

Full Length Research Paper

Predicting chromium (VI) adsorption rate in the treatment of liquid-phase oil-based drill cuttings

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Accepted 19 March, 2008

The adsorption rate of chromium (VI) on commercial activated carbon during the treatment of the flocculation effluent of liquid-phase oil-based drill-cuttings has been investigated in terms of contact time and initial chromium (VI) ion concentration. Homogenizing 1 g of the activated carbon with 100 ml of the flocculation effluent of known initial concentrations (1.25 → 6.25 mg/l, in turn) in a flask, at a constant stirring speed of 80 rpm at 25°C for 180 min, the pseudo-second-order kinetics was observed to be more suitable in predicting the adsorption rate of chromium (VI) ion in the treatment process as experimental data fitted the model relatively better than the pseudo-first-order kinetics with $R^2 = 0.9999$. Adsorption took place in two steps: an initial high rate step before reaching a plateau at equilibrium in the low rate step. Equilibrium was attained in a contact time of 60 min and the equilibrium adsorption capacity of the activated carbon was 78.6%. Equilibrium adsorption data fitted the Freundlich isotherm well with $R^2 = 0.981$. The intensity of adsorption was 1.32, which indicates a strongly favourable adsorption. This showed that a large proportion of the chromium (VI) ion was adsorbed at low concentration of the adsorbate in solution.

Key words: Carbon adsorption, kinetic models, drill cuttings, chromium removal.

INTRODUCTION

The injection of the flocculation effluent of liquid-phase oil-based drill-cuttings (LP-OBDC) into the ground, as currently being done by oil drilling and exploration and production (E and P) waste management companies in Nigeria, has been described as the best available technology (BAT) for the disposal of this type of drilling

waste (Akinlade et al., 1996). Apart from being heavily laden by suspended matter and oil/grease (Table 1), it has also been observed that this flocculation effluent contains chromium (a pollutant heavy metal) at concentrations that could seriously threaten the life of edaphic systems as well as people who depend on local ground water if it is continually injected into the ground without further remedial treatment measures (Okparanma, 2007). Moreso, conventional methods such as precipitation, oxidation and reduction, ion exchange, membrane filtration and evaporation are prohibitively expensive for removing metals from dilute solutions containing 1 to 100 mg/l of dissolved metal (Volesky, 1990). But in the recent past, sorption process has been used to remove heavy metals from different industrial effluents (Ho, 2006; Tsekova et al., 2006; Romero et al., 2006; Wankasi et al., 2006; Abia and Asuquo, 2006; Zou et al., 2007; Parvathi et al., 2007; Igwe and Abia, 2007; Ayotamuno et al., 2007; Gök et al., 2008). The sorption of chromium from

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Abbreviations

APHA- American Public-Health Association; ASTM - American Society for Testing and Materials; BAT- Best Available Technology; DPR - Department of Petroleum Resources
FE - Flocculation Effluent ; IRS - Infra-red Spectrophotometer;
LP-OBDC -Liquid-Phase Oil-Based Drill-Cuttings; PAC - Powdered Activated-Carbon; THC -Total Hydrocarbon Content; TSS - Total Suspended Solids.

Table 1. Chemical compositions of untreated and flocculation effluent of LP-OBDC.

Parameter	Waste stream		
	Untreated LP-OBDC	Flocculation Effluent of LP-OBDC	DPR (2002) Limits
Oil/Grease (mg/l)	1,649,724	67,300	10
Total Suspended Solids (mg/l)	13,700	610	30
Chromium (mg/l)	5.26	5.01	0.03
pH	8.5	7.4	7.8

aqueous solutions by activated carbon of none-living biomass origin and microbes alike has also been widely reported (Hussein et al., 2004; Demirbas et al., 2004; Ahalya et al., 2005; Nomanbhay and Palanisamy, 2005; Popuri et al., 2007). But the present study reports about the sorption of chromium by activated carbon from the flocculation effluent of liquid-phase oil-based drill cuttings (LP-OBDC), which is heavily laden by oil/grease and suspended solids (Table 1).

Adsorption is the adhesion of a chemical substance (adsorbate) onto the surface of a solid (adsorbent). The most widely used adsorbent is activated carbon, which is commercially available in two main variants – Norit Row 0.8 Supra and Norit SA4. Activated carbon can be prepared either by physical or chemical means using a variety of starting materials such as coconut shell and shell hull of palm tree (Gueu et al., 2007), water hyacinth ash (Uddin et al., 2007) and cornelian cherry, apricot stone and almond shell (Demirbas et al., 2004). But the most popular source of activated carbon is wood charcoal (Abe, 1988) and wood charcoal has been reported to be chromium-free (Yoshiyuki et al., 2005). Activated carbon has a relatively large surface area to mass ratio of 1091.951 m²/g and total pore volume to mass ratio of 0.582 cm³/g. It consists mainly of micro-pores (of pore width; 20Å) with some mesopores of pore width up to 60Å. It is also rich in acidic functional groups with the lactonic group being the most abundant (Gunawan et al., 2007). In carbon adsorption processes, knowledge of the adsorption kinetics (i.e. the rate of solute uptake, which dictates the residence time of sorbed solute at the solid-liquid interface) is important because information from it is an indispensable tool in the large-scale process design (Ho and McKay, 1999a). This study also compares the suitability of two predictive models (i.e. pseudo-first- and pseudo-second-order kinetic models) in analyzing the adsorption rate of chromium (in terms of initial concentration and contact time) onto powdered activated carbon.

MATERIALS AND METHODS

Experiments

This experiment was conducted in two steps: firstly, by mixing 1 g of

commercial PAC with 100 ml of the flocculation effluent (FE) of known initial chromium concentration in a flask, using a variable-speed STUART Magnetic Stirrer set at 80 rpm at 25°C. The residual concentration of chromium in solution, (C in mg/l), was measured after different stirring times: 5, 10, 15, 30, 60, 120, and 180 min. By equilibrium of masses, the adsorption *q* (mg/g) was found for each period. Stirring over time was to enable adsorption equilibrium time to be determined. Secondly, trial runs in equilibrium of adsorption were carried out to determine the performance characteristics of the activated carbon. At 25°C, four different flasks (i.e. contactors) containing 1 g of PAC and 100 ml of the flocculation effluent were stirred in turn during the equilibrium time determined earlier in step 1. Thereafter, four different initial chromium concentrations; 1.25, 2.5, 5.01 and 6.25 mg/l were tested. Finally, the amount of chromium retained in equilibrium *q_e* (mg/g) was calculated for each contactor.

Laboratory analysis

Total chromium was analyzed using a UNICAM-969 Atomic Absorption Spectrophotometer (AAS) by measuring the light absorbance at a specific wavelength of 357.9 nm according to APHA (1998) method 3111C. A standard solution of chromium was used to calibrate the equipment beforehand. Oil/Grease (i.e. total hydrocarbon content, THC) was analyzed according to ASTM (1999) method D3921 using a SHIMADZU Infra-red Spectrophotometer (IRS) by measuring the light absorbance at the wavelength range of 3333 – 3704 nm. Bonny-Light crude was used to calibrate the equipment beforehand. Total suspended solid (TSS) was analyzed according to APHA (1998) method 2540D. pH was analyzed with a WTW MULTI-340 pH-meter according to APHA (1998) method 4500-H⁺.

Theory

To observe the kinetics of the adsorption mechanism of chromium onto the PAC, experimental results were fitted to pseudo-first- and pseudo-second-order kinetic models. Pseudo-first-order kinetic expression, integrated and linearized, according to Lagergren (1898); is given as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (1)$$

According to Ho and McKay (1999a), pseudo-second-order kinetic model, integrated and linearized, is given as;

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

The values of the parameters K_1 and K_2 were determined by regression analysis by fitting on a number of experimental data points. Then, q_e was calculated for each model and compared with its experimental value.

Adsorption isotherm is an expression relating the amount of adsorbate and the equilibrium concentration of the solute in the fluid at a given temperature. The Freundlich isotherm is an empirical model, which considers the surface of the adsorbent as heterogeneous and is given by:

$$Q_e = K_F C_e^{1/n} \quad (3)$$

The value of n indicates whether or not the adsorption is favourable. The more favourable the process is, the lower the value of n in the range; [$1 < n < 10$]. The parameters K_F , Q_e and n were determined by regression by fitting on a number of experimental data points. The Langmuir's isotherm is a theoretical model, which supposes that the maximum adsorption consists in a saturated monolayer of molecules of adsorbate on the surface of the adsorbent considered as homogenous and is given by:

$$\frac{C_e}{q_e} = \frac{C_e}{Q^o} + \frac{K_L}{Q^o} \quad (4)$$

The parameters Q^o and K_L were determined by regression by fitting on a number of experimental data points. From the Langmuir model, the separation factor r , according to Calvo et al (2001) cited in Rozada et al. (2005), may be given by:

$$r = \frac{1}{1 + K_L C_o} \quad (5)$$

Adsorption is favourable if $r < 1$; unfavourable if $r > 1$; linear if $r = 1$; irreversible if $r > 0$.

RESULTS AND DISCUSSION

Chemical characteristics of the LP-OBDC

Table 1 shows the pertinent chemical characteristics of the LP-OBDC *vis-à-vis* the effluent quality discharge standard of the Department of Petroleum Resources (DPR) of the Nigerian government. As it can be observed from Table 1, all the parameters far exceed the safe limits spelt out by the regulatory body; thereby making the untreated and flocculation effluent of the LP-OBDC unsafe for sub-surface injection.

IR spectra studies

The IR spectra shown in Figure 1a are for the oil/grease (O and G), that is, the total hydrocarbon content (THC) analysis of the untreated LP-OBDC. Comparing this spectra with that in Figure 1b for the blank, it is observed that peaks occurred at $3000 - 2700 \text{ cm}^{-1}$, indicating the presence of oil/grease in the range. Therefore, it can be

inferred that absorption occurred in the wavelength range of $3333 - 3704 \text{ nm}$.

Sorption kinetics and effect of contact time on chromium uptake rate

The adsorption rate of chromium (VI) onto powdered activated carbon (PAC) at different initial chromium concentrations is shown in Figure 2. The results show that sorption took place in two steps: a high rate step and a low rate step. In the high rate step, 74% of adsorbent saturation capacity was reached in 10 min of contact; before reaching a plateau at equilibrium in the low rate step. This behaviour is corroborated by the findings of Ho and McKay (1999a; b). Sorption, and indeed sorption equilibrium time, is influenced by contact time, pH, temperature, sorbent concentration, nature of the solute and its concentration (Ho and McKay, 2000). But it has been reported that equilibrium time is in the range of 15 min and 10 days (Aksu and Kutsal, 1991; Nourbakhsh et al., 1994) cited in Cossich (2002). In this study, for the range of initial chromium concentrations tested ($1.25 \rightarrow 6.25 \text{ mg/l}$), it is observed from Figure 1 that equilibrium was reached within a contact time of 60 min. It is further observed from Table 2 that the value of the equilibrium concentration deduced with the pseudo-second-order kinetics (i.e. $q_e = 3.96 \text{ mg/g}$) is comparable with its experimental value of 3.94 mg/g ; with the value of the correlation coefficient close to unity ($R^2 = 0.9999$). On the other hand, the value of the equilibrium concentration deduced with the pseudo-first-order kinetics ($q_e = 3.47 \text{ mg/g}$) is quite different from its experimental value of 3.94 mg/g ; with the value of the correlation coefficient far from unity ($R^2 = 0.2889$). This result shows that experimental data fitted the pseudo-second-order kinetics relatively better than the pseudo-first-order model. By implication, the pseudo-second-order model may be more suitable in predicting chromium (VI) adsorption in the treatment process. Demirbas et al. (2004) reported a similar result for chromium (VI) adsorption onto the activated carbon prepared from cornelian cherry, apricot stone and almond shell. Furthermore, a number of sorption systems for chromium (VI), which followed the pseudo-second-order kinetics has been widely reported (Ho and McKay, 1999a).

Adsorption capacity of the powdered activated carbon (PAC) at equilibrium

Equilibrium adsorption capacity of the PAC at the adsorbent dose of 10 g/l of effluent is shown in Table 3; where it is observed that the PAC adsorbed the highest amount of chromium of 1.60 mg/g (representing 64% adsorption) at an initial chromium concentration, C_o of 2.50 mg/l . This

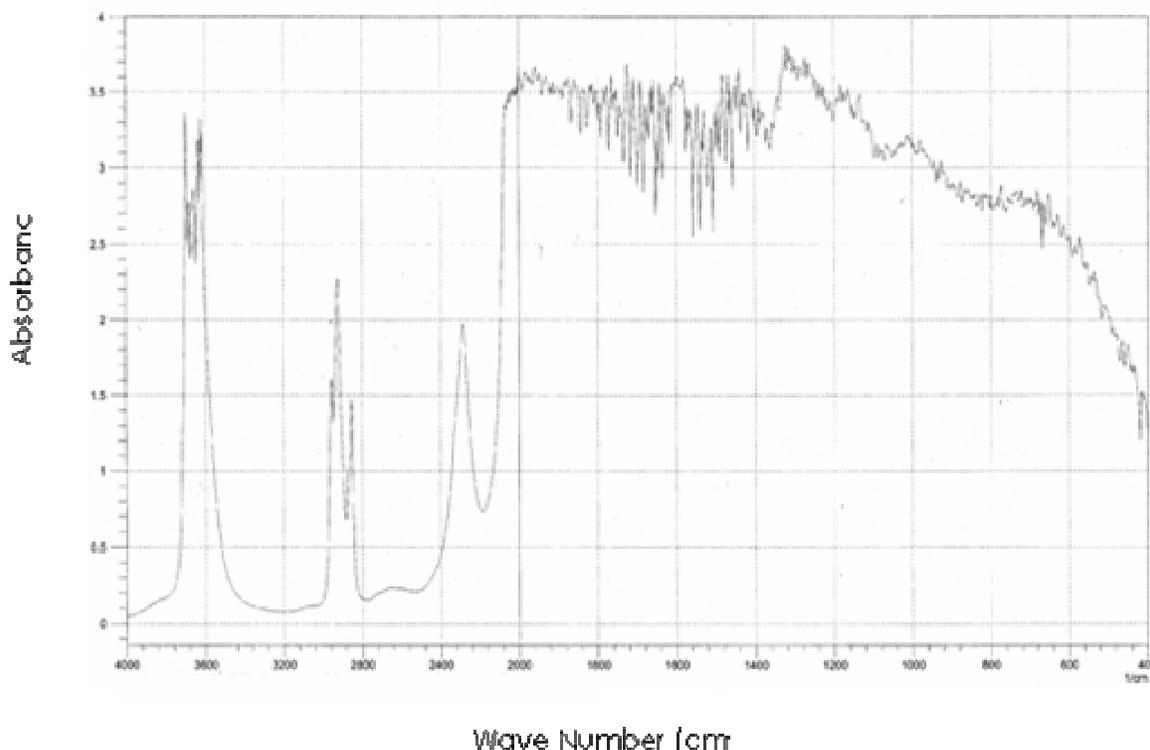


Figure 1a. IRS spectra for the untreated liquid-phase oil-based drill cuttings (LP-OBDC).

Table 2. Comparison of kinetics parameters for Cr^{6+} adsorption in the treatment of the flocculation effluent of LP-OBDC.

Pseudo-first order kinetics	Pseudo-second order kinetics
$K_1 = 9.84 \times 10^{-5} \text{ (min}^{-1}\text{)}$	$K_2 = 3.664 \times 10^{-1} \text{ (g/mgmin)}$
$q_e \text{ (experimental)} = 3.94 \text{ (mg/g)}$	$q_e \text{ (experimental)} = 3.94 \text{ (mg/g)}$
$q_e \text{ (calculated)} = 3.47 \text{ (mg/g)}$	$q_e \text{ (calculated)} = 3.96 \text{ (mg/g)}$
$R^2 = 0.2889$	$R^2 = 0.9999$

result indicates a high adsorbate loading at a low initial adsorbate concentration, which, according to Ahalya et al. (2006), is partly due to the availability of sufficient binding sites in the biomass to bind metal ions when present in few numbers. Table 4 compares the Freundlich and Langmuir isotherm parameters. Although the values of the parameters n and r of the Freundlich and Langmuir models respectively point to the fact that the adsorption was favourable, it is observed from Table 4 that experimental data fitted the Freundlich isotherm (Figure 3) relatively better than the Langmuir isotherm (Figure 4); with the correlation coefficient of the former

being closer to unity than that of the latter. As stated earlier, a strongly favourable adsorption indicates that a large proportion of chromium (VI) is adsorbed at a very low initial chromium concentration in solution. The maximum equilibrium adsorption capacity of 3.94 mg/g (representing 78.6% equilibrium adsorption capacity) reported in this study is comparable with those reported by other researchers as shown in Table 5.

Conclusion

The adsorption of chromium (VI) onto powdered activated

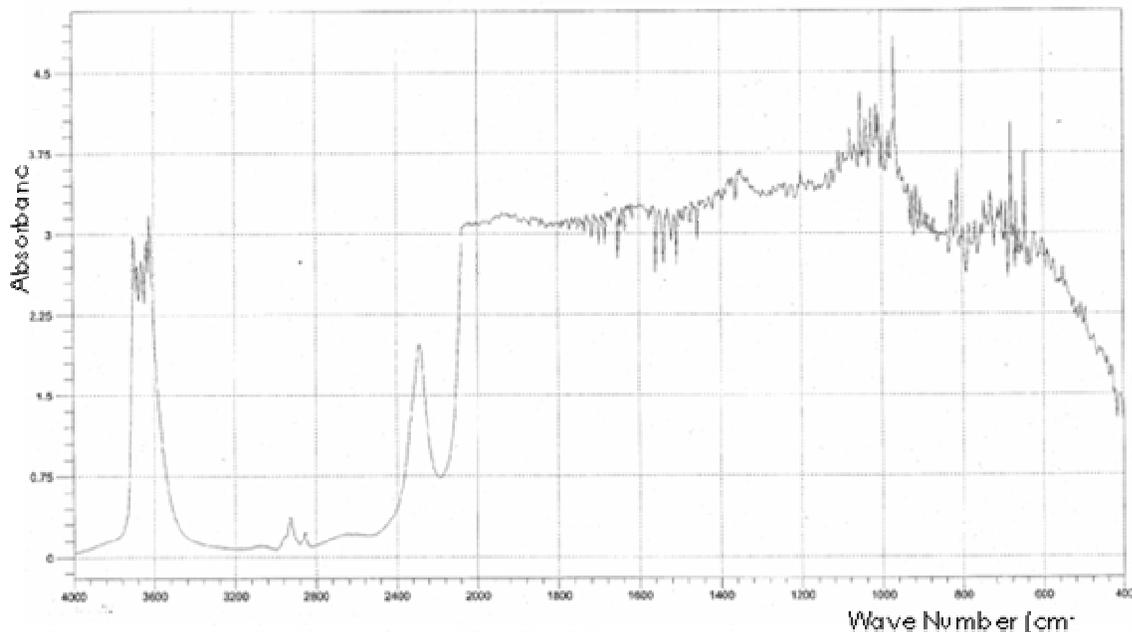


Figure 1b. IRS spectra for blank solution.

Table 3. Equilibrium adsorption capacity of the PAC at 10g of PAC per litre of effluent.

C _o (mg/l)	C _e (mg/l)	Q _e = C _o - C _e (mg/g)
1.25	0.94	0.31
2.50	0.90	1.60
5.01	3.59	1.42
6.25	3.36	2.89

Table 4. Comparison of isotherm parameters for Cr⁶⁺ adsorption in the treatment of the flocculation effluent of LP-OBDC.

Freundlich isotherm	Langmuir isotherm
K _F = 0.768 (mg ^{1/n} /g.mg ^{1/n})	K _L = 17.825 mg/l
Q _e = 3.94 (mg/g)	Q ^o = 10.81 mg/g
n = 1.32	r = 0.01
R ² = 0.981	R ² = 0.6113

carbon (PAC) in the tertiary treatment of the flocculation effluent of liquid-phase oil-based drill-cuttings (laden by suspended matter and oil/grease) fitted the pseudo-second-order kinetics relatively better than the pseudo-first-order kinetics with R² ≈ 1.00. This shows that the pseudo-second-order kinetics could be used to predict chromium (VI) adsorption onto the PAC in the treatment

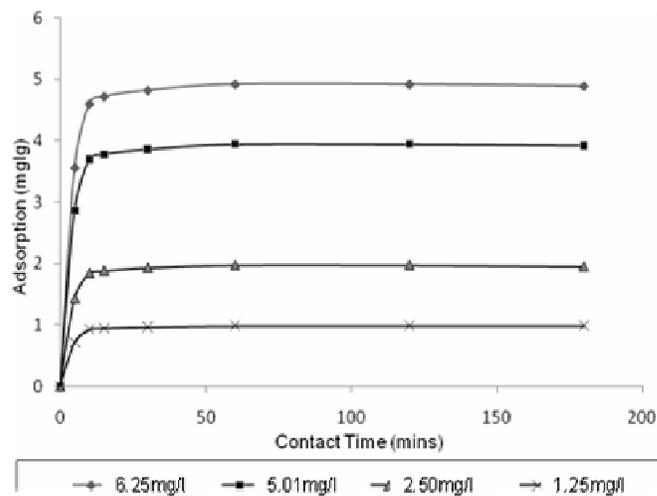
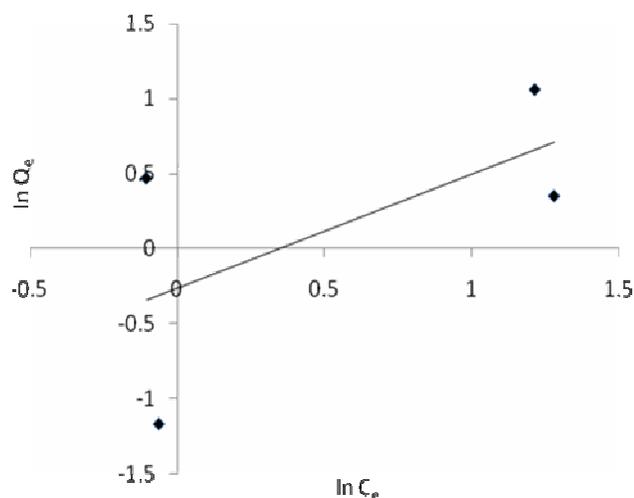
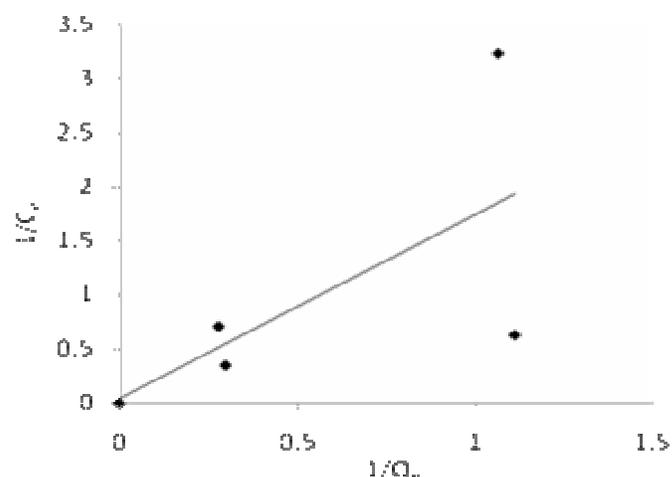


Figure 2. Adsorption rate of Cr⁶⁺ onto PAC at different initial Cr⁶⁺ concentrations for the flocculation effluent of LP-OBDC.

process. Adsorption kinetics (in terms of initial chromium concentration and contact time) took place in two steps: an initial high rate step and a low rate step before reaching a plateau at equilibrium. The high rate step reached 74% of adsorbent saturation capacity in a contact time of 10 min. Equilibrium was reached in a contact time of 60 min. The equilibrium concentration of the chromium (VI) at the adsorbent dose of 10 g/l of effluent was 3.94 mg/g,

Table 5. Comparison of sorption capacities of different adsorbents for Cr⁶⁺.

Adsorbent	Waste water	Adsorption Capacity (%)	Reference
<i>Sargassum sp.</i>	Aqueous solution of Cr ³⁺	60.0	Cossich et al (2002)
<i>Pseudomonas sp.</i>	Waste water	38.0	Hussein et al (2004)
Activated Carbon	Aqueous solution of Cr ⁶⁺	99.9	Demirbas et al (2004)
Activated Carbon	Aqueous solution of Cr ⁶⁺	99.9	Ahalya et al (2005)
Activated Carbon	Aqueous solution of Cr ⁶⁺	52.0	Nomanbhay and Palanisamy (2005)
Activated Carbon	Flocculation effluent of LP-OBDC	78.6	This study

**Figure 3.** The Freundlich isotherm for PAC.**Figure 4.** The Langmuir isotherm for PAC.

which shows that the PAC was able to adsorb up to 78.6% of the chromium (VI) at equilibrium. Equilibrium adsorption capacity data fitted the Freundlich isotherm relatively better than the Langmuir isotherm with $R^2 = 0.981$. The adsorption intensity constant, $n = 1.32$, which shows that the adsorption was strongly favourable.

Nomenclature

C = Concentration in the liquid phase over a time period t (mg/l)

C_e = Concentration in the liquid phase at equilibrium (mg/l)

C_0 = Initial concentration (mg/l)

K_1 = Pseudo-first order kinetic constant (in min^{-1}) for the adsorption

K_2 = Pseudo-second order kinetic constant for the adsorption (g/mg.min)

K_F = Freundlich constant indicating the capacity of adsorption (in $\text{mg}^{1/n}/\text{g} \cdot \text{mg}^{1/n}$)

K_L = Langmuir constant related with affinity for the

adsorption sites (in mg/l)

n = Dimensionless constant indicating intensity of adsorption

q = Adsorption over a time period t (mg/g)

q_e = Adsorption at equilibrium (mg/g)

Q_e = Adsorption capacity at equilibrium (in mg/g)

Q^0 = The maximum adsorption capacity per unit of mass of adsorbent for a complete monolayer on the surface (in mg/g)

r = Separation factor (dimensionless)

R^2 = Correlation Coefficient (dimensionless)

t = Time (min)

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