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Removal of Pb^{2+} and Cr^{6+} ions from aqueous solution by earthworm cast soil

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The problem of removing pollutants from aqueous wastewater is growing with the increase in water pollution owing to enhanced industrial activities. Three earthworm cast soil types were studied. Modified and unmodified types were prepared and used for removal of lead and Chromium ions. At about 298 K, the earthworm cast soil types, modified and unmodified removed lead and Chromium ions from aqueous solution. Both equilibrium and dynamic sorption experiments showed that physically and chemically modified earthworm cast soils removed lead and chromium ions better than the unmodified form. The equilibrium data fitted well into Langmuir and Freundlich isotherms. The unmodified earthworm cast soil with a dynamic equilibrium constant, K_c of 266 performed better in lead(ii) ion removal than chromium(vi) ion with a dynamic equilibrium constant of 4 at 298 K. $\Delta G°$, the standard free energy change of adsorption of Pb^{2+} and Cr^{6+} onto unmodified earthworm cast soil is negative which implied spontaneity and feasibility of adsorption process. The cheapness and the local availability of this soil type give it an added advantage for effluent treatment in heavy metals removal in the environment.

Key words: Earthworm cast soil, equilibrium and dynamic adsorptions, heavy metals, effluent, langmuir and freundlich isotherms.

INTRODUCTION

Modification of materials for adsorption process has been studied. They have been found to be useful in heavy metals removal of waste water (Adediran et al., 2005; Adediran et al., 1999, Kumar and Dara, 1981; Eromosele and Otitolaye, 1994; Okiemen, 1985). Agricultural wastes such as rice husk, bean husk and corn husk contain cellulose that possess some ion exchange properties due to the presence of a small number of carboxyl groups in their structure. Modification improves the metal ion binding capacity of the materials. For example, cellulose matrix can be modified to become positively or negatively charged by introducing acidic or basic group. Clay, a natural occurring cation exchanger has been modified by chemical and physical means. These have increased the exchange ion capacity of the heavy metal like Cu^{2+} and Pb^{2+}. Because of the recent utilization of clay for building, its cheapness and availability has been a serious problem.

The earthworm cast soils are formed in the tropical regions of Africa where the rainfall is about 60 inches. The earthworm cast soils resemble hardened clay when dried and its composition is mainly silicate in form of sodium silicate and aluminate. They possess sites that can be modified by physical and chemical means. Modification opens up more binding and exchanging sites of the material. This may or may not increase the sorption and exchange capacity of such materials.

Several inorganic materials have been used in the removal of metal ions from solution. Elizabeth et al. (2003) studied the removal of some metal ions using solid adsorbents such as sand, coal and alumina. Modification of the carbon surface has been shown to increase

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Abbreviations: UEI, Unmodified Earthworm Cast Soil from Ileapa; **UEB,** Unmodified Earthworm Cast Soil from Ibadan; **EIAO,** Earthworm Cast Soil from Ilorin activated with orthophosphoric acid; **EBAO,** Earthworm Cast Soil from Ibadan activated with orthophosphoric acid; **PAEI,** Physically Activated Earthworm Cast Soil from Ilorin; **PAEB,** Physically Activated Earthworm Cast Soil from Ibadan.

the sorption of metals from their solution. Mustafa (2002) studied adsorption of Hg^{2+}, Pb^{2+} and Cd^{2+} on activated carbon modified with tetraoxosulphate(vi) acid and observed a significant increase in metal ions adsorption. Adediran et al. (1999) studied the adsorption chromatography of Zn^{2+}, Cu^{2+}, Ni^{2+} and Pb^{2+} using cellulose modified urea and thiourea. It was observed that unmodified substrate sorbed the metal in the range of 69.9 - 86.5% while the modified cellulose performed in the range of 94.2 - 95.4%. Ogbeifun et al. (1989) carried out sorption study on the removal of Pb^{2+} from aqueous solution with thiolated melon seed-husks. Their equilibrium sorption demonstrate that high proportion between 45 and 65% of the initial amount of Pb^{2+} ions were removed from solution by 3.3% thiolated melon seed-husks.

Earthworm cast soil is cheaply available in rain forest regions and is of no value other than enriching the soil. A number of research work have been carried out on removal of heavy metals from solution by clay, and modification of clay surfaces improved its adsorption capacity (Mockovciaková and Orolínová, 2009; Oliveira LCA et al., 2004; Oliveira LCA et al., 2003; Karaham et al., 2006; Marinkovski et al., 2006). The need to search into method of heavy metals removal such as lead and chromium from solution by earthworm cast soil, instead of clay has been our concerned for sometime now for economic reasons. This paper therefore reports the use of earthworm cast soil for removal of Pb^{2+} and Cr^{6+} from aqueous solution.

EXPERIMENTAL

Collection and treatment of samples

The earthworm cast soils were collected from Ileapa and agricultural research farm, University of Ibadan, Ibadan, Nigeria. Earthworm cast soils were air dried at room temperature for 2 weeks and non solid materials like wood, stones and dirts were removed by handpicking. Samples were mechanically ground into fine particles using a porcelain mortar and pestle. The samples were sieved to <2 mm diameter size. This was used as unmodified substrate. The samples were coded UEI* and UEB.

Earthworm cast soils were chemically modified by using 1 M H_3PO_4. H_3PO_4 is a milder inorganic acid, and was used for modification so as to open up the earthworm cast soil for large surface area availability. 100 cm^3 of 1 $moldm^{-3}$ H_3PO_4 was added to 100 g of unmodified earthworm cast soils powder; this was heated until a paste was formed. This mixture was then filtered and washed with de-ionised water to a pH 5.0. The resulting substrate was filtered and the residue was oven-dried at 353 K for 24 h. The samples are named EIAO and EBAO.

Earthworm cast soil was subjected to physical activation at 1073 K for 3 h in a muffle furnace to enhance the adsorption capacity. The samples were labelled PAEI and PAEB.

ADSORPTION EXPERIMENT

Dynamic adsorption of metal ions

Dynamic adsorption of Pb^{2+} and Cr^{6+} ions by unmodified earthworm cast was carried out using a glass column of 30 cm long. Glass wool was introduced into the glass column and 20 g of dry adsorbent were packed by constant tapping after each successive introduction into the column so as to effect even distribution of packing in the column. Glass bead were added on top of the column to prevent floating and separation of adsorbent particles. Distilled water was run slowly through the column for 72 h for equilibration. 100 cm^3 of 40 mg/l of Pb^{2+} and Cr^{6+} metal ions were run through the column and the first 15 cm^3 of the eluent was discarded. The flow rate was determined to be 1 cm^3/min. The amounts of Pb^{2+} and Cr^{6+} ions left in solution were determined by atomic absorption spectrophotometer (SP-9 Pye Unicam).

Equilibrium adsorption

The equilibrium adsorption of metal ions by unmodified and modified earthworm cast was carried out by shaking 4 g of the substrate with 100 cm^3 of Pb(ii) and Cr(vi) ion solutions of different concentrations (10 - 50 mg/l). Solution in Pyrex reagent bottles were shaken using thermostated electrical shaker at 298 K for 3 h. All the experiments were carried out at 298 K except otherwise stated. The mixtures left were filtered and the filtrate analysed for Pb^{2+} and Cr^{6+} ions concentration. Blank solutions without adsorbent were also shaken and the concentrations of metal ions were determined using atomic absorption spectrophotometer. This was used as initial concentration. In the determination of adsorption capacity, adsorption metal uptake at equilibrium, q_e (mg/g) was calculated using the adsorption system mass balance:

$$q_e = \frac{V(C_i - C_f)}{S}$$

Where V = volume of solution (ml), S = amount of dry adsorbent/substrate (g), C_i = initial metal concentration (mg/l) and C_f = final metal concentration (mg/l). C_f is also, C_e, the metal concentration at equilibrium.

Time dependence study

The effect of contact time on the adsorption of Pb^{2+} and Cr^{6+} from aqueous solution using chemically modified earthworm cast was investigated. 4 g of the substrate together with 100 cm^3 of 40 mg/l of Pb^{2+} and Cr^{6+} ion solutions were shaken using thermostated electrical shaker at 298 K between 5 and 120 min. The mixtures were filtered and the filtrate analysed for Pb^{2+} and Cr^{6+} ions concentration using atomic absorption spectrophotometer (SP-9 Pye Unicam) and adsorption metal uptake was calculated.

Adsorption models

Freundlich and Langmuir isotherm models were used for interpreting the metal adsorption equilibrium. They are the earliest, most common and simplest known relationships describing the adsorption phenomenon (Jalali et al., 2002).
The linearized form of Freundlich isotherm is given as;

$$\log q_e = \log K + \left(\frac{1}{n}\right)\log C_e$$

Where q_e is the heavy metal adsorbed on the biosorbent (mg/g); C_e is the final concentration of metal (mg/l) in the solution; K is an empirical constant that provides an indication of the adsorption capacity of biosorbent; and n is an empirical constant that provides

Table 1. Equilibrium adsorption of Pb^{2+} and Cr^{6+} by UEI.

Metal ions	Initial conc. (mg/l)	Final conc. (mg/l)	Amount adsorbed (mg/l)	Amount adsorbed, q_e (mg/l)	% adsorbed	% mean adsorbed
	10.00	9.09	0.91	0.02	9.10	
	20.00	18.08	1.92	0.05	9.60	
Pb^{2+}	30.00	27.09	2.91	0.07	9.70	9.58
	40.00	36.08	3.92	0.10	9.80	
	50.00	45.15	4.85	0.12	9.70	
	10.00	9.69	0.31	0.01	3.10	
	20.00	18.48	1.52	0.04	7.60	
Cr^{6+}	30.00	27.67	2.33	0.06	7.77	6.96
	40.00	36.90	3.10	0.08	7.75	
	50.00	45.72	4.25	0.11	8.56	

Table 2. Equilibrium adsorption of Pb^{2+} and Cr^{6+} by UEB.

Metal ions	Initial conc. (mg/l)	Final conc. (mg/l)	Amount adsorbed (mg/l)	Amount adsorbed, q_e (mg/l)	% adsorbed	% mean adsorbed
	10.00	9.04	0.96	0.02	9.60	
	20.00	18.02	1.98	0.05	9.90	
Pb^{2+}	30.00	27.02	2.98	0.07	9.93	9.87
	40.00	36.01	3.99	0.10	9.98	
	50.00	45.02	4.98	0.12	9.96	
	10.00	9.10	0.89	0.02	9.00	
	20.00	18.41	1.59	0.04	7.95	
Cr^{6+}	30.00	27.75	2.25	0.06	7.50	8.11
	40.00	36.85	3.15	0.08	7.88	
	50.00	45.88	4.12	0.10	8.24	

Table 3. Equilibrium adsorption of Pb^{2+} and Cr^{6+} by EIAO.

Metal ions	Initial conc. (mg/l)	Final conc. (mg/l)	Amount adsorbed (mg/l)	Amount adsorbed, q_e (mg/l)	% adsorbed	% mean adsorbed
	10.00	0.71	9.29	0.23	92.88	
	20.00	0.42	19.58	0.49	97.92	
Pb^{2+}	30.00	0.68	29.32	0.73	97.72	97.12
	40.00	0.87	39.13	0.98	97.84	
	50.00	0.37	49.63	1.24	99.26	
	10.00	5.99	4.01	0.10	40.10	
	20.00	7.48	12.52	0.31	62.60	
Cr^{6+}	30.00	5.25	24.75	0.62	82.50	70.58
	40.00	6.76	33.24	0.83	83.10	
	50.00	7.69	42.31	1.06	84.62	

an indication of the intensity of adsorption. The Freundlich isotherm equation is an empirical equation based on the sorption on a heterogeneous surface which is an indication that the binding sites are not equivalent or independent (Jalali et al., 2002). The model that assumes a monolayer adsorption, Langmuir isotherm model in a linearized form is given as;

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{b}{q_{max}\ C_e}$$

Where q_{max} is the heavy metal adsorbed on the biosorbent (mg/g) under given conditions; b is a coefficient related to the affinity

Table 4. Equilibrium adsorption of Pb^{2+} and Cr^{6+} by EBAO.

Metal ions	Initial conc. (mg/l)	Final conc. (mg/l)	Amount adsorbed (mg/l)	Amount adsorbed, q_e (mg/l)	(%) adsorbed	(%) mean adsorbed
	10.00	0.00	10.00	0.25	100.00	
	20.00	0.00	20.00	0.50	100.00	
Pb^{2+}	30.00	0.00	30.00	0.75	100.00	97.92
	40.00	4.03	35.97	0.90	89.93	
	50.00	0.17	49.83	1.25.	99.66	
	10.00	8.84	1.16	0.03	11.60	
	20.00	5.56	14.44	0.36	72.20	66.17
Cr^{6+}	30.00	8.01	21.99	0.55	73.30	
	40.00	9.53	30.47	0.76	76.18	
	50.00	1.21	48.79	1.22	97.58	

Table 5. Equilibrium adsorption of Pb^{2+} and Cr^{6+} by PAEI.

Metal ions	Initial conc. (mg/l)	Final conc. (mg/l)	Amount adsorbed (mg/l)	Amount adsorbed, q_e (mg/l)	% adsorbed	% mean adsorbed
	10.00	0.09	9.91	0.25	99.14	
	20.00	0.07	19.93	0.50	99.66	
Pb^{2+}	30.00	0.13	29.87	0.75	99.58	99.51
	40.00	0.08	39.92	1.00	99.81	
	50.00	0.32	49.68	1.24	99.36	
	10.00	7.50	2.50	0.06	25.00	
	20.00	5.13	14.87	0.37	74.35	
Cr^{6+}	30.00	7.51	22.49	0.56	74.97	65.82
	40.00	9.56	30.44	0.76	76.10	
	50.00	10.66	39.34	0.98	78.68	

Table 6. Equilibrium adsorption of Pb^{2+} and Cr^{6+} by PAEB.

Metal ions	Initial conc. (mg/l)	Final conc. (mg/l)	Amount adsorbed (mg/l)	Amount adsorbed, q_e (mg/l)	% adsorbed	% mean adsorbed
	10.00	0.20	9.80	0.24	97.97	
	20.00	0.20	19.80	0.50	99.01	
Pb^{2+}	30.00	0.38	29.62	0.74	98.75	99.05
	40.00	0.15	39.85	1.00	99.62	
	50.00	0.03	49.97	1.25	99.93	
	10.00	9.58	0.42	0.01	4.20	
	20.00	5.67	14.33	0.36	71.65	
Cr^{6+}	30.00	7.85	22.15	0.55	73.83	60.67
	40.00	9.71	30.29	0.76	75.73	
	50.00	11.02	38.98	0.97	77.96	

between the adsorbent and adsorbate.

RESULTS AND DISCUSSION

The results of the experiment are shown in Table 1 - 8 and Figure 1 - 5. Table 1 - 6 show the results of equilibrium adsorption of Pb^{2+} and Cr^{6+}, the percentage mean of adsorption of Pb^{2+} onto UEI, UEB, EIAO, EBAO, PAEI and PAEB are 9.58, 9.87, 97.12, 97.92, 99.51 and 99.05 respectively. The percentage mean of adsorption of Cr^{6+} onto UEI, UEB, EIAO, EBAO, PAEI and PAEB are 6.96, 8.11, 70.58, 66.17, 65.82 and 60.67 respectively.

With initial concentration of 40 mg/l, it can be seen from dynamic adsorption data (Table 7) that earthworm cast soil has greater capacity for Pb^{2+} removal than Cr^{6+}.

Table 7. Dynamic adsorption of Pb^{2+} and Cr^{6+} by UEB.

Metal ions	Initial conc. (mg/l)	Final conc. (mg/l)	Amount adsorbed (mg/l)	Amount adsorbed, q_e (mg/g)	% adsorbed
Pb^{2+}	40.00	36.01	3.99	0.10	9.98
Cr^{6+}	40.00	36.32	3.68	0.09	9.20

Table 8. Langmuir and Freundlich adsorption parameters of Cr^{6+} by PAEI and PAEB.

	Langmuir parameters			Freundlich parameters		
	q_{max}	b	R^2	K	n	R^2
PAEI	0.062	-0.03	0.992	0.04	0.8	0.981
PAEB	0.049	-0.03	0.999	0.16	0.7	0.994

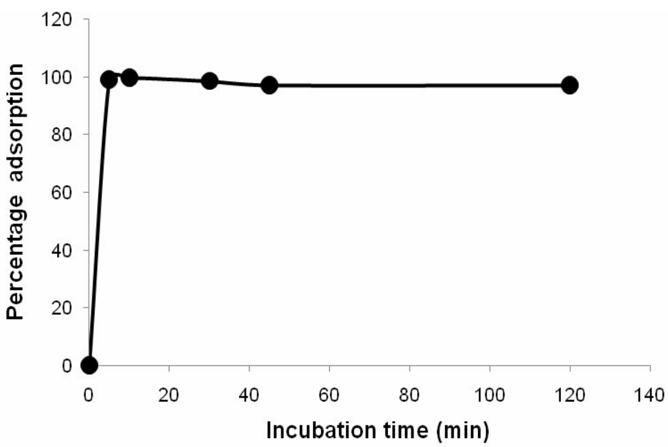

Figure 1. Dependence of contact time of adsorption of Pb(ii) ion by EBAO.

This could be due to the nature of the anions. Hydrated sphere of Pb^{2+} is smaller than that of Cr^{6+}, and the adsorption capacity depends on the size of the hydrated ion.

ΔG^0, the standard free energy of adsorption ($KJmol^{-1}$) can be written as;

$$\Delta G^0 = -RTlnK_c$$

Where R is the universal gas constant (8.314 $KJmol^{-1}K^{-1}$), T is the temperature in Kelvin and K_c is the equilibrium constant. The equilibrium constant can be expressed as;

$$K_c = \frac{C_{ad}}{C_e}$$

Where C_{ad} is the mg of adsorbate adsorbed per litre and C_e the equilibrium concentration of solution in mg per litre (Sarin et al., 2006). At 298 K, the equilibrium constant K_c of adsorption of Pb^{2+} on UEB is 266 while that of Cr^{6+} is 4. ΔG, the free energy change of adsorption process is -14 $KJmol^{-1}K^{-1}$ and -3 $KJmol^{-1}K^{-1}$ for dynamic adsorption of Pb^{2+} and Cr^{6+} onto UEB.

Time dependence study

The time dependence study revealed the fast kinetics process of adsorption of Pb^{2+} by chemically modified earthworm cast. As shown in Figure 1, a very short time of agitation is needed for removal of Pb^{2+} from solution. Maximum adsorption was observed at 5 min of agitation, this is an indication that Pb^{2+} binds very fast to earthworm cast soil. The equilibrium was reached after 20 min. A fast kinetics process of adsorption is an indication that the adsorption of Pb^{2+} onto earthworm cast soils is a chemical controlled reaction rather than a diffusion-controlled process (Ho et al., 2000).

Analysis of adsorption isotherms

Figures 2 and 3 show the conformity of our data with Langmuir and Freundlich isotherms. The data fitted well to both Langmuir and Freundlich. Both the Freundlich and Langmuir isotherms can be used to modelize biosorption data from dilute aqueous solutions (Loukidou et al., 2005). The conformity of our data to both adsorption isotherms is an indication that a monolayer adsorption and heterogeneous surface condition may coexist under the investigated experimental conditions. The Langmuir and Freundlich adsorption parameters as well as the correlation coefficient (R^2) for Cr^{6+} onto UEIP and UEBP are shown in Table 8. The values of the parameters show that earthworm cast soils are good adsorbent for the uptake of Pb^{2+} and Cr^{6+} from solution. This is an indication that earthworm cast soils would serve as good adsorbent for removal of heavy metals in polluted water.

The ability of heavy metals removal in solution by earthworm cast varied depending on the nature of the

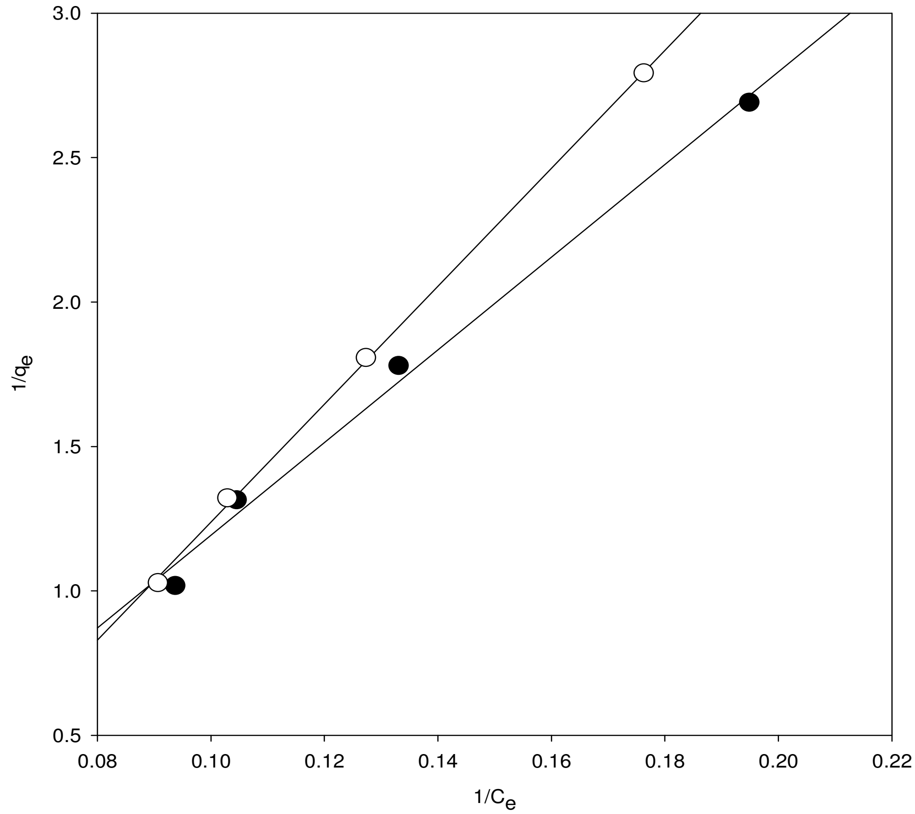

Figure 2. Langmuir isotherm for Cr^{6+} by (open circles) PAEI and (closed circles) PAEB.

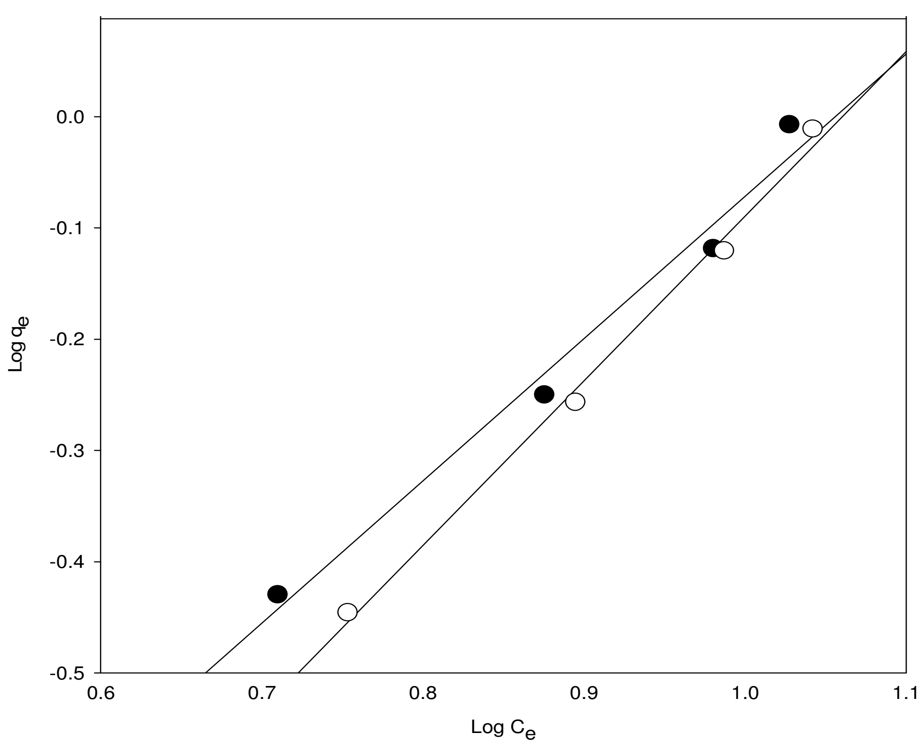

Figure 3. Freundlich isotherm for Cr^{6+} by (open circles) PAEI and (closed circles) PAEB.

cast earthworm cast soil. Earthworm cast soil is an effective adsorbent for Pb(ii) and Cr(vi) removal from aqueous solution owing to their high binding ability, availability and low cost.

Conclusion

Earthworm cast soils are good adsorbent of heavy metals in solution. Modification of earthworm cast soil either by physical or chemical methods increased its capacity for removal of heavy metals in solutions. Modification provides larger surface area for adsorption. The adsorptive capacity of earthworm cast soils for Pb^{2+} removal is greater than Cr^{6+} removal from aqueous solution. The dynamic equilibrium constant and standard free energy change are greater for Pb^{2+} adsorption process than Cr^{6+} adsorption process. From our findings, unmodified and modified earthworm cast soils are good adsorbent for heavy metals removal from aqueous solution. The adsorption process is spontaneous and feasible.

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