

Removal of Cr and Pb from Spent Engine Oil using Waste Plastic Materials as Adsorbents

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Abstract— Used engine oil from automobile was treated with five different types of plastic waste materials (plastic water bottles, vegetable oil gallons and engine oil gallons) to investigate the adsorptive removal potential of heavy metals associated with wear of the automobile engines. Atomic Absorption spectral analysis of the used oil showed the presence of chromium (Cr) 41.6 mgL⁻¹ and Lead (Pb) 37.7 mgL⁻¹. After treatment with wasteplastics; Final-product plastic (FPP) bottles, Goshen-water plastic (GWP) bottles and Waterfirst plastic (WFP) bottles, equilibrium concentration of Cr reduced to 12.5, 13.4 and 13.1 mgL⁻¹ and Pb reduced to 14.4, 15.6 and 14.9 mgL⁻¹ respectively. Engine oil wasteplastic gallon (EOG) also reduced equilibrium concentrations of Cr to 10.9 mgL⁻¹ and Pb to 12.7 mgL⁻¹ while vegetable oil wasteplastic gallon (VOG) decreased concentrations of Cr to 10.7 mgL⁻¹ and Pb to 14.1 mgL⁻¹. A thermodynamic study showed that the Gibbs free energy of adsorption for the plastic bottles and gallons were found to be in the range -0.746 and -2.754 KJmol⁻¹, which indicates that physical adsorption prevailed throughout the process. The adsorption of heavy metals on the plastic materials used during the study followed the modified Arrhenius-type equation.

Index Terms— Spent engine oil, waste plastics, heavy metals, adsorption, free energy, activation energy.

1 INTRODUCTION

Spent engine oil obtained from vehicle engines and machineries contains wear metals and other impurities which accumulate during lubrication of the moving parts in the engine. Indiscriminate disposal of spent engine oil in the environment poses threat to living organisms because of the presence of heavy metals in the waste oils. These heavy metals have become a major environmental concern because they are extremely toxic and have the tendency to bioaccumulate in food chain even at low concentrations (Para *et al*, 2004). About 80% spent engine oil discarded into the environment posed widespread contamination and possible environmental pollution with heavy metals such as Cu, Ni, Pb, and Zn. The concentrations of these heavy metals in soils and water receiving spent engine oil investigated using atomic absorption spectro photometer showed that their concentrations exceeded the permissible limits (Warmate *et al*, 2011). This problem could be remedied by curbside collection and re-refining of spent engine oil and putting in place an appropriate legislation.

Lead is a toxic metal even at low concentrations. It is a poisonous heavy metal which forms complexes with Oxogroups in enzymes to affect virtually all steps in the process of haemoglobin synthesis and porphyrin metabolism, hence associated with health conditions like seizures and mental retardation (Bansal *et al*, 2009) despite its useful applications. The removal and recovery of these metals have become very important because of their detrimental effects on the environment (Odoemelam *et al*, 2011).

Conventional methods for removing these heavy metals from solution include chemical precipitation, ion exchange, solvent extraction, membrane separation processes, reverse osmosis, flocculation and electrodialysis. Most of these methods suffer from drawbacks such as high capital and operational costs or the disposal of the residual metal sludge (Odoemelam *et al*, 2011). Several methods have been studied

for the development of cost-effective adsorbents successfully (Demirbas *et al*, 2004; Abia and Asuquo, 2006; Kumar and Kirthika, 2009; Odoemelam *et al*, 2011; Radnia *et al*, 2011; Wambu *et al*, 2011). The technical feasibility of low cost adsorbents for the removal of heavy metals has been reviewed and concluded that the use of low cost adsorbents may contribute to the sustainability of the environment with potential commercial benefits (Babel *et al*, 2003). In recent years, a number of adsorptive materials like waste ashes and PET (Zhan and Itoh, 2003), use of zeolites (Ali *et al*, 2010), egg shale powder, date palm kernel powder as adsorbent and acid activated date palm kernel (Nabi *et al*, 2010) have been used in the treatment of wastewater and oil as the case may be by adsorption. This particular work presents the use of different plastic waste materials as adsorbents for the removal of Chromium and Lead from spent engine oil.

2 MATERIALS AND METHODS

2.1 Materials

Five waste-plastic samples namely; Water first plastic (WFP*) bottles, Final product plastic (FPP**) bottles, Goshen-water plastic (GWP***) bottles, vegetable oil gallon (VOG****) and engine oil gallon (EOG*****) were collected from waste bins while the spent engine oil was obtained from an automobile workshop in Makurdi town, Nigeria. The labels on the wasteplastic materials were removed and the plastics were dismembered, thoroughly washed with liquid soap and water, rinsed with enough distilled water and air-dried. They were shredded into smaller sizes, ground into chips, sieved with a 2mm sieve to obtain a powder with good and uniform particle distribution and stored in polyethylene bags for subsequent analysis and application.

2.2 Physicochemical Characterization of the Adsorbents

The adsorbents pH, bulk density and porosity were determined as described by Itodo *et al.*, (2010). The adsorbent pH was determined by adding 1.0 g of the sample into 100 mL of distilled water and stirred for 1 h at regular interval. The mixture was then filtered and the pH of the filtrate was determined using a Hanna HI 9024 pH meter. The bulk density, expressed in g/mL was determined using the tapping method (Itodo *et al.*, 2010). The adsorbent porosity was determined using the saturation method by adding 3.0 g of sample into 100 mL distilled water and was allowed to stand for 48 h. The mixture was then filtered and the filtrate volume measured. The iodine adsorption ratio (IAR) was determined as described by Malik *et al.*, (2006). 1.0 g portions of the adsorbent was slurred in excess (25 mL, 0.05 M) iodine solution in a beaker. The mixture was then stirred vigorously for 10 min and filtered through a funnel impregnated with glass wool. 20 mL of the filtrate was back-titrated with 0.1 M sodium thio-sulphate solution. The iodine ratio was calculated as mole of iodine adsorbed per gram of adsorbent. The adsorbent attrition factor (AF) was determined using the procedure described by Toles *et al* (2000) which is based on the measurement of the percentage of the adsorbent retained in a 2 mm sieve after 1.0 g was stirred with magnetic stirrer in 100 mL acetate buffer of pH 4.0 for 4 h, which was calculated based on the weight loss of the adsorbent after the stirring and it is reported as percentage attrition. Cation exchange capacity (CEC) was obtained according to the method described by Kandah *et al* (2008). 2.0 g portion of adsorbent was left for 4 h in an excess of 33 mL of 1.0 M sodium acetate solution. It was then filtered and washed with 33 mL isopropyl alcohol. The procedure was repeated thrice but without washing with the alcohol at the last round. Thereafter, the residue adsorbent was washed with 33 mL of 1.0 M ammonium acetate solution and the concentration of the displaced Na in the filtrate determined by a buck scientific Atomic Absorption Spectrophotometer (AAS) model VGP 210.

*, **, *** = water first (WF), final product (FP), Goshen water (GW):
 Company name of water supplies
 ****, ***** = vegetable oil gallon (VOG) and engine oil gallon (EOG):
 Type of oil plastic

2.3 adsorption studies

The initial concentrations of Cr and Pb in the spent engine oil were determined by measuring 100 mL of untreated spent engine oil into five different beakers, the first beaker was kept at room temperature of 305 K while the rest (one at a time) had their temperature raised to 315, 325, 335, and 345 K respectively in a warm water bath. A one in ten dilution of each of the oil was done with kerosene in a labeled specimen bottle in preparation for AAS analysis. The same procedure was carried out for 100 mL spent engine oil after being treated with 5.0 g adsorbent by stirring for 30 min while the temperature were being raised and filtered. The equilibrium concentrations of the metals were then determined by a buck scientific Atomic

Absorption Spectrophotometer model VGP 210 (Jabar *et al*, 2011).

2.4 Adsorption thermodynamics

The thermodynamic properties of the adsorbents were determined using the Van't Hoff's equation (Venkatraman *et al*, 2009) as expressed in equation (2).

$$\ln K_{ad} = -\Delta H^{\circ}/RT + \Delta S^{\circ}/R \quad (2)$$

$$K_{ad} = C_{ad}/C_e \quad (3)$$

$$\Delta G^{\circ} = -RT \ln K_{ad} \quad (4)$$

Where ΔH° is change in enthalpy (kJmol^{-1}), ΔS° is change in entropy ($\text{Jmol}^{-1}\text{K}^{-1}$), ΔG° is change in Gibb's free energy (kJmol^{-1}), R is the gas constant ($8.314 \text{ Jmol}^{-1}\text{K}^{-1}$), T is temperature in kelvin, K_{ad} is the adsorption thermodynamic equilibrium constant, C_{ad} is the amount of metal adsorbed onto the adsorbent per liter of the analyte solution at equilibrium in mgL^{-1} and C_e is the equilibrium concentration (mgL^{-1}) of metal left unadsorbed in the analyte solution.

3 RESULTS AND DISCUSSION

3.1 Physicochemical Characteristics of Adsorbents

Results for Physicochemical Characterization of the adsorbents (FPP, WFP, GWP, EOG and VOG) are shown in Table 1.

The pH of adsorbents influences the species and extent of adsorption. VOG has the highest pH value of 7.78 followed by EOG with pH of 7.53, GWP with pH 7.28, WFP with pH 6.80 and FPP with pH 6.71.

The bulk density of adsorbents indicates the mass of the adsorbent that can be contained in a filter of a given capacity during the design of an adsorption column and the quantity of the treated liquid retained. The bulk density of the adsorbents increases in the order $\text{EOG} < \text{VOG} < \text{WFP} < \text{FPP} < \text{GWP}$ with values 0.1702 g/mL, 0.1951 g/mL, 0.3200 g/mL, 0.3478 g/mL and 0.4211 g/mL respectively as shown in Table 1. Porosity indicates the efficiency of an adsorbent during adsorption process. The porosity of the adsorbents decreases in the order $\text{EOG} > \text{VOG} > \text{FPP} > \text{WFP} > \text{GWP}$ with values of 12 mL, 10 mL, 9.5 mL, 9 mL and 8 mL respectively.

Iodine adsorption ratio also measures the adsorptive performance of an adsorbent. These plastic adsorbents show increase in iodine adsorption ratio in the order $\text{WFP} < \text{GWP} < \text{FPP} < \text{VOG} < \text{EOG}$ with values of 0.0205 mol/g, 0.0455 mol/g, 0.0550 mol/g, 0.0890 mol/g and 0.0915 mol/g respectively. Attrition factor is the measure of the resistance of an adsorbent to mechanical abrasion and indicates the mechanical strength of that adsorbent during transportation, handling and regeneration. The attrition factor of the adsorbents increases in the order $\text{EOG} < \text{VOG} < \text{FPP} < \text{WFP} < \text{GWP}$ with values 1%, 3%, 8%, 11% and 17% respectively. Cation exchange capacity measures the quantity of adsorptive sites adsorbent possesses. The CEC of the adsorbents under investigation increases in the order

GWP < WFP < FPP < VOG < EOG with values 2.50 mg/L, 3.50 mg/L, 3.75 mg/L, 6.25 mg/L and 7.50 mg/L respectively.

3.2 Adsorption Studies

The equilibrium adsorption of the metals by the adsorbents is shown in Table 2. From the generated data, VOG has a slightly alkaline pH of 7.78 at which Cr metal was preferentially adsorbed at all the experimental temperatures than Pb although the amount adsorbed decreases as the temperature increases from 305 to 345 K. The trend of adsorption was thus; Cr (30.9 mgL⁻¹) > Pb (23.6 mgL⁻¹). At the pH of 7.53, the adsorption for EOG was thus; Cr (30.7 mgL⁻¹) > Pb (25.0 mgL⁻¹). For GWP with the pH of 7.28, the trend was thus; Cr (28.2 mgL⁻¹) > Pb (22.1 mgL⁻¹). At the pH of 6.80 and 305 K temperature for WFP, the trend was; Cr (28.5 mgL⁻¹) > Pb (22.8 mgL⁻¹). FPP with the pH of 6.71 and at 305 K adsorbed Cr (29.1 mgL⁻¹) > Pb (23.3 mgL⁻¹). It was observed that the adsorption was most favored at neutral pH.

The bulk density of the adsorbents increases in the order EOG < VOG < WFP < FPP < GWP while the amount of metal species adsorbed decreased in somewhat same order. The general observation could be explained based on the difference in bulk densities of the various adsorbents, the higher the density of the adsorbents, the lower the pore size volume hence the adsorption of metal ions will be reduced. The adsorption capacity of the adsorbents decreases as their porosity values decreases in the order EOG < VOG < FPP < WFP < GWP. The porosity as well as the cation exchange capacity also explains the observed behavior of the adsorbents. The porosity of adsorbents plays an important role in the adsorption of metal ions. Adsorbents with high porosity will also have increased rate of adsorption. The porosity and CEC of the adsorbents was observed to decrease in the order; EOG > VOG > WFP > FPP > GWP, hence another possible reason for the observed trend of adsorption for the adsorbents.

The adsorptive performance of the adsorbents decreases as their IAR decreases in the order EOG > VOG > FPP > GWP > WFP. However, GWP with a little higher IAR value of 0.0455 mol/g adsorbed lesser amount of metals than WFP with lower IAR value of 0.0205 mol/g.

The adsorbents have attrition factor (AF) values increasing in the order EOG < VOG < FPP < WFP < GWP but showed decrease in adsorption performance in the same order implying an increase in the AF leads to low adsorption capacity or vice versa. The adsorption capacity of the adsorbents decreases in the order EOG > VOG > FPP > WFP > GWP as the CEC decreases in the same order.

3.3 Thermodynamic Parameters

The Van't Hoff plots of $\ln K_{ad}$ against $1/T$ for Cr are shown in figures 1 and 2 while those for Pb are as given in figures 3 and 4. All the plots are straight lines with slopes equal to $-\Delta H^\circ/R$ and intercepts equal to $\Delta S^\circ/R$. K_{ad} and ΔG° were calculated from equations (3) and (4).

Table 3 highlights the regression equations for the various plots in figures 1, 2, 3 and 4. The thermodynamic parameter

values are as presented in Table 4. The values of ΔH° for the adsorption of the metals onto all the adsorbents were negative and in the range of -1.593 to -2.475 kJmol⁻¹. These negative values indicate the exothermic nature of the adsorption process. The positive values of ΔS° for the adsorption of Cr onto VOG, WFP, GWP and EOG show that the freedom of the metals is not too restricted during the process. The value of ΔS° for the metals adsorbed onto all other adsorbents is negative indicative of improved orderliness and decreased randomness at the adsorbent-analyte interface. The values of ΔG° for the metals and the adsorbents were negative at all the temperatures considered. The negative values of ΔG° show the spontaneous nature of adsorption of the metals onto the adsorbents. It is of note that ΔG° up to -20.0 kJmol⁻¹ is consistent with the electrostatic interaction between the adsorption sites and the metal showing physical adsorption while ΔG° values more negative than -40.0 kJmol⁻¹ involve charge sharing or transfer from the adsorbent surface to the metal ion to form a coordinate bond, indicating chemical adsorption (Michael et al, 2005). The ΔG° values obtained in this study for these metals, are less than -2.754 kJmol⁻¹, signifying that the adsorption process occurred through physical mechanism.

In order to further support asserted adsorption mechanism, activation energy E_a and sticking probability S^* were estimated from the experimental data. They were calculated using a modified Arrhenius equation (equation 5) related to surface coverage, θ , of adsorbed species (Chaudhari and Lee, 2008).

$$S^* = (1-\theta) \exp(-E_a/RT) \quad (5)$$

$$\theta = (1 - C_e/C_o) \quad (6)$$

Equation (5) is rearranged as in equation (7).

$$\ln(1 - \theta) = \ln S^* + E_a/RT \quad (7)$$

The S^* must lie in the range $0 < S^* < 1$ and is temperature dependent. It indicates the measure of the potential of an indefinite attachment of an adsorbate on an adsorbent. The plot of $\ln(1 - \theta)$ against $1/T$ gave linear plots with intercepts at $\ln S^*$ and slopes of E_a/R as shown in Table 4.

The magnitude of E_a for physisorption is usually not more than 4.2 kJmol⁻¹ but between 8.4 and 83.7 kJmol⁻¹ for chemisorption (Kumar, 2011). The negative values of E_a are indicative of exothermic adsorption process. The low values of E_a which ranged between -0.924 and -1.662 kJmol⁻¹ and the high sticking probability as $0 < S^* < 1$ further confirmed that physical adsorption actually prevailed during the adsorption process.

4 FIGURES AND TABLES

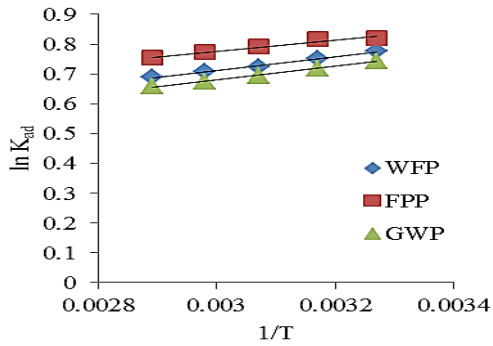


Figure 1 Adsorption of Cr onto WFP, FPP and GWP at 305 - 345K

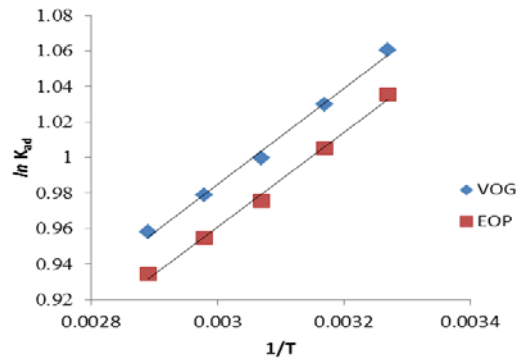


Figure 2 Adsorption of Cr onto VOG and EOG at 305 - 345K

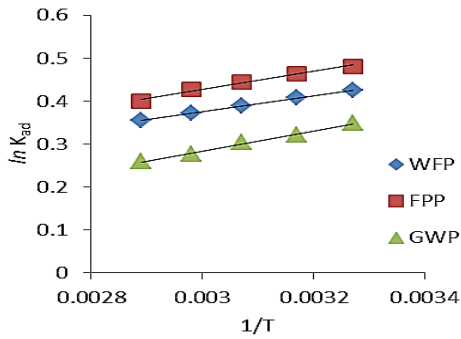


Figure 3 Adsorption of Pb onto WFP, FPP and GWP at 305-345 K

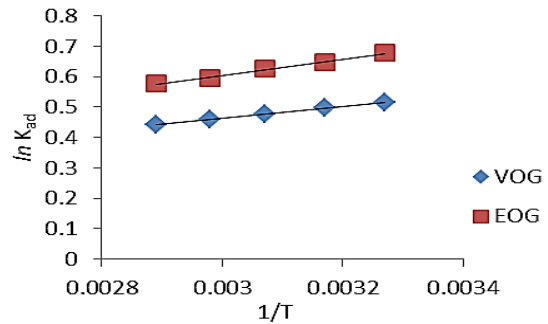


Figure 4 Adsorption of Pb onto VOG and EOG at 305 - 345 K

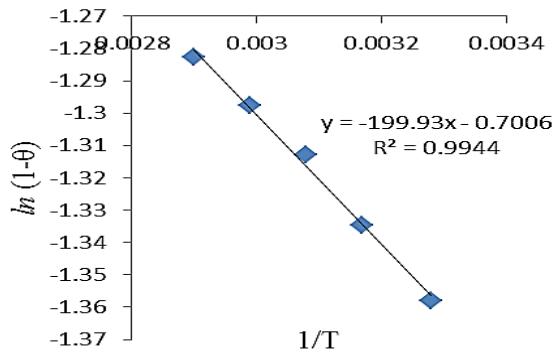


Figure 5 Sticking probability and adsorption activation energy for Cr

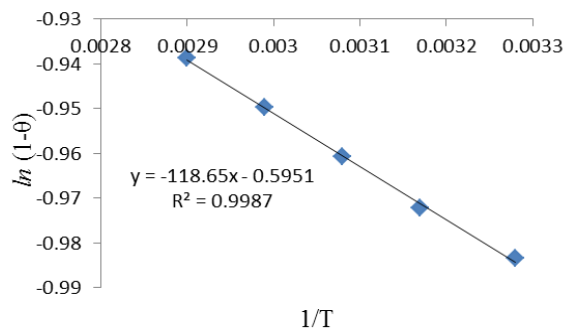


Figure 6 Sticking probability and adsorption activation energy for Pb

Table 1: Physicochemical Properties of the Plastic Adsorbents

Property	FPP	WFP	GWP	EOG	VOG
pH	6.71	6.80	7.28	7.53	7.78
Bulk density (g/mL)	0.3478	0.3200	0.4211	0.1702	0.1951
Porosity (mL)	9.5	9.0	8.0	12.0	10.0
IAR (mol/g)	0.0550	0.0205	0.0455	0.0915	0.0890
AF (%)	8.0	11.0	17.0	1.0	3.0
CEC (mg/L)	3.75	3.50	2.50	7.50	6.25

Table 2 Equilibrium adsorption of Cr and Pb onto plastic adsorbents

Adsorbent	T (K)	Cr		Pb	
		C _o (mg/L)	C _e (mg/L)	C _o (mg/L)	C _e (mg/L)
VOG	305	41.6	10.7	37.7	14.1
	315	41.8	11.0	37.8	14.3
	325	42.0	11.3	37.9	14.5
	335	42.1	11.5	38.0	14.7
	345	42.2	11.7	38.1	14.9
WFP	305	41.6	13.1	37.7	14.9
	315	41.8	13.4	37.8	15.1
	325	42.0	12.7	37.9	15.3
	335	42.1	13.9	38.0	15.5
	345	42.2	14.1	38.1	15.7
FPP	305	41.6	12.5	37.7	14.4
	315	41.8	12.8	37.8	14.6
	325	42.0	13.1	37.9	14.8
	335	42.1	13.3	38.0	15.0
	345	42.2	13.5	38.1	15.3
GWP	305	41.6	13.4	37.7	15.6
	315	41.8	13.7	37.8	15.9
	325	42.0	14.0	37.9	16.1
	335	42.1	14.2	38.0	16.4
	345	42.2	14.4	38.1	16.6
EOG	305	41.6	10.9	37.7	12.7
	315	41.8	11.2	37.8	13.0
	325	42.0	11.5	37.9	13.2
	335	42.1	11.7	38.0	13.5
	345	42.2	11.9	38.1	13.7

Table 3 Regression equations for adsorption of Cr and Pb onto plastic adsorbents

Adsorbent	Cr	Pb
WFP	$y = 269.83x + 0.1753$	$y = 184.09x + 0.176$
FPP	$y = 188.3x + 0.2122$	$y = 210.22x + 0.2035$
GWP	$y = 227.38x + 0.0017$	$y = 236.49x + 0.4262$
VOG	$y = 269.83x + 0.1753$	$y = 190.0x + 0.106$
EOG	$y = 265.92x + 0.1631$	$y = 263.35x + 0.1855$

Table 4: Thermodynamic Parameters for the Adsorption of Cr and Pb onto Adsorbents

Metal	Adsorbent	$-\Delta H^\circ$ (kJmol ⁻¹)	ΔS° (JK ⁻¹ mol ⁻¹)	$-E_a$ (kJmol ⁻¹)	S^*	$-\Delta G^\circ$ (kJmol ⁻¹)				
						305K	315K	325K	335K	345K
Cr	VOG	2.214	1.530	1.662	0.497	2.688	2.697	2.702	2.729	2.754
	WFP	1.950	0.067	1.309	0.529	1.978	1.964	1.972	1.977	1.979
	FPP	2.214	-0.208	1.385	0.520	2.155	2.148	2.135	2.145	2.151
	GWP	1.769	0.341	1.273	0.533	1.876	1.886	1.864	1.894	1.893
	EOG	2.475	0.524	1.628	0.499	2.637	2.645	2.648	2.646	2.668
Pb	VOG	1.765	-1.455	0.986	0.552	1.319	1.309	1.297	1.281	1.262
	WFP	1.593	-1.646	0.924	0.569	1.090	1.074	1.054	1.031	1.033
	FPP	1.674	-1.463	1.073	0.582	1.217	1.205	1.216	1.198	1.147
	GWP	1.950	-3.500	1.142	0.650	0.888	0.838	0.811	0.780	0.746
	EOG	2.211	-1.596	1.142	0.596	1.724	1.702	1.702	1.671	1.664

5 CONCLUSION

Waste plastic bottles and gallons can be used effectively as adsorbents for removing heavy metal pollutants like Cr and Pb from used engine oil and other related sources. EOG adsorbent is the most effective for removing such metals from such sources. This is followed consecutively in the order VOG, FPP, WFP and GWP. The adsorption mechanism that prevailed is physical adsorption, signifying electrostatic attractions in the removal process. For all the materials, the adsorption capacity decreased as the temperature was raised and it increases when the pore size is increased. The neutral pH of the adsorbents used in the study was shown to favor the heavy metal adsorption. The negative values of ΔG° indicate that the process occurred through physical adsorption.

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