

Synthesis, Characterisation and Application of Capped Chromic Oxide Nanoparticle (CCONP) for the Removal of Cd²⁺ and Pb²⁺ ion from Aqueous Solution

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Abstract

This research was designed to ascertain the removal efficiency of Cd²⁺ and Pb²⁺ ion from aqueous solution using capped chromic oxide nanoparticle (CCONP) synthesized by method of co-precipitation and thermal degradation of chromic hydroxide (Cr(OH)₃), stabilized and capped using polyvinyl alcohol (PVA). The physicochemical characterization of the synthesized CCONP was evaluated using x-ray diffractograms (XRD), scanning electron microscope (SEM) and Fourier Transform infrared spectrophotometer (FTIR). The CCONP obtained was more of crystalline than amorphous with very small particles inapparently soft agglomerates with a size of 7.7 nm. The amount of Cd²⁺ and Pb²⁺ ions before and after treatment of the aqueous solution was evaluated using atomic absorption spectrometer (AAS). Adsorption experiments were conducted in batches and the adsorption property of CCONP was studied using adsorption isotherm models and optimized using response surface methodology (RSM) Analysis. The adsorption isotherm models revealed that the adsorption process of Cd²⁺ and Pb²⁺ ions onto CCONP was a physical process, favorable and exothermic. The energy of affinity for Pb²⁺ ions on CCONP was higher. The adsorption process for Cd²⁺ ions on CCONP was spontaneous and the adsorption capacity of CCONP for Pb²⁺ ions was higher. However, optimisation analysis revealed that the cadmium ions were slightly more adsorbed on CCONP and removed from the aqueous solution compared to lead ions. This observation was in agreement with the k_F values obtained from Freundlich isotherm in which the k_F value for cadmium ions (59.52) was higher than that of lead (51.99).

Keywords: Capped, Chromic oxide, Nanoparticle, Optimization, Adsorption Isotherm.

Introduction

Water is one of the most important resources for human life, despite its abundance on the earth, majority of the water bodies contains different types of impurities - organics and inorganics (Mohan *et al.* 2011). Research and development of remedial techniques in the removal of heavy metals from aqueous solution vis-à-vis polluted water, has become a necessity to bring about an improvement in the quality of water for human existence and longevity. Thus there is need for the development of an affordable nanomaterial with increased affinity, capacity and selectivity for heavy metals and other contaminants in water.

Nanotechnology has the potential to revolutionize the remediation of contaminated water, agriculture and food industry (Wani and Shah, 2012). The growth in the applications of nanoparticles in solving environmental problem is rapid and still a new area. Nanotechnology could be applied at both ends of the environmental spectrum, to clean up existing contaminants and to decrease or prevent its generation. Exceptional properties such as small size effect, large surface effect and quantum tunnel effect is possessed by matters at nano-scale and they provide a variety of surprising and interesting uses (Salata, 2004; Sovan, *et al.*, 2011; Rathore, *et al.*, 2012). Nanoparticles tend to aggregate and interact with environmental media because of their charged surface and surface potential (Cornell and Schwertmann, 2003). Nanoparticle's properties can vary dramatically under different electrical, photological, and thermodynamic conditions (Mahdi *et al.* 2012; Rathore, *et al.* 2012). Several synthetic methods have been developed for generation of nanoparticles, such as chemical, photochemical, electrochemical, radiolytic, co-precipitation, sol gel, mechanochemical reaction and sonochemical methods etc. (Rakesh and Netkal, 2013; Ramesh *et al.*, 2012). Chromium (III) particle is associated with lipid and glucose digestion. The lack of chromium (III) is related with cardiovascular illness and diabetes. An intake of 50 to 200 µg of chromium (III) per day is recommended for adults (Calder, 1988; Pechova and Pavlata, 2007). In aqueous solution, Cr⁶⁺ is poisonous, while the danger of the less versatile Cr³⁺ is moderately low. (Manahan, 1992; DEFRA, 2002).

The objective of this study was to synthesize, characterize CCONP and evaluate its efficiency in removing Cd²⁺ and Pb²⁺ ions from aqueous using adsorption isotherm models and response surface methodology.

Materials and Methods

Adsorbates Preparation

Aqueous solutions of lead (II) and cadmium (II) were prepared from their nitrate salts and their actual concentrations confirmed with atomic absorption spectrophotometer (AAS).

Capped Chromic Oxide Nanoparticle (CCONP) Synthesis

Chromium (III) oxide nanoparticle (CONP) was synthesized using the thermal degradation method adapted from Tavares *et al.* (2014) and Sadjadi and Khalilzadegan (2015), with slight modifications. A solution of 5.0 mmol of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was dissolved in 40 ml of distilled water containing 2.0 % (w/v) of polyvinyl alcohol (PVA) to get chromic (Cr^{3+}) ions solution (solution A) and a solution of 20.0 mmol of NaOH was dissolved in 50 ml of distilled water containing 2.0 % (w/v) of polyvinyl alcohol (PVA) (solution B). Solution B was added drop wise into a 200 ml reaction vessel containing solution A at a rate of one drop per second while the dropping lasted under vigorous stirring (using Stuart SD162 heat-stir) at 1300 rpm. The reacting system was further stirred at 90°C for 2 hr. The $\text{Cr}(\text{OH})_3$ nanoparticle formed was allowed to cool for at least 6 hr after which the product was separated by centrifugation at 5,800 rpm for 15 min (using MPW-53) and washed three times with distilled water. The synthesized $\text{Cr}(\text{OH})_3$ nanoparticle was dried in an oven at 105°C for 6 hr to avoid the oxidation of Cr^{3+} to Cr^{6+} . Finally the $\text{Cr}(\text{OH})_3$ nanoparticle was calcined at 400°C for 5 hr to obtain CONP which was allowed to cool in a desiccator for 24 hr, ground and sieved through 400 mesh size sieve.

In order to modify the surface of chromic oxide nanoparticle, so as to reduce or eliminate aggregation/agglomeration as well as water uptake, the post-precipitation addition method of capping metal oxide nanoparticle adapted from Li *et al.* (2013), with slight modifications was used in modifying the surface of the synthesized chromic oxide nanoparticle. Polyvinyl alcohol (PVA) was used as its capping agent. 1.5 % solution of polyvinyl alcohol (PVA) was added to the dried chromic oxide nanoparticle obtained until slurry or paste was formed. The slurry was oven dried at 105°C for 12 hr and allowed to cool in a desiccator for 24 hr. The dried polyvinyl alcohol (PVA) capped chromic oxide nanoparticle was ground and sieved through 400 mesh size sieve.

Physicochemical Characterization Techniques

The physicochemical characterization of the synthesized capped chromic oxide nanoparticle was evaluated using x-ray diffractograms (XRD,

Empyrean diffractometer system equipped with a copper tube); scanning electron microscope (SEM; Phenom pro suite desktop scanning electron microscope) and Fourier Transform infrared spectrophotometer (FTIR).

Adsorption Isotherm Studies

The effect of adsorbent dose, adsorbate concentration, time, and pH on the removal of Cd^{2+} and Pb^{2+} were investigated. The adsorption process of Cd^{2+} ions onto capped chromium (III) oxide nanoparticle was studied using the batch adsorption isotherm experiments. The batch adsorption isotherm experiments were conducted by varying adsorbent dose, contact time, pH and concentration of Cd^{2+} ions (at 50 mg/l). Cd^{2+} ions concentrations were varied from 10 to 50 mg/l, at optimum CCONP dose, contact time, pH and agitation speed of 300 rpm to obtain the optimum concentration of Cd^{2+} ions adsorbed. Pb^{2+} ions were also treated in the manner. The equilibrium concentration of the heavy metal ions in the treated samples were determined using atomic absorption spectrophotometer (Buck scientific model VGP-210).

Adsorption Isotherm Model

An adsorption process can be best understood by use of adsorption isotherms models. Adsorption isotherm is a graph that associates the amount of adsorbed substance (adsorbate) on the adsorbent as a function of pressure (for gases) or concentration (for liquids) at constant temperature with the unadsorbed substance concentration (equilibrium concentration, C_e) in the solution. Information on the affinity between the adsorbent-adsorbate, adsorption capacity of the adsorbent, surface area, porosity and adsorption heat can be obtained from adsorption isotherms (Yildiz, 2017).

The equilibrium amount of adsorbate adsorbed (or adsorption capacities) and adsorption efficiency from the aqueous solution were calculated using equations 1 and 2 respectively:

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

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

Where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g); C_0 is the initial concentration of adsorbate (mg/l); C_e is the equilibrium concentration of adsorbate (mg/l) left in solution; M is the adsorbent mass (g); and V is the volume of the aqueous solution (l) (Kocaoba *et al.* 2007; Erdem *et al.* 2004). The data obtained from the adsorption processes were

analyzed using the Langmuir, Freundlich, Dubinin-Radushkevick (DRK) and Temkim isotherm model.

Response Surface Methodology (RSM) Analysis

Response surface methodology - an empirical modeling technique derived for the evaluation of the relationship of a set of controlled experimental factors and observed results - was utilized and a 'Three-factor-three-level' Box-Behnken Design (BBD) was adopted in order to study the response pattern and determine the optimum combination of the initial metal concentration, adsorbent dosage and contact time for optimizing the amounts of lead and cadmium ions adsorbed from their aqueous solutions using the CCONP adsorbents (Myers *et al.* 2009).

The values of the process variables considered for this analysis is shown in Table 1.

Table 1: Coded and Actual Levels of the factors for the three factor BBD

Independent variables	Unit	Symbol	Coded and actual value		
			-1	0	1
Initial concentration	(mg/l)		10	30	50
Adsorbent dosage	(g)		0.01	0.03	0.05
Contact time	(min.)		20	60	100

A total of 15 experimental runs with three variables for each individual response were designed according to BBD of Design Expert 8.6.0 using 3 center points. A Box Behnken experimental design matrix with responses is shown in Table 2.

Table 2: Box Behnken Experimental Design Matrix with Responses

Runs	Initial concentration (mg/l)	Adsorbent dosage (g)	Contact time (min)	CONP	
				Amount Adsorbed (mg/l)	
				Lead	Cadmium
	A	B	C		
1.	10	0.03	100	16.22	15.05
2.	30	0.03	60	48.59	37.26
3.	50	0.03	20	79.48	60.93
4.	30	0.01	100	140.70	115.35
5.	30	0.05	20	30.47	26.77
6.	30	0.01	20	152.35	133.85
7.	10	0.03	20	15.55	14.95
8.	30	0.03	60	48.59	37.26
9.	10	0.01	60	48.66	45.15

10.	30	0.03	60	48.59	37.26
11.	10	0.05	60	9.38	7.69
12.	30	0.05	100	28.14	23.07
13.	50	0.05	60	46.90	38.45
14.	50	0.03	100	80.60	61.35
15.	50	0.01	60	185.79	240.03

Results and Discussion

Characterization of CONP

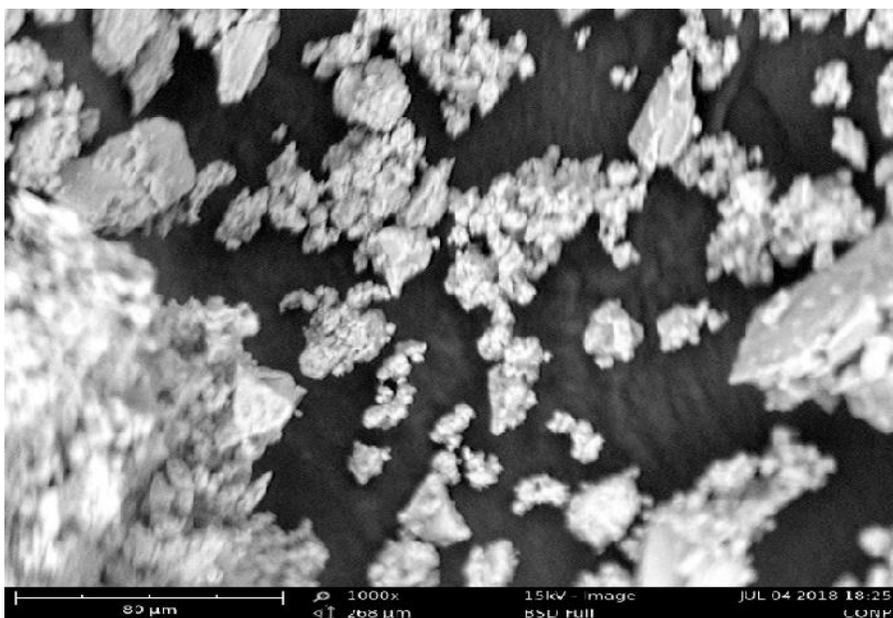


Figure 1: SEM Image of capped Chromic oxide Nanoparticle (CONP)

The SEM revealed that the morphology of the synthesized nanoparticle (CCONP) obtained was more of crystalline than amorphous with very small particles in apparently soft agglomerates (Fig. 1).

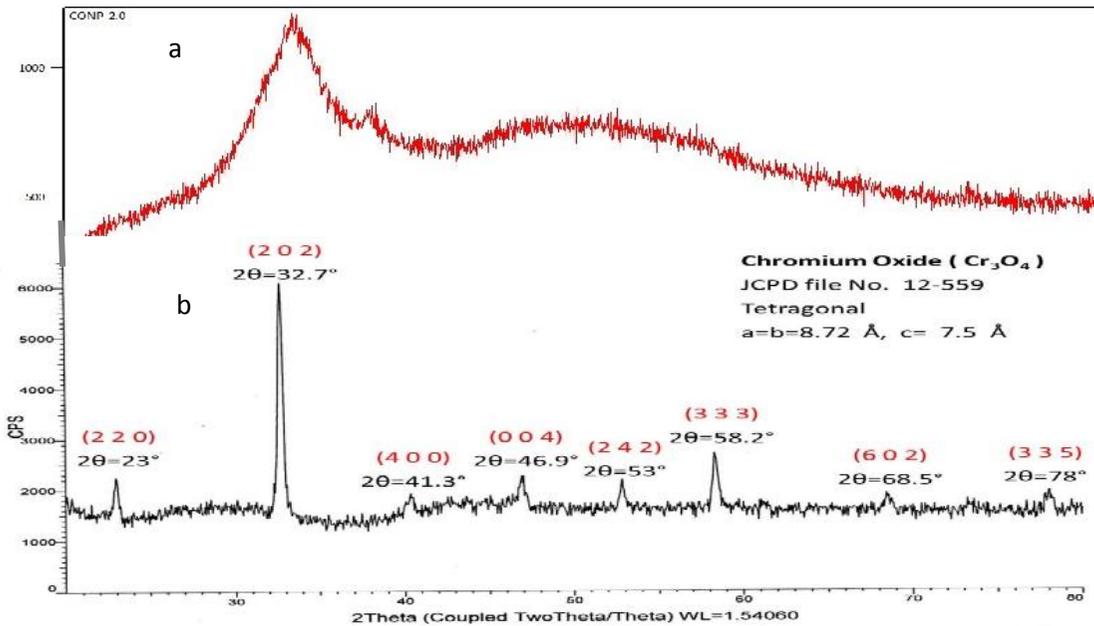


Figure 2: XRD Image of capped chromic oxide nanoparticle (a) and chromic oxide standard (b).

In the x-ray diffraction, some prominent peaks were considered and corresponding d-values were compared with standard. The x-ray diffractogram shows peaks only due to Cr₂O₃ and no peak is detected due to any other material or phase, indicating a high degree of purity of the synthesized CCONP. The broadening of the x-ray diffraction lines and the sharpness of the peaks, as seen in Fig. 2 reflected that the nanoparticles were of higher degree of crystallinity and good crystal growth of the oxide nanoparticles. Average particle size (L) of the particles was calculated from the high intensity peak using the Debye-Scherrer equation.

$$L = K / B \cos \theta \quad (3)$$

L= particle size, B (2θ) = full width at half maximum (FWHM, the broadening of the x-ray peak, in radians), K= Scherrer constant (0.94), λ is the x-ray wavelength, and θ is the peak position in degree. The particle size was found to be 7.7 nm.

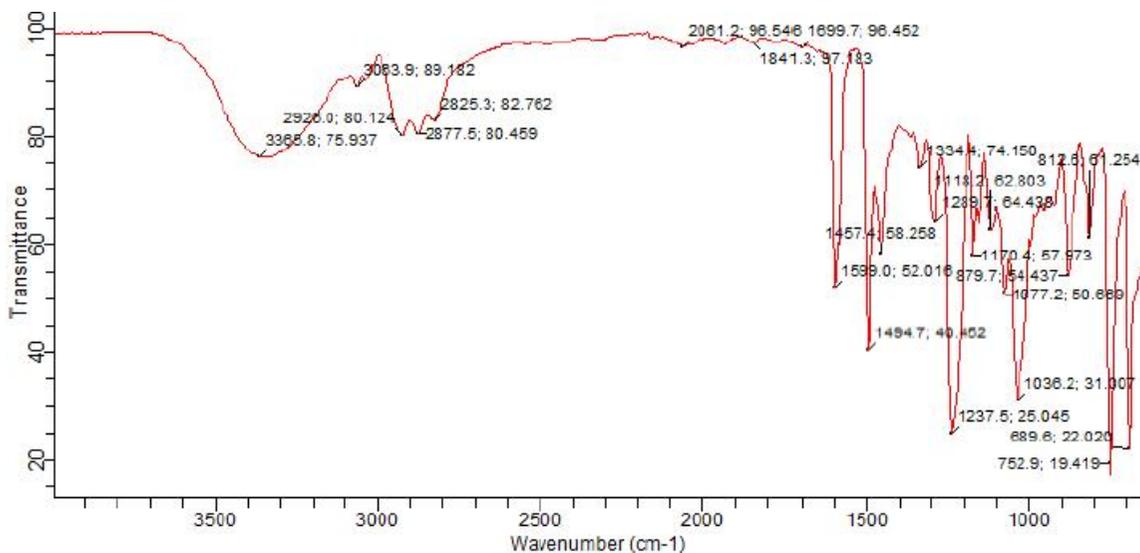


Figure 3: Fourier Transform Infrared Spectrum of capped chromic oxide Nanoparticle (CCONP).

The FTIR spectra shown in Fig. 3, was expressed in tabular form in Table 3

Table 3: The wave numbers and their corresponding functional groups from FTIR Spectrum of capped chromic oxide nanoparticle (CONP)

Wave number (cm ⁻¹)	Functional group
3368.80	corresponds to N-H bond belonging to secondary amine group (R ₂ NH)
3083.90 and 2920.00	corresponds to O-H stretch band, belonging to the carboxylic acid groups -COOH,
1699.70	corresponds to C=O stretch belonging to amide (RCONH ₂)
1599.00 and 1454.70	corresponds to the stretching vibration of C=C stretch, conjugated alkene – an arene
1237.50 and 1170.40	corresponds to strong appearance of C-O stretch for acids (RCOOH), esters (RCOOR), and anhydrides (R(COO) ₂)
689.60, 762.90 and 879.70	corresponds to Cr-O-Cr vibrations due to metal oxides of Chromium-oxide stretching

The functional groups identified on capped chromic oxide Nanoparticle (CCONP) FTIR spectrum, such as O-H, C=O, -C=C- (arene), shown in Fig 3 and Table 3, will promote negatively-surface-charged character of CCONP due to availability of electrons, hence increasing its chances of removing heavy metals from aqueous solution. The C-O stretch bond on CCONP belonging to the carboxylic acid groups can also result in the formation of

negatively-charged carboxylate ions (COO^-) with a strong coordinative affinity in forming chelate complexes towards metal ions (Shen *et al.*, 2009). The metal oxide (M-O-M; Cr-O-Cr) functional group infers the presence of chromic oxide. Octahedral hexaquo ion, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ tends to hydrolyze with increasing pH, resulting in the formation of polynuclear complexes containing OH⁻ bridges which can greatly increase the negative charges on the surface of CCONP hence promoting its ability to adsorb heavy metals from aqueous (Weckhuysen *et al.*, 1996).

Adsorption Study and Response Surface Methodology (RSM) Analysis

The adsorption isotherm parameters determined from the plots of their adsorption isotherms and response surface methodology (RSM) Analysis (Table 4; Fig 4a and 4b) were used in predicting the removal behavior and adsorption efficiency of the Cd^{2+} and Pb^{2+} ions by CCONP.

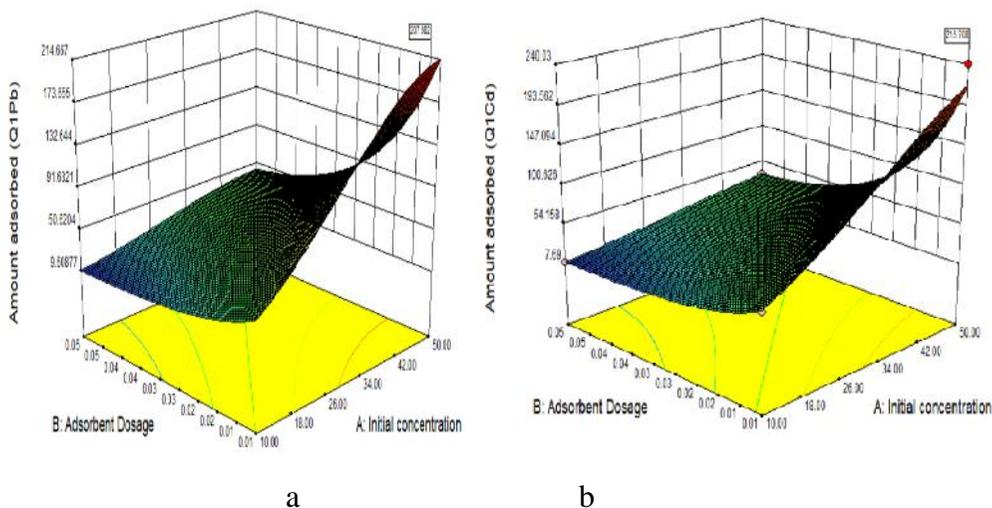


Figure 4: Response surface plots showing the interaction effects of initial concentration and adsorbent dosage on the amounts of (a) lead (b) cadmium adsorbed respectively by the CONP adsorbent.

The isotherm parameters obtained from the adsorption isotherm and response surface methodology (RSM) Analysis is presented in the Table 4.

Table 4: Adsorption isotherm parameter models and response surface methodology (RSM) Analysis value obtained for adsorption of Cd²⁺ and Pb²⁺ ions onto CCONP

Models	Parameters	Cd ²⁺	Pb ²⁺
Langmuir isotherm model	q _{mL} (mg/g)	78.74	370.37
	K _L (l/mg)	0.17	0.17
	R _L	0.10	0.11
	R ²	0.87	0.70
Freundlich isotherm model	K _F	59.52	51.99
	n _F	1.97	1.15
	R ²	0.98	0.99
Dubinin–Radush-kervik (DRK) Isotherm model	q _{mD} (mg/g)	71.16	75.24
	(mol ² J ⁻²)	-6 x 10 ⁻⁸	-1 x 10 ⁻⁸
	E (KJ mol ⁻¹)	2.89	7.07
	R ²	0.84	0.89
Temkin Isotherm model	b (J mg ⁻¹)	155.62	72.38
	B (l g ⁻¹)	16.03	34.46
	K _T	2.13	5.21
	R ²	0.89	0.96
Response Surface Methodology (RSM) Analysis	Optimal values		
	Initial Concentration (mg/l)	50.00	47.93
	Adsorbent dosage (g)	0.01	0.01
	Contact time (min)	60.00	67.10
	Amount adsorbed (mg/g)	215.71	206.34
	R ² – R squared	0.94	1.00

From Langmuir isotherm, the values of q_{mL} revealed that CCONP has a higher adsorption capacity for Pb²⁺ ions, these values were corroborated by the q_{mD} values of DRK isotherm. Their adsorption must have taking place only at specific localized sites on its surface. Pb²⁺ and Cd²⁺ ions had high heat of adsorption, high binding affinity on the adsorbent and the immobilization of the adsorbate onto the sorbent was favorable (Table 4).

Freundlich isotherm revealed that there was no monolayer adsorption but a multilayer adsorption properties consisting of heterogeneous surface of the adsorbent in terms of adsorption regions and energy, the adsorption was a physical process and it indicated a favorable adsorption process for Cd²⁺ and Pb²⁺ ions. Based on their n_F values, which indicates the extent of adsorption mechanism and formation of relatively stronger bonds between adsorbate and adsorbent, revealed that the n_F values of Cd²⁺ and Pb²⁺ ions were 1.97 and 1.15 respectively. The higher the n_F values the better its adsorption mechanism and formation of relatively stronger bonds. This

implies that Cd^{2+} ions formed the relatively stronger bonds with the adsorbent CCONP and a better adsorption mechanism.

The Dubinin- Radush-Keveick (DRK) isotherm revealed that the adsorption of Cd^{2+} and Pb^{2+} ions were exothermic. The activity coefficient constant () for Pb^{2+} ions is low, thus supporting the fact that the adsorption capacity of lead ions was relatively higher than that of Cd^{2+} ions. The mean free energy or energy of affinity (E) between the adsorbate and the adsorbent was in favour of Pb^{2+} ions hence confirming the higher adsorption capacity (q_m) of the lead ions onto the CCONP adsorbent (Table 4). The sorption process of the adsorbate Pb^{2+} and Cd^{2+} on the capped CCONP adsorbent is a physical process since the E value calculated from the DRK isothermal model is lower than 8 kJ/mol thus agreeing with the prediction from Freundlich isotherm model (Table 4).

Temkin isotherm revealed that Pb^{2+} ions had higher adsorption potential or maximum binding energy (B and K_T) to the CCONP adsorbent also this indicated that Pb^{2+} ions had higher adsorption capacity onto the CCONP adsorbent and this was corroborated by the heat of adsorption (b) value which shows that the Pb^{2+} ion has the stronger interaction with the adsorbent CCONP, hence a higher adsorption capacity onto CCONP. This value agrees with the prediction from Langmuir and DRK isotherm models. The values of the calculated b (a constant related to heat of sorption, J/mg) were positive for Cd^{2+} and Pb^{2+} an indication that the reaction is exothermic and their adsorption was a physical process (Table 4).

From Fig. 4(a) it was observed that the initial concentration increased from 10 to 50 mg/l and adsorbent dosage decreased from 0.05 to 0.01 g, the amount of Pb^{2+} ions adsorbed by the CCONP adsorbent increased from 9.5 to 215 mg/g and the optimal value of Pb^{2+} ions adsorbed at a contact time of 67.10 min was 206.34 mg/l (Table 3). Fig. 4(b), revealed that initial concentration increased from 10 to 50 mg/l and adsorbent dosage decreased from 0.05 to 0.01 g, the amount of Cd^{2+} ions adsorbed by the CCONP adsorbent increased from 7.8 to 245 mg/g and the optimal value of Cd^{2+} ions adsorbed at a contact time of 60 min was 215.71 mg/l (Table 3). From these observations, the interaction between initial concentration and adsorbent dosage have an overall positive impact on the adsorption of Pb^{2+} and Cd^{2+} ions by the CCONP adsorbent and the Cd^{2+} ions was slightly more adsorbed and removed from the contaminated water compared to Pb^{2+} ions.

Conclusion

Capped Chromic oxide nanoparticle adsorbed Pb^{2+} and Cd^{2+} ions favorably and exothermically through a physical process (physiosorption). The adsorption isotherm revealed that CCONP had a higher adsorption capacity for Pb^{2+} ions compared to Cd^{2+} ions. However, the optimization study using response surface methodology revealed that the cadmium ions were slightly more adsorbed and removed from the polluted water compared to lead ions, this observation was in agreement with the k_F values obtained from Freundlich isotherm in which the k_F value for Cd^{2+} ions (59.52) was higher than that of Pb^{2+} ions (51.99) indicating that cadmium ions has a higher adsorption capacity. This study revealed that CCONP was effective for the removal of Cd^{2+} and Pb^{2+} ions.

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