EISSN: 2707-0425

East African Journal of Science, Technology and Innovation, Vol. 1 (2): 2020

Synthesis, Characterisation and Application of Chromic Oxide-*Lophira Alata* Carbonized Sawdust Nanocomposite (COLACSN) in Removing Cd^{2+} and Pb^{2+} ions from aqueous solution

[1]OKUO, J. M., [1*]MOSES, O.

[1,] Department of Chemistry, Faculty of Physical Sciences, University of Benin, Benin City, Nigeria

***Corresponding author**: okponmwense.moses@uniben.edu

Abstract

The aim of this research is to examine the efficiency of removing cadmium-II and lead-II ions from aqueous solution using chromic oxide-*lophira alata* carbonised sawdust nanocomposite (COLACSN) synthesized by modified co-precipitation and thermal degradation method. The physicochemical characterization of chromic oxide-*lophira alata* carbonised sawdust nanocomposite was evaluated with the use of x-ray diffractograms (XRD), scanning electron microscope (SEM) and Fourier-Transform infrared spectrophotometer (F-TIR). The nanocomposite was amorphous with some degree of crystallinity, smooth and spherical in shape with a particles size of 12.05 nm in apparently soft agglomerates. The quantity of cadmium-II and lead-II 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 COLACSN was studied using isotherm models and Response Surface Methodology (RSM). The adsorption isothermal study revealed that the adsorption manner was physical and favorable for the accumulation of Cd^{2+} and Pb^{2+} ions on to chromic oxide-*lophira alata* carbonised sawdust nanocomposite. The chromic oxide-*lophira alata* carbonised sawdust nanocomposite had high adsorption capacity for Pb^{2+} ions. The accumulation process of Pb^{2+} ions was exothermic and possesses a high interaction with the adsorbent chromic oxide-*lophira alata* carbonised sawdust nanocomposite. The optimization analysis revealed that the Pb^{2+} ions were more adsorbed compared to Cd^{2+} ions with optimum adsorption capacities of 191.50mg/g and 66.20mg/g respectively. These values agreed with the k_F values obtained from Freundlich isotherm. This implies that the chromic oxide-*lophira alata* carbonised sawdust nanocomposite was more effective in the removal of Pb^{2+} ions.

Keywords: *Adsorption Isotherm, chromic Oxide,* Sawdust, *Nanocomposite,* Optimization.

Cite as: *Okuo J. M., Moses O., 2020 Synthesis, Characterisation and Application of Chromic Oxide-Lophira Alata Carbonized Sawdust Nanocomposite (COLACSN) in Removing Cd2+ and Pb2+ ions from aqueous solution, East African Journal of Science, Technology and Innovation 1(2).*

Received: 25/06/19
Accepted: 06/01/20
Published: 02/03/20

Introduction

Contaminated water is one of the main sources of illnesses worldwide, therefore the search for pollutants free water is inevitable and indispensable to human health and existence, (Pink, 2006; Savage and Diallo, 2005).

Water pollutants include pathogenic and non-pathogenic microorganisms, organic or inorganic (Hashem 2014; Sushma and Richa 2015). Various methods implemented for removing heavy metals from contaminated water include coagulation, membrane separation, flocculation, filtration, chemical treatment and adsorption (Westerhoff *et al.,* 2016).

Adsorption has more benefits than other techniques because of its simple plan that is, its design is easy to carry out for both batch and continuous method of treating contaminated water, with little monetary value and lack of sludge development. Natural and synthetic materials of different kinds have been utilized in removing heavy metals by adsorption these include clay, seaweed, biomass, activated carbon, resin, and mesoporous silica etc. (Gupta *et al.,* 2015).

Utilization of nanomaterials is seen as a potential with unique prospects to advance more affordable and environmentally adequate water decontamination procedures which could help in resolving or greatly reduce the problems of heavy metals contaminants in water (Gupta *et al.,* 2015; Sadegh *et al.,* 2014). Nanomaterials behave significantly in a different way from composite materials because of their quantum effects and surface effects. These dynamics influence the chemical reactiveness of nanomaterials, in addition to their optical, magnetic, electrical and mechanical properties (Abhilash, 2012; Singh *et al.,* 2013).

The ultimate goal of synthesizing nanocomposite is to design a material that has the capability to get rid of heavy metals from contaminated water very quickly, proficiently and within sensible costs. Nanocomposite is a material having nano fillers dispersed in a matrix, its structure is a matrix-filler combination, where the fillers like particles, fibers, or fragments are surrounded and bound together as discrete units by the matrix (Singh *et al.,* 2013; Baksi and Biswas, 2014).

The significant characteristic that make nanomaterials chiefly eye-catching as sorbents are their greater surface areas compared to bulk particles and they can also be functionalized with different chemical groups to increase their attraction towards target compounds, thus, serving as high capacity/selectivity and recyclable ligands for poisonous metal ions, radionuclides, organic and inorganic solutes/anions in aqueous solutions. (Savage and Diallo, 2005; Westerhoff *et al.,* 2016).

Lead, cadmium and mercury are the "Big Three" toxic categories of heavy metals because of their acute toxicity to humans and the environment (Gallego *et al.,* 2012). Lead exists in Inorganic and Organic form. Inorganic lead is a general metabolic poison, enzyme inhibitor and has the ability to replace bone calcium, remain there long time and make the bone susceptible to breaking. Organic lead is even more poisonous than inorganic lead (Niu *et al.,* 2009). Lead can cause several unwanted effects, such as: Disruption of the biosynthesis of haemoglobin and anaemia; a rise in blood pressure; kidney damage; miscarriages and subtle abortions; disruption of nervous systems; brain damage; declined fertility of men through sperm damage; diminished learning abilities of children; behavioural disruptions of children, such as aggression, impulsive behavior and hyperactivity; lead can enter a foetus through the placenta of the mother thereby causing serious damage to the nervous system and the brains of unborn children. (Khlifi and Hamza-Chaffai, 2010; Giaccio *et al.,* 2012; Zhang *et al.,* 2013).

Cadmium can accumulate in the kidneys and liver of humans. Chronic cadmium poisoning produces proteinuria and formation of kidney stones, lung and prostate cancer. There is evidence of a link between cadmium and hypertension. Other health effects caused by cadmium include: diarrhoea, stomach pains and severe vomiting; bone fracture; reproductive failure and possibly even infertility; damage to the central nervous system; damage to the immune system; psychological disorders; possibly DNA damage or cancer development. (Ebau *et al.,* 2012).

Chromium (III) particle is a basic follow component associated with lipid and glucose digestion. It is normally viewed that practically all the chromium in sustenance is available as chromium (III) particle, its deficiency is related with cardiovascular illness and diabetes (Manahan, 1992, Department for Environment Food and Rural Affairs (DEFRA) and Environment Agency (EA), 2002). The Cr^{6+} ion is poisonous in aqueous solution or in water, whereas the danger of Cr^{3+} ions which is less mobile is moderately low, as such, Cr^{3+} particle is generally latent, less versatile, less bioavailable and effectively adsorbed on mineral surfaces. Carbonized saw dust is a good adsorbent for heavy metals, however, a nanoparticle oxide activated carbonized saw dust can be more efficient, effective, recyclable and economically viable in tackling heavy metals contaminated water.

The objective of this study was to synthesize, characterize Chromic oxide-*lophira alata* Carbonized Sawdust nanocomposite (COLACSN) and evaluate the efficiency of COLACSN in removing Cd^{2+} and Pb^{2+} ions from aqueous solution using 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).

Chromic Oxide-Lophira Alata Carbonized Sawdust Nanocomposite (COLACSN) Synthesis

Chromic oxide-*lophira alata* Carbonized Sawdust nanocomposite (COLACSN) was prepared by the co-precipitation method adapted from Moafi *et al.,* (2016) and Hasanzadeh *et al.,* (2016), with slight modifications. 20 mmole of sodium hydroxide (NaOH) in 50 ml distilled water containing 2.0 % (w/v) of PVA was added drop wisely to 5 mmole of $Cr(NO_3)_3$ in 40 ml of distilled water containing 2.0 % (w/v) of PVA in a 200 ml reaction vessel, after the last drop of NaOH solution, the reaction was stirred for 30 min to allow for formation of $Cr(OH_3)_3$ after which 2.0 g *lophira alata* carbonized sawdust was added into the reaction vessel and stirred continuously for another 120 minutes at 90 °C (using Stuart SD162 heat-stir magnetic stirrer) at 1300 rpm to allow for formation of *lophira alata* carbonized sawdust-$Cr(OH_3)_3$ nanocomposite, until a consistent dark-greyish colloidal suspension was formed and stirring continued for another 2 hr. The product formed was allowed to cool down for at least 6 hr after which it was centrifuged and rinsed three times with sufficient distilled water and dried for at least 6 hr in an oven at 105 °C and cooled in a desiccator for 24 hr, the material obtained was calcined at 400°C for 5 hr to obtain COLACSN.

Physicochemical Characterization Techniques

The physicochemical characterization of the synthesized COLACSN was evaluated using X-ray diffractograms (XRD, Figs. 2.) Scanning electron microscope (SEM, Fig. 1) was used to obtain the images which revealed their morphologies and Fourier-Transform infrared spectrophotometer (FT-IR; Fig. 3) was used in determining functional groups present on the synthesized COLACSN.

Adsorption Isotherm Studies

The effect of adsorbent dosage, time, and pH on removal of Cd^{2+} and Pb^{2+} were investigated as follows. The adsorption process of Cd^{2+} ions onto COLACSN was studied using the batch adsorption isotherm experiments, because the quantities of aqueous solution treated are small in amount (see Table 4). The batch adsorption isotherm experiments were conducted by varying adsorbent dosage, contact time, pH and constant concentration of Cd^{2+} ions (50 mg/l). Cd^{2+} ions concentration were varied from 10 to 50 mg/l, at optimum COLACSN dose, contact time, pH and agitation speed of 300 rpm to obtain the optimum concentration of Cd^{2+} ion. The adsorption process of Pb^{2+} ions onto COLACSN was also studied using the batch adsorption isotherm experiments (see Table 4). The batch adsorption isotherm experiments were conducted by varying adsorbent dosage, contact time, pH and constant concentration of Pb^{2+} ions (50 mg/l). Pb^{2+} ions concentration were varied from 10 to 50 mg/l, at optimum COLACSN dose, contact time, pH and agitation speed of 300 rpm to obtain the optimum concentration of Pb^{2+} ion. The equilibrium concentration of the Cd^{2+} and Pb^{2+} ions in the treated samples was determined using atomic absorption spectrophotometer (Buck scientific model VGP-210).

The equilibrium amount of adsorbate adsorbed (adsorption capacities) and adsorption efficiency were calculated using equation 1 and 2 respectively:

$$q_e = \frac{(C_o - C_e)v}{M} \tag{1}$$

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

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 adsorption processes were analyzed using the Langmuir, Freundlich, Dubinin-Radushkevick (DRK), Temkim and Flory-Huggins Adsorption Isotherm Models (Table 4).

Response Surface Methodology (RSM) Optimization Study

The relationship between a set of controlled experimental factors and observed results was evaluated using an empirical modelling

The values of the process variables considered for this analysis are shown in Table 1 technique known as the response surface methodology (RSM). 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 dose and contact time for the optimization of the amounts of lead and cadmium ions adsorbed from their aqueous solutions using the adsorbents (Myers *et al.,* 2009).

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	X_1	10	30	50
Adsorbent dosage	G	X_2	0.01	0.03	0.05
Contact time	min.	X_3	20	60	100

A total of 15 experimental runs with three variables for 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)	COLACSN Amount Adsorbed (mg/l)	
	A	B	C	Lead	Cadmium
1.	10	0.03	100	10.15	12.30
2.	30	0.03	60	49.04	6.95
3.	50	0.03	20	40.88	6.45
4.	30	0.01	100	147.40	20.85
5.	30	0.05	20	14.71	2.09
6.	30	0.01	20	49.04	6.95
7.	10	0.03	20	8.14	1.49
8.	30	0.03	60	49.04	6.95
9.	10	0.01	60	48.85	8.99
10.	30	0.03	60	49.04	6.95
11.	10	0.05	60	9.77	1.80
12.	30	0.05	100	13.13	67.48
13.	50	0.05	60	7.88	37.49
14.	50	0.03	100	50.75	61.52
15.	50	0.01	60	245.25	38.69

Results

Characterization of chromic oxide-lophira alata carbonized sawdust nanocomposite (COLACSN)

The morphology of the synthesized nanocomposite (COLACSN) is shown in Figure 1.

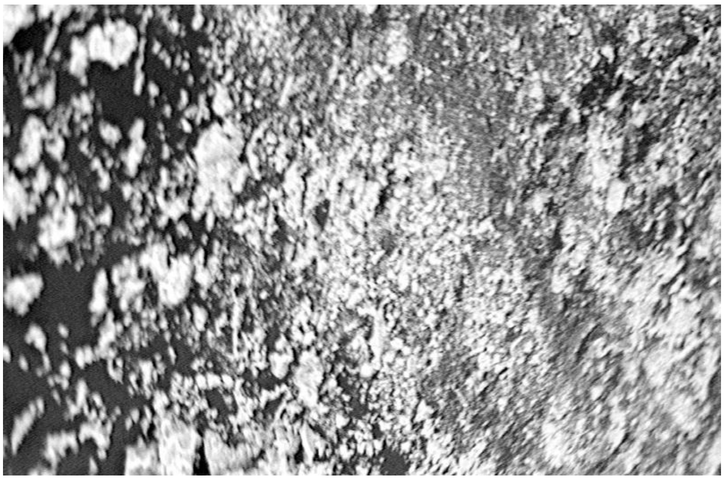

Fig1. SEM Image of COLACSN

The XRD Image comparing the images of synthesized Chromic oxide nanoparticle (a), chromic oxide-*Lophira Alata* carbonised sawdust nanocomposite (b) and chromic oxide standard (c) is shown in figure 2.

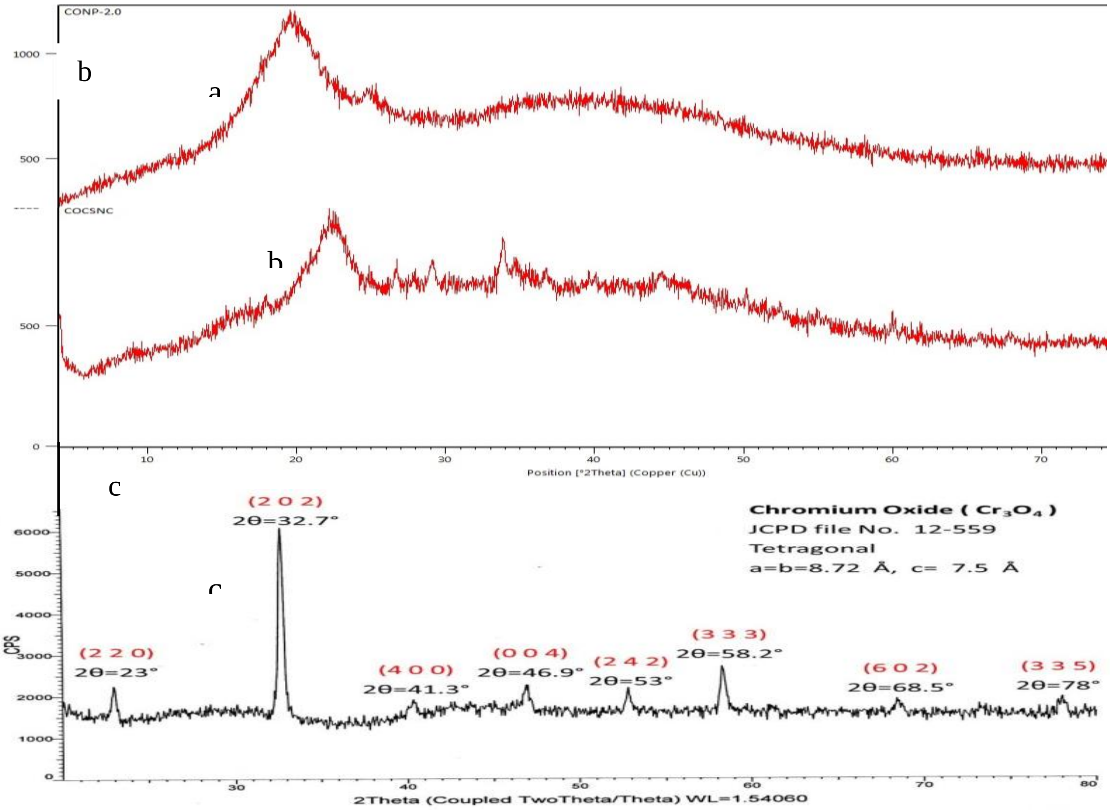

Figure 2: XRD Image of Chromic oxide nanoparticle (a), chromic oxide-*Lophira Alata* carbonised sawdust nanocomposite (b) and chromic oxide standard (c).

The Fourier Transform Infrared Spectrum of COLACSN and a Table showing the wave number and their corresponding functional in FTIR Spectrum of COLACSN are shown in Figure 3 and Table 3 respectively.

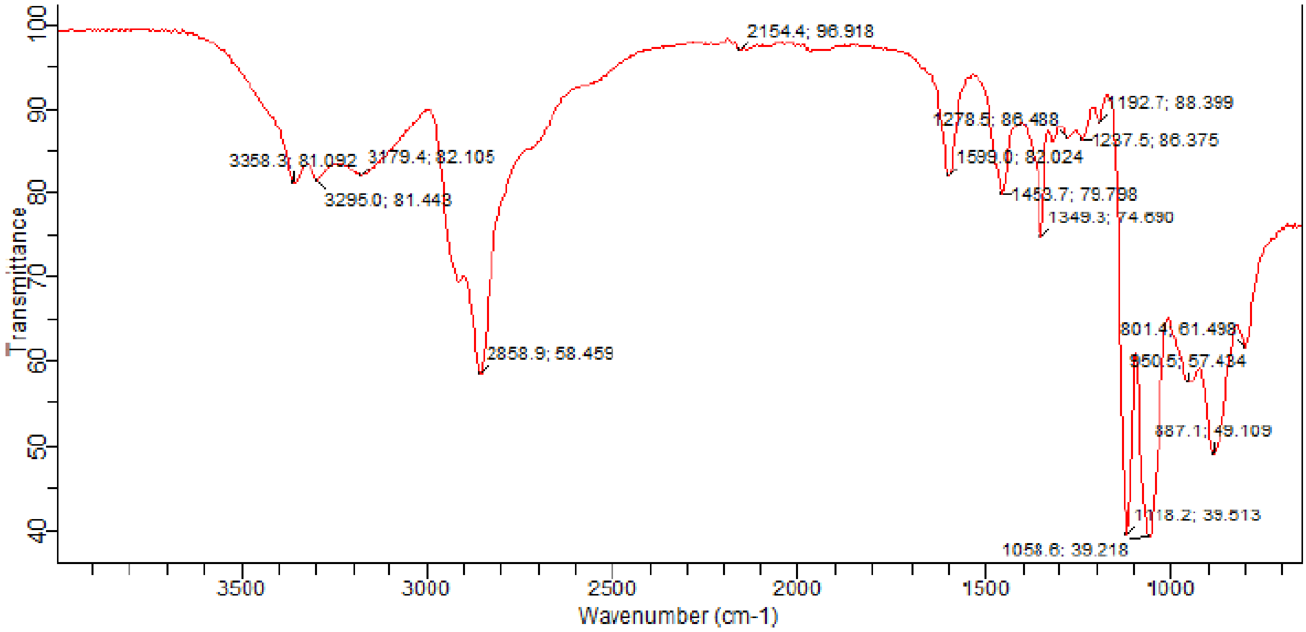

Fig. 3: Fourier Transform Infrared Spectrum of COLACSN

Table 3: Wave Number and their Corresponding Functional in FTIR Spectrum of COLACSN.

Wave number (cm^{-1})	Functional group
3368.30	corresponds to a O-H bond stretch belonging H_2O may be due to presence moisture (or ROH and ArOH)
3295.00	corresponds to a secondary amine group (R_2NH)
3179.40	corresponds to a primary amine group (RNH_2)
2164.40	corresponds to nitrile (RC≡N) or alkyne (RC≡CH) stretch band
1599.00	corresponds to amines RNH_2 or amides ($RCONH_2$)
1192.70 and 1227.60	corresponds to C-O stretch bond belonging acids (RCOOH), esters (RCOOR) and anhydrides ($R(COO)_2$)
801.40	corresponds to M-O (Cr-O) stretching

Adsorption Study and Response Surface Methodology (RSM) Optimisation Study

Isotherm parameter models and response surface methodology (RSM) analysis value obtained for adsorption of Cd^{2+} and Pb^{2+} ions onto COLACSN and 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 COLACSN adsorbent are shown in Table 4 and Figure 4 respectively.

Table 4: Isotherm parameter models and response surface methodology (RSM) Analysis value obtained for adsorption of Cd^{2+} and Pb^{2+} ions onto COLACSN

Models	Parameters	Cd^{2+}	Pb^{2+}
Freundlich isotherm model	K_F	8.08	278.04
$\log q_e = \text{loq} k_f + (1/n_f) \log C_e$	n_F	1.94	0.40
	R^2	0.82	0.97
Dubinin –Radush-kervik (DRK) Isotherm model	q_{mD} (mg g-1)	25.09	329.77
$\ln q_e = \ln q_m - \beta . \varepsilon^2$	β ($mol^2 J^{-2}$)	-4.00×10^{-7}	-1.00×10^{-7}
	E (KJ mol^{-1})	1.12	2.24
	R^2	0.63	0.99
Temkin Isotherm model	b (J mg^{-1})	266.15	18.46
$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e$	B (l g^{-1})	9.37	135.09
	K_T	1.92	6.01
	R^2	0.64	0.98
Response Surface Methodology (RSM) Analysis	Optimal values		
	Initial Concentration (mg/l)	49.29	50.00
	Adsorbent dosage (g)	0.02	0.01
	Contact time (min)	99.93	60.00
	Amount adsorbed (mg/g)	66.20	191.50
	R^2	1.00	0.76

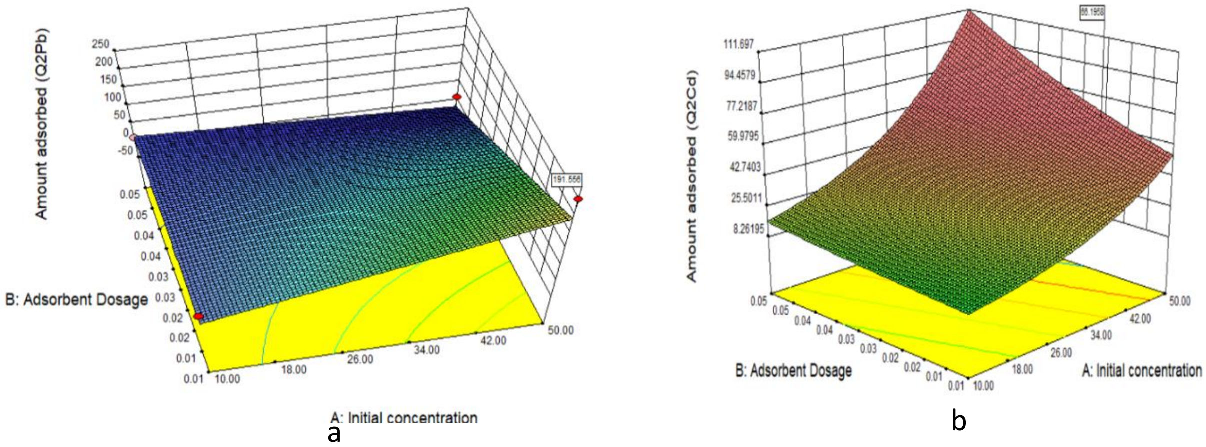

Figure 4: Response surface plots showing the interaction effects of initial concentration and adsorbent dosage on the amounts of (a) lead (b) cadmium adsorbed respectively by the COLACSN adsorbent.

Discussion

Characterization of chromic oxide-lophira alata carbonized sawdust nanocomposite (COLACSN)

The morphology of the synthesized nanocomposite (COLACSN) from the SEM analysis revealed it was smooth and spherical in shape with very small particles in apparently soft agglomerates.

The x-ray diffractogram, revealed peaks resulting from COLACSN and no peak was detected as a result of any other material or phase, thus indicating that the degree of purity of the synthesized material was high. However, the peak shifted slightly from those of chromic oxide nanoparticles (CONP) and standard chromic oxide X-ray diffractogram when compared with COLACSN, this could be as a result of its nanocomposite nature, that is a case of having nano fillers dispersed in a matrix of carbonised saw dust, whereby the nanoparticles are surrounded and bound together as discrete units by the carbonised saw dust.

The broadening of the x-ray diffraction lines reflects that the nanocomposite is amorphous and the sharpness of the peaks shows some level of crystallinity and good crystal growth of the chromic oxide nanoparticles in the nanocomposite. An average particle size (t) of the particles was calculated from the high intensity peak using the Debye-Scherer equation.

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

L= particle size, B (2θ) = full width at half maximum (FWHM, the broadening of the X-ray peak, in radians), (the broadening of the x-ray peak, in radians), K= Scherer constant (0.94), λ is the x-ray wavelength, and θ is the peak position in degree. The particle size was found to be 12.05 nm.

The FTIR spectra expressed in tabular form (Table 3), revealed that the functional groups identified on COLACSN were O-H, -NH, -NH_2, -C≡N, -$CONH_2$ and -C≡CH, these are functional groups that tend to promotes negatively-surface-charged character of COLACSN due to availability of electrons and oxygen carrying surface, hence increasing its chances of removing heavy metals from aqueous solution. The C-O stretch bond on COLACSN belonging to the carboxylic acid groups can result in the formation of negatively-charged carboxylate ions (COO^-) with a strong coordinative attraction in forming chelate complexes towards metal ions (Shen et al., 2009). The metal oxide (M-O; Cr-O) functional group infers the presence of chromic oxide. Chromic ions (Cr^{3+}) is always an octahedral hexaquo ion, $Cr(H_2O)_6^{3+}$ in acid solution and it tends to hydrolyze with increasing OH^-, resulting in the formation of polynuclear complexes containing OH^- bridges which can greatly increase the negative charges on the surface of COLACSN thereby promoting its ability to adsorb heavy metals from heavy metal polluted water (Weckhuysen *et al.*, 1996).

Adsorption Study and Response Surface Methodology (RSM) Optimisation Study

The Freundlich isotherm (Table 4) fitted well to the sorption data of Pb^{2+} and Cd^{2+} ions from the contaminated water onto COLACSN. The adsorption process was physical and favourable for the Cd^{2+} and Pb^{2+} ions adsorption onto COLACSN. The $n_{F,}$ value revealed that Cd^{2+} ions formed a relatively stronger bonds with the adsorbent COLACSN and a better adsorption mechanism, however, the k_F values revealed that Pb^{2+} ions had the stronger adsorption capability on the adsorbent.

Dubinin-Radush-kevick (DRK) isotherm (Table 4) revealed that the Pb^{2+} adsorption was exothermic. The activity coefficient constant (β) for Pb^{2+} ions was lower with a value of -1.00 x $10^{-7}mol^2\ J^{-2}$, this implies a high adsorption capacity for lead ions. The mean free energy or energy of affinity (E) between the Pb^{2+} ions and COLACSN also confirmed a high adsorption capacity (q_m) of the lead ions on the COLACSN adsorbent and the adsorption process was physical since the E value calculated from the DRK isothermal model is lower than 8kJ/mol thus agreeing with the prediction from Freundlich isotherm model.

Temkin isotherm (Table 4) revealed that Pb^{2+} ions had a higher maximum binding energy (K_T) to the adsorbent COLACSN. The heat of adsorption, b-value shows that the Pb^{2+} ions had a strong interaction with the adsorbent, this value agrees with the inference from DRK isotherm models. The value of the calculated b was a positive value of 18.46 J mg^{-1} for Pb^{2+} ions and 266.15 J mg^{-1}, an indication that the adsorption process was exothermic.

The 3-D response surface plots (Figure 4) for the amounts of Pb^{2+} and Cd^{2+} ions adsorbed by the COLACSN adsorbent revealed that as the metal ion initial concentration increased from 10 to 50 mg/l and adsorbent dose decreased from 0.05 to 0.01 g, the amount of Pb^{2+} adsorbed by adsorbent increased from 7.6 to 240 mg/g and the optimal value of Pb^{2+} ions adsorbed was 191.50 mg/l at a time of 60.00 min. As the initial concentration increased from 10 to 50 mg/l and adsorbent dosage decreased from 0.01 to 0.05 g, the amount of Cd^{2+} ions adsorbed by the adsorbent increased from 8.2 to 103.6 mg/g and the optimal value of Cd^{2+} ions adsorbed was 66.20 mg/l at a time of 99.93 min. The response surface plots revealed that 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 COLACSN adsorbent and the Pb^{2+} ions was more adsorbed and removed from the aqueous solution compared to Cd^{2+} ions.

The isotherm parameters determined from the slopes and intercepts of the linear plots of the adsorption isotherms and optimisation study were used in predicting the removal behavior and adsorption efficiency of the Cd^{2+} and Pb^{2+} ions by COLACSN.

Conclusion

Chromic oxide-carbonized sawdust nanocomposite prepared was found to be smooth and spherical in shape with a particles size of 12.05 nm in apparently soft agglomerates. The adsorption process of COLACSN for Cd^{2+} and Pb^{2+} ions is physical and favorable and it had a high adsorption capacity for Pb^{2+} ions, the adsorption process of Pb^{2+} ions was exothermic and possesses a high interaction with the adsorbent. The response surface methodology optimization study revealed that Pb^{2+} ions were more adsorbed and removed from the heavy metal polluted water compared to Cd^{2+} ions with an optimum values of 191.50 and 66.20mg/g respectively. This observation was in agreement with the k_F values obtained from Freundlich isotherm in which the k_F value for Pb^{2+} ions (278.04) was higher than that of Cd^{2+} ions (8.04) indicating that COLACSN had a higher adsorption capacity for Pb^{2+} ions. This implies that the COLACSN was more effective in the removal of Pb^{2+} ions.

References

Abhilash B. D. P. (2012). Synthesis of zinc-based nanomaterials: A biological perspective. IET Nanobiotechnology. 6(4), 144–148.

Baksi S. & Biswas S., (2014). Nanocomposites – An overview. The Scitech Journal. 1(5), 22-30.

Department for Environment Food and Rural Affairs (DEFRA) & Environment Agency (EA) (2002). Contaminants in soil: Collation of toxicological data and intake values for humans. Chromium. R&D Publications TOX 4. Environment Agency. Bristol.

Ebau, W., Rawi, C.S.M., Din, Z. & Al-Shami, S.A. (2012). Toxicity of cadmium and lead on tropical midge larvae, *chironomus kiiensis tokunaga* and *chironomus javanus kieffer* (Diptera: *Chironomidae*). Asian Pacific Journal of Tropical Biomedicine, 2(8), 631-634.

Erdem, E., Karapinar, N. & Erdem Donat, R., (2004). The removal of heavy metal cations by natural zeolites. J. Colloid. Interface. Sci. 280, 309-314.

Gallego, S.M., Pena, L.B., Barcia, R.A., Azpilicueta, C.E., Iannone, M.F., Rosales, E.P.,

Zawoznik, M.S., Groppa, M.D. & Benavides, M.P. (2012). Unravelling cadmium toxicity and tolerance in plants: Insight into Regulatory Mechanisms. Environmental and Experimental Botany, 83(0), 33-46.

Giaccio, L., Cicchella, D., De Vivo, B., Lombardi, G. & De Rosa, M. (2012). Does heavy metals pollution affects semen quality in men? A Case of study in the metropolitan area of Naples (Italy). Journal of Geochemical Exploration, 112(0), 218-225.

Gupta V. K., Tyagi I., Sadegh H., Shahryari-Ghoshekandi R., Makhlouf A. S. H. & Maazinejad B., (2015). Nanoparticles as adsorbent; a positive approach for removal of noxious metal ions: A review. Science, Technology and Development. 34(3), 195-214,

Hasanzadeh M., Ansari R., & Ostovar F., (2016). Synthesis and application of CeO_2/sawdust nanocomposite for removal of As (III) ions from aqueous solutions using a fixed bed column system. Global NEST Journal. 19(1), 7-16.

Hashem E. A., (2014). Nanotechnology in water treatment, case study: Egypt. Journal of Economics and Development Studies. 2 (3), 243-259.

Khlifi, R. & Hamza-Chaffai, A. (2010). Head and neck cancer due to heavy metal exposure via tobacco smoking and professional exposure: A review. Toxicology and Applied Pharmacology, 248(2), 71-88.

Kocaoba, S., Orhan Y. & Akyüz T., (2007). Kinetics and equilibrium studies of heavy metal ions removal by use of natural zeolite. Desalination. 214, 1-10.

Manahan, S. E. (1992). Toxicological chemistry, an Import of CRC Press. Lewis publishers. Boca Raton, 449.

Moafi H. F., Ansari R. & Ostovar F., (2016). Ag_2O/sawdust nanocomposite as an efficient adsorbent for removal of hexavalent chromium ions from aqueous solutions. J. Mater. Environ. Sci. 7 (6), 2051-2068.

Myers, R.H., Montgomery, D.C. & Anderson-Cook, C.M. (2009). Response surface methodology: Process and product optimization using designed experiments. John Wiley & Sons, Inc., Hoboken, New Jersey, USA.

Niu, H., Deng, W., Wu, Q. & Chen, X. (2009). Potential toxic risk of heavy metals from sediment of the Pearl River in South China. Journal of Environmental Sciences, 21(8), 1053-1058.

Pink, D. H. (2006). Investing in tomorrow's liquid gold, Available at http://finance. yahoo.com/columnist/trenddesk/3748.yahoo and http://finance. yahoo.com/columnist/article/trenddesk.3748.

Sadegh, H., Shahryari-Ghoshekandi R. & Kazemi M., (2014). Study in synthesis and characterization of carbon nanotubes decorated by magnetic iron oxide nanoparticles. Int. Nano Lett., 4, 129-135.

Savage N. & Diallo M. S., (2005). Nanomaterials and water purification: Opportunities and challenges. Journal of Nanoparticle Research 7, 331–342.

Shen Y. F., Tang J., Nie Z. H., Wang Y. D., Ren Y. & Zuo L., (2009). Preparation and application of magnetic Fe_3O_4 nanoparticles for wastewater purification. Sep. Purif. Technol. 68, 312–329.

Singh, S., Barick, K. C. and Bahadur, D. (2013). Functional oxide nanomaterials and nanocomposites for the removal of heavy metals and dyes. Nanomater. Nanotchnol. 3(20). www.intechopen.com

Sushma D. & Richa S., (2015). Use of nanoparticles in water treatment: A review. International Research Journal of Environment Sciences. 4 (10), 103-106.

Weckhuysen B. M., Wachs I. E. & Schoonheydt R. A., (1996). Surface chemistry and spectroscopy of chromium in inorganic oxides. Chem. Rev. 96, 3327−3349.

Westerhoff P., Alvarez P., Li Q., Gardea-Torresdey J. & Zimmerman J., (2016). Overcoming implementation barriers for nanotechnology in drinking water treatment.

Environmental Science Nano. 3 (6), 1225–1522

Zhang, R., Zhou, L., Zhang, F., Ding, Y., Gao, J., Chen, J., Yan, H. & Shao, W. (2013). Heavy metal pollution and assessment in the tidal flat sediments of Haizhou Bay,China. Marine Pollution Bulletin, 74(1), 403-412.