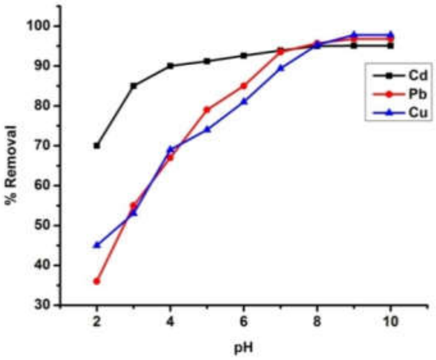

Figure 4. Effect of pH on Cd(II), Pb(II) and Cu(II) adsorption.

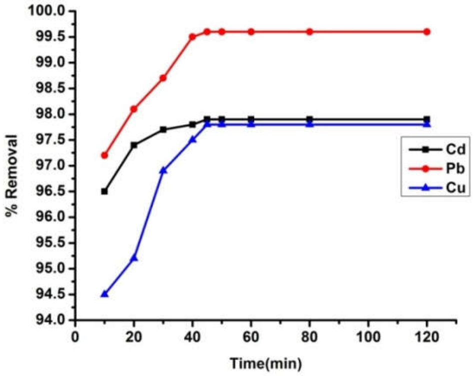

Figure 5. Effect of contact time on Cd(II), Pb(II) and Cu(II) adsorption.

Effect of amount of adsorbent

The effect of amount of chromium doped NiO was studied by carrying out experiments using 30 mL of trace metals (Pb, Cd and Cu) with a concentration of 1 mg/L with a dosage ranging from 0.05 g to 0.5 g (Figure 6). The percentage removal efficiency of trace metals increased up to 99% with the increase in the amount of dosage up to 0.15 g of adsorbent and then remained constant with increase in the adsorbent dose. Removal % of trace metals increased rapidly till maximum removal is attained at optimum dosage, i.e. 0.15 g because of high availability of exchangeable sites. The effect of various parameters such as pH, contact time and adsorbent dosage is given in Table 1.

Table 1. Optimum conditions for adsorption of metal onto chromium doped NiO.

Parameters	Cd(II)	Pb(II)	Cu(II)
pH	9.0	9.0	9.0
Contact time (min)	45	45	45
Adsorbent dose (g)	0.15	0.15	0.15

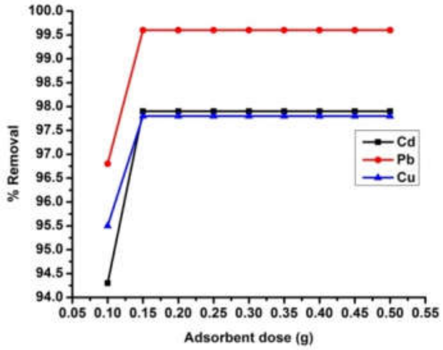

Figure 6. Effect of adsorbent dose on Cd(II), Pb(II) and Cu(II) adsorption.

Sorption process

It was additionally shown that the powder material synthesized via solution combustion route has negative surface charge over the whole pH range studied (Figure 7). According to the literature [28, 29], low pH values are unfavorable for metal ion adsorption, since in that range they are present in solution in free form as M^{n+} (Cd^{2+}, Cu^{2+} and Pb^{2+}), hence in this case there is an electrostatic repulsion between the cation and the more positively charged surface of the adsorbent. With increasing pH, the adsorbent surface becomes more negatively charged more OH^- groups are generated and this fact allows metal ions, such as Cd(II) , Pb(II), and Cu(II) to be adsorbed more effectively. In a strongly basic environment, the anions $M(OH)^-$ are formed, and these forms of metal ions, like cadmium or lead hydroxides, strongly interact with the surface of the inorganic oxide adsorbent, making adsorption easier.

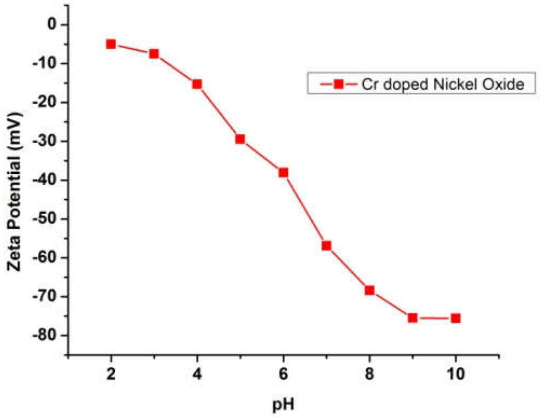

Figure 7. Metal ions (Pb, Cd and Cu) interation with chromium doped NiO adsorbent surface atdiffernt pH values.

Adsorption isotherm

The interaction between solutes and sorbents is well described in an adsorption isotherm. For the design and optimization of adsorption process, developing an appropriate isotherm model viz., Langmuir adsorption isotherm, Freundlich adsorption isotherm, Temkin adsorption isotherm and D-R isotherms for the adsorption is required. However, the equilibrium adsorption isotherms play a vital role in calculating the adsorption capacity of metal ions and diagnosing the nature of adsorption onto chromium doped NiO nanometal oxide. The information gained from this present work was checked with Langmuir, Freundlich, Temkin and D-R models.

Langmuir isotherm

This isotherm method is one of the widely used for explaining the adsorption of solutes onto a solid substance in a solution. With the formation of monolayer coverage of adsorbates on adsorbents, the adsorption takes place on finite number of adsorption sites and was given in the following equation.

$$q_e = q_m K_L C_e/(1+K_L C_e) \quad (3)$$

The linearized form of Langmuir can be written as follows

$$C_e/q_e = 1/q_m K_L + C_e/q_m \quad (4)$$

where q_e is the solid-phase equilibrium concentration (mg g^{-1}); C_e is the liquid equilibrium concentration of heavy metals (Pb, Cd, Cu) in solution (mg L^{-1}); K_L is the equilibrium constant related to the affinity of binding sites (L mg^{-1}); and q_m is the maximum amount of the heavy metals (Pb ,Cd ,Cu) per unit weight of adsorbent for complete monolayer coverage (Figure 8).

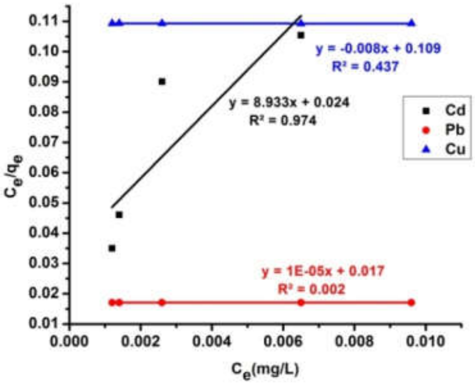

Figure 8. Langmuir adsorption isotherm of Pb(II), Cd(II) and Cu(II) onto Cr doped NiO nanostructure.

Freundlich isotherm

The Freundlich isotherm describes adsorption where the adsorbent has a heterogeneous surface with adsorption sites that have different energies of adsorption. The energy of adsorption varies as a function of the surface coverage (q_e) and is represented by Freundlich constant K_F (L g^{-1}) in Equation:

$$q_e = K_F C^n_e \quad (5)$$

where K_F is roughly an indicator of the adsorption capacity and n is the heterogeneity factor which has a lower value for more heterogeneous surfaces. In most references, Freundlich adsorption Eq. (5) may also be expressed as

$$\ln q_e = \ln K_F + 1/n\, C_e \quad (6)$$

All the correlation coefficients, R^2 value, and the constants obtained for the models show that the Langmuir and Freundlich isotherms fitted with cadmium(II) and only Freundlich isotherm fitted with lead(II) and copper(II) ions. Freundlich isotherm is suitable equation to describe the adsorption equilibrium of heavy metals (Pb, Cd, Cu) on the Cr doped NiO (Figure 9).

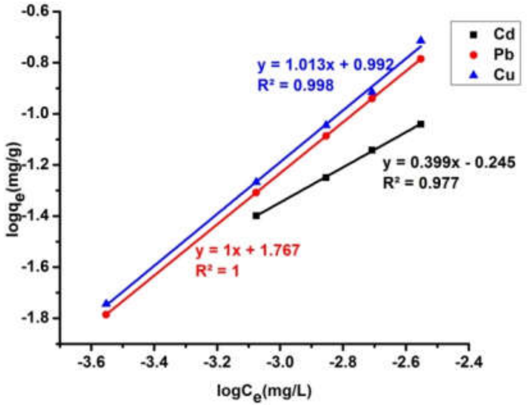

Figure 9. Freundlich adsorption isotherm of Pb(II), Cd(II) and Cu(II) onto Cr doped NiO nanostructure.

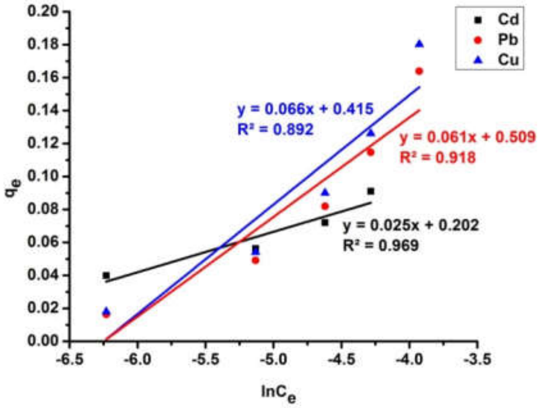

Figure 10. Temkin adsorption isotherm of Pb(II), Cd(II) and Cu(II) onto Cr doped NiO nanostructure

Temkin isotherm

The Temkin isotherm contains a factor that explicitly takes into account the adsorbing species–adsorbate interactions; the isotherm is given by a linearized expression as

$$q_e = RT/b_t \ln A_t + RT/b_t \ln C_e \qquad (7)$$

where B_T = RT/b (R is the universal gas constant (8.314 J/mol K), T is temperature (K), BT is the Temkin constant related to adsorption energy (kJ/mol), and K_T is the binding constant at equilibrium corresponding to the maximum binding energy (L/mg). The values of K_T and B_T were calculated from the intercept and slope of the plot of q_e vs. ln C_e (Figure 10).

Dubinin- Radushkevich isotherm model

The nature of adsorption can be also determined by analyzing the equilibrium data using the Dubinin–Radushkevich model (D-R). The D-R model is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The model has often been shown to fit both high activities of the solute and the intermediate range of concentrations. The adsorption energy is evaluated on the basis of the Dubinin–Radushkevich equation. D-R adsorption isotherm of Pb(II), Cd(II) and Cu(II) onto Cr doped NiO nanostructure is shown in Figure 11.

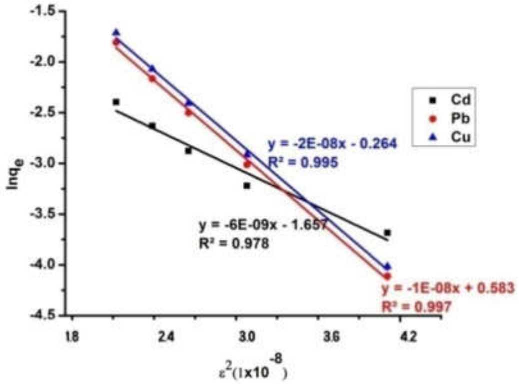

Figure 11. D-R adsorption isotherm of Pb(II), Cd(II) and Cu(II) onto Cr doped NiO nanostructure

The data related to adsorption isotherms are given in Table 2.

Table 2. Adsorption isotherm models of cadium(II), lead(II) and copper(II) ions using chromium doped nickel oxide nano particles.

Isotherm model	Parameters	Cd(II)	Pb(II)	Cu(II)
Langmuir model	Qm (mg/g)	0.1119	-	-125
	K_L (L/mg)	372.3	-	0.07339
	R^2	0.974	0.002	0.437
Freundlich model	1/n	0.399	0.987	1.013
	n	2.506	1.013	0.987
	Kf (mg/g)	1.75	58.4	9.817
	R^2	0.971	1	0.998
D-R model	Q_m (mg/g)	5.243	1.7914	1.3021
	β (mol^2/kJ^2)	$6x10^{-9}$	$1x10^{-8}$	$2x10^{-8}$
	E ($kJmol^{-1}$)	9.1	7.0	5.0
	R^2	0.977	0.997	0.995
Temkin	A_t (L/mg)	3229.23	4205.7	537.96
	B	0.025	0.061	0.066
	bt	99102.88	40615.9	37538.93
	R^2	0.969	0.918	0.892

Kinetics of adsorption

The main aim of adsorption kinetics is to determine the rate-determining step. To set up an equilibrium time and rate of sorption of contaminants in solution, the uptake of adsorbates as function of time is usually taken. Adsorption mechanisms or dynamics were generally checked by substituting the experimental values of adsorption in the kinetic models. The following discussed four kinetic models viz., pseudo first and second order, intraparticle diffusion and Elovich model, were the general models used for explaining, solid-liquid adsorption systems.

Pseudo first order model

In order to predict adsorption kinetic model, pseudo-first-order and pseudo-second-order kinetic models were applied to the data. The pseudo first-order model assumes that the rate of change of solute uptake with time is directly proportional to difference in saturation concentration and amount of solid uptake with time.

$$\ln(q_e\text{-}q_t)=\ln q_e\text{-}k_1t \qquad (7)$$

where q_e and q_t are the amounts of heavy metals adsorbed per unit mass of the adsorbent (mg g^{-1}) at equilibrium and time t, respectively, and k_1 is the rate constant of adsorption (min^{-1}). When ln (q_e-q_t) was plotted against time, a straight line should be obtained with a slope of $-k_1$, if the first-order kinetics is valid. Figure 12 represents pseudo first order reaction.

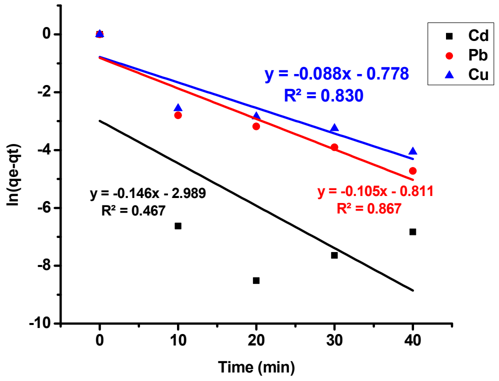

Figure 12. Kinetic pseudo first order reaction of Cr doped NiO.

Pseudo second order model

The pseudo-second-order model is in the following form:

$$t/q_t = t/q_e + 1/(k_2q_e^2) \qquad (8)$$

where q_e and q_t represent the amount of heavy metals adsorbed (mg g^{-1}) at equilibrium and at any time, k_2 in the rate constant of the pseudo-second-order equation (g mg^{-1} min^{-1}). A plot of t/q_t versus time (t) would yield a line with a slope of $1/q_e$ and an intercept of $1/(k_2q^2_e)$, if the second-order model is a suitable expression. The plot between ln ($q_e - q_t$) versus time t shows the pseudo-first-order model and the plot of t/qe versus time t shows the pseudo-second-order model.

The kinetic model with a higher correlation coefficient R^2 was selected as the most suitable one. It was found that application of pseudo-second-order kinetics provides better correlation coefficient of experimental data than the pseudo-first-order model for the heavy metals (Pb, Cd, Cu) onto adsorbent. The good correlation coefficients were obtained by fitting the experimental data to Eq. (8), indicating that the adsorption process on Cr doped NiO is pseudo second order. The pseudo second-order kinetic model was found to be appropriate for describing kinetics of metal adsorption. The values of rate constant were calculated from the slope of the Figures 13.

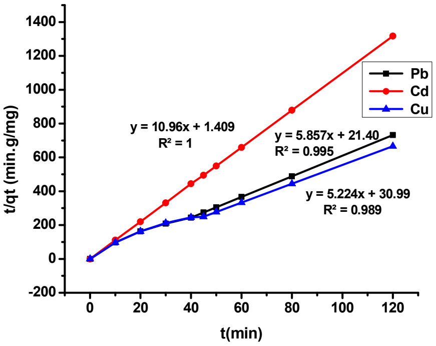

Figure 13. Kinetic pseudo second order reaction of Cr doped NiO.

Elovich kinetic model

The Elovich kinetic model generally expressed as

$$q_t = 1/\beta \ln\alpha\beta \; + 1/\beta \ln t \tag{9}$$

where α is the initial adsorption rate (mg/g.min), β is the desorption constant (g/mg) during any experiment. A plot of q_t vs ln(t) should give a straight line where in $1/\beta$ and $1/\beta \ln(\alpha\beta)$ correspond to the slope and intercept. Its use is currently adapted for the modeling of experimental data obtained for aqueous solutions. Elovich kinetic model of Cr doped NiO is shown in Figure 14.

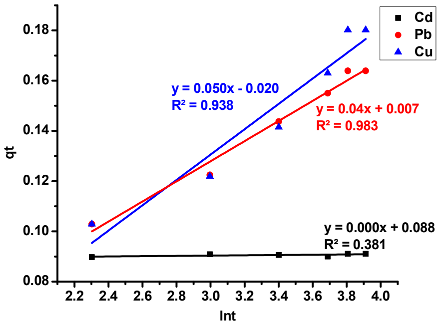

Figure 14. Elovich kinetic model of Cr doped NiO.

Intraparticle diffusion

Intraparticle diffusion describes the movement of species from the bulk of the solution to the solid phase. The possibility of intra-particle diffusion resistance was identified using the following intra-particle diffusion model.

$$q_t = k_i\ t^{0.5} + C \qquad (10)$$

where C is constant and k_i is the intra particle diffusion rate constant (mg/g min$^{1/2}$), q_t (mg/g) is the amount adsorbed at a time, $t^{1/2}$ is the square root of time (min$^{1/2}$). The intra particle diffusion rate constant was determined from the slope of the linear plot q_t versus $t^{1/2}$ (Figure 15). The larger the intercept, greater is the contribution of the surface adsorption in the rate limiting step. The data and results related to the adsorption kinetics are given in Table 3.

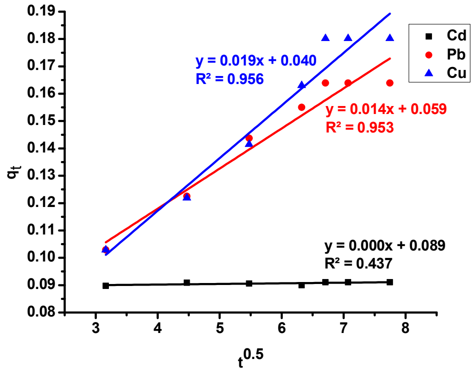

Figure 15. Intraparticle diffusion model of Cr doped NiO.

Table 3. Adsorption kinetic parameters of Pb^{2+}, Cd^{2+}, Cu^{2+} by Cr doped NiO particle.

Kinetic model	Parameters	Cd(II)	Pb(II)	Cu(II)
Pseudo kinetic first order	K_1	0.146	-0.105	-0.088
	Cal Q_e (mg/g)	0.05033	0.444	0.459
	Exp. Q_e (mg/g)	0.09108	0.1639	0.1802
	R^2	0.467	0.867	0.830
Pseudo kinetic second order	K_2	85.6	1.7398	0.9937
	Cal Q_e (mg/g)	0.09124	5.857	5.224
	Exp. Q_e (mg/g)	0.09108	6.1012	5.549
	R^2	1	0.995	0.989
Elovich model	α	-	20.9	29.8
	β	-	25	20
	R^2	-	0.983	0.938
Intraparticle diffusion	K_{id}	-	0.014	0.019
	R^2	0.437	0.953	0.956

CONCLUSION

Adsorption of metal ions Pb(II), Cd(II) and Cu(II) on chromium doped nickel nano metal oxide was examined. Chromium-doped nickel oxide was synthesized by combustion technique using glycine as a fuel. In this work, transmission electronic microscopy (TEM), scanning electronic microscopy (SEM) and X-ray diffraction (XRD) were applied to study the compositional and structural information of chromium doped nickel oxide. Brunauer–Emmett–Teller (BET) studies were used to measure the surface area. The BET surface area of Cr doped nickel oxide was found to be 76 m^2/g. Batch equilibrium experiments were performed to study the removal efficiency of metal ions Pb(II), Cd(II) and Cu(II). The effects of different parameters such as contact time, pH and adsorbate dose on the adsorption process were investigated. The adsorption kinetics well fitted using a pseudo-second-order kinetic model. SEM and TEM images showed that of particles was mostly agglomerated with an average size 10 nm. Adsorption isotherms studies are also performed. The results from Freundlich isotherm shows that the system can be comfortably applicable for the removal of the Cd(II), Pb(II) and Cu(II) metals at a concentration range of 0.1-1.0 mg/L. The K_F value of lead ion is higher than that of cadmium and copper, so adsorption is more efficient towards lead ion. From the kinetic studies, pseudo second order well fitted with the obtained data, i.e. experimental value good agreement with calculated value and also correlation coefficient R^2 values are nearly equal to 1. This study confirms adsorption process was controlled by chemisorption process. The formation of hydroxide on the surface of chromium doped nickel oxide could be the main factor of cations removal due to its high adsorption affinity for aqueous solutes. The thermodynamic parameter ΔG^o value shows that the removal of heavy metals lead(II), cadmium(II), and copper(II) ions from aqueous solutions by using chromium doped nickel oxide nanoparticles was spontaneous in nature and ΔS^o values for above metal ions shows an increase in the disorder of the solid-solution interface during adsorption at 298 K. The ΔH^o value indicates that the process is endothermic in nature. Chromium-doped nickel oxide may offer a potential remediation method for the removal of metals from water and environment.

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