International Journal of Engineering Sciences & Research Technology

(A Peer Reviewed Online Journal)
Impact Factor: 5.164

✚ IJESRT

Chief Editor	Executive Editor
Dr. J.B. Helonde	Mr. Somil Mayur Shah

IJESRT

INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

INVESTIGATION OF Cr (VI) IONS ADSORPTIVE REMOVAL FROM AQUEOUS SOLUTION ONTO TiO2-AC COMPOSITE: NON-LINEAR EQUILIBRIUM MODELING AND KINETICS

Sali Mouhamadou[1], Constant Tcheka*[2], Raphael Djakba[1], Narcisse Dobe[3], Gilbert Mando[1] & Massai Harouna[2,4]

[1]Department of Chemistry, Faculty of Science, University of Maroua, Cameroon,
[2]Department of Chemistry, Faculty of Science, University of Ngaoundéré, Cameroon
[3]Department of Fundamental Science, Faculty of Mines and Petroleum Industries, University of Maroua, Cameroon
[4]Department of Chemistry, Chemical Engineering & Mineral Industries School, University of Ngaoundéré, Cameroon

ABSTRACT
The present work dedicated to the removal of Cr(VI) ions in aqueous solution onto a synthetized TiO_2-AC composite. Composite characterization was carried out by determining of the point of zero charge pH_{pzc}, iodine number, methylene blue index and FT-IR spectra. Adsorption experiments were conducted in batch mode and the influences of composite quantity, contact time, Cr(VI) ions concentration, ionic strength, and pH were studied. The highest adsorption were obtained in acid medium, with lowest adsorbent quantity (0.01 g) and initial solution concentration of 10 ppm. The results of kinetic studies revealed that Cr(VI) adsorption process on TiO_2-AC composite followed pseudo second-order kinetic model. Non-linear regression was applied to equilibrium data and Langmuir, Freundlich, Dubinin-Radushkevich, and Temkin isotherm models were used for evaluation of adsorption parameters. The best-fitting was estimated based on correlation coefficient R^2 value and the calculation of error deviations between experimental and predicted equilibrium adsorption data, using non-linear analysis. The results showed that Freundlich model describing adsorption process the best. The isotherm parameters from Langmuir and Freundlich models revealed that Cr(VI) adsorption mechanism on the composite is linear, spontaneous, and endothermic follows chemisorption process.

KEYWORDS: AC-TiO_2 composite, Cr(VI), adsorption isotherm, kinetics, error analysis.

1. INTRODUCTION

Environmental contamination by chromium has become a global concern because of its major role in industry [1,2]. Chromium is widely used in leather tanning, electroplating, paint manufacture, wood treatment, metallurgy, and mining [3, 4]. Significant amounts of chromium are introduced into the environment through poorly regulated disposal of chromium containing waste [5]. As a result, chromium concentrations in surface and drinking waters can exceed the World Health Organization's maximum allowable concentration of 0.05 mg L^{-1} [6]. Cr (VI) due to its potential carcinogen and acutely toxic effects for humans (such as epigastria, nausea, vomiting, severe diarrhea, and internal hemorrhage, dermatitis, and liver and kidney damage), animals, plants, and microorganisms has attracted enormous interest [7]. Therefore, removal of Cr (VI) from aqueous solutions before its release is also an important environmental issue.

Several treatment methods including chemical and electrochemical precipitation, oxidation/reduction processes, ion exchange, membrane separation, flotation, solvent extraction, evaporation, adsorption, and phytoremediation have been focused on the wastewater contaminated with chromium. Most of these methods are effective but required a large quantity of chemicals and/or high energy [8]. Among of these methods, the adsorption process is

a promising remediation technology due to its generally low cost, easy operation, and good efficiency which can be applied to remove various organic or inorganic contaminants in an eco-friendly and high-efficiency way. Many

adsorbents including activated carbon, clay and composite were used to remove chromium from aqueous solution. Recently, the interlocking nature of composite structure is helpful in creating a porous materials with good properties such as high porosity, mechanical strength, higher surface area and durability even under harsh conditions [9]. These properties of composite make it a potential candidate for possible water purification applications and this motivated about testing its capability towards removal of heavy metal ions in aqueous solution. In this study, an adsorbent composite from TiO_2 and *bauhinia reticula* seed hulls based activated carbon was prepared and used as adsorbent for Cr (VI) ions adsorption. The kinetics of Cr(VI) adsorption onto the synthesized material has been examined. The effects of several performance parameters, such as pH, contact time and adsorbent dosage on the adsorption efficiency, etc. are investigated in detail which suggest the potential application scope of the composite towards purification.

2. MATERIALS AND METHODS

Material and chemicals
Bauhinia Reticulata seed hulls used as precursor of activated carbon preparation in this work was collected in Mayo-Oulo, Mayo-Louti Subdivion in the North Region, Cameroon. The biomass precursor collected was first washed using distilled water to remove dust. The sample powder was obtained after scrubbing, drying, crushing and sieving with standardized sieves for getting the biomass fraction less than 80 μm size, and stored in a glass bottle for preparation of activated carbon. Potassium dichromate $K_2Cr_2O_7$ was supplied from Sigma-Aldrich, USA. All other reagents used in the present work, such as phosphoric acid H_3PO_4, hydrochloric acid HCl, sodium hydroxide $NaOH$ and titanium isopropoxide $Ti[OCH(CH_3)_2]_4$, were analytical grade. Cr(VI) ions stock solution with concentration of 1000 mg/L was prepared by dissolving an appropriated quantity of $K_2Cr_2O_7$ salt in distilled water. Working solutions with desired concentrations of Cr(VI) ions were prepared by successive dilution of the stock solution.

Preparation of AC-TiO₂ composite
Preparation of the composite was carried out by taking 30 g of biomass powder of *bauhinia* which were mixed with 2M phosphoric acid in the weight Ratio of 1:3, after 24 hours the mixture was dried in a dry air oven at 60 °C for 12 hours. The resulting powder activated carbon (AC) was then mixed with prepared gel solution of 0.4 M titanium isopropoxide at weight ratio of 1:3. After 24 hours the mixture was dried in a dry air oven at 60 °C for 12 hours. The final mixture was carbonized in a Nabertherm furnace. The heating started at room temperature with an increment of 5°C/min up to final temperature of 400 °C. The residence time of the sample at the final stabilized temperature of 400 °C was 1hours. After heat treatment, the composite was cooled down to room temperature. The resulting composite (AC-TiO₂) was stored in polyethylene bottles for characterization and further Cr(VI) adsorption experiments.

Characterization of the composite
Surface charge indicated by point of zero charge (pHzpc) and acidity or basicity of the composite surface was determined using the modified method described by El-Nahas [10], 0.1 g of the composite was added to 25 mL of 0.1 M *NaCl* solution then, pH of the solution was adjusted in the range between 2 to 12 using *NaOH* or *HCl* diluted solutions. The mixture was stirred at a speed of 120 rpm at room temperature for 24 hours. After stirring operation completed, the solution was filtered and the surface charges were measured using KMOOM Tri-meter (Waterproof, EC/pH&TEMP) instrument. The existence of possible functional groups on the surface of the composite was analyzed by Fourier transform infrared spectrophotometry (FT-IR) using a PerkinElmer Spectrum 100 FT-IR spectrophotometer at the range of wavenumber between 4000 and 500 cm⁻¹ while the porosity (in term of micropores and mesorpes quantity) was verified using iodine number (IN) and methylene blue index (MB Index) as described by Harouna et *al*. [24].

Adsorption experiments
Kinetic adsorption experiments of Cr(VI) ions were carried in batch mode technic at experimental conditions of pH 4.8, temperature (30 °C), agitation speed (120 rpm), and AC-TiO₂ composite adsorbent dose of 0.05 g. In a typical run, conical flasks (50 mL) were filled with 20 mL of Cr (VI) ions solution with original known

concentration. The reaction solutions were then agitated for specific period of contact time varying from 2 min to 30 min. After a given contact time period, stirring was stopped, and the solid was separated from the liquid phase

(solution) by simple filtration operation using a whatman paper N°1. The residual concentration of Cr(VI) ions in aqueous solution was determined by measuring the solution absorbance using UV-visible spectrophotometry at the wavelength of 373 nm corresponding to the maximum absorbance. The effect of pH of the solution on the adsorption of Cr(VI) ions was studied over the pH range of (1−2.5), and desired pH value was obtained by adjustment using 0.1 M *NaOH* 0.1 M *HCl* solutions. The influence of ionic strength was also explored by adding *NaCl* solution with concentration range from 100 to 500 ppm. For equilibrium isotherm study, the experiment was carried out at three different concentration of Cr(VI) ions of 10, 20 and 30 mg/L. The adsorbed amount of Cr (VI) ions at equilibrium time, q_e (mg/g) was calculated using the following equation (1):

$$q_{e=} \frac{(C_o - C_e)V}{m} \tag{1}$$

where C_o and C_e are initial and equilibrium concentrations of Cr(VI) ions solution (mg/L), respectively, V is the total volume of Cr(VI) ions solutions (L), and m stands for the mass of adsorbent (g).

Best-fitting isotherm model estimation
Non-linear regression is presented in several paper as the most recurrent used method to optimization of fitting analysis and to decide on the best fit isotherm models with experimental data [12]. In the present work, best-fitting of nonlinear isotherm model onto Cr((VI) ions adsorption data was chosen based on the correlation coefficient R^2 values and calculation of five error functions using Microsoft Excel SOLVER function-spreadsheet method. These error functions include sum square error, hybrid functional error, average relative error, sum of absolute error, nonlinear chi-square [13].

Chi-square test (χ^2)

The Chi-square statistic test is basically the sum of the square of the differences between the experimental data and theoretically predicted data from models [14]. Its equation is expressed as:

$$\chi^2 = \sum \frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,cal}} \tag{2}$$

Residual root mean square error (RMSE)
The residual root mean square error function is defined by the following equation (3) [15]:

$$RMSE = \sqrt{\left(\frac{1}{n-2}\sum_{i=1}^{n}(Q_{e,exp} - Q_{e,cal})\right)^2} \tag{3}$$

Average relative error (ARE)
This error estimation tool [16], is presented by equation (4):

$$ARE = \frac{100}{n-p}\sum_{i=1}^{n}\left|\frac{Q_{e,cal} - Q_{e,exp}}{Q_{e,exp}}\right|_i \tag{4}$$

Sum of absolute errors (EABS)
The Sum of absolute errors [17], is given by equation (5):

$$EABS = \sum_{i=1}^{n}(q_{e,cal} - q_{e,exp}) \tag{5}$$

The hybrid fractional error function (HYBRID)
HYBRID error function (equation 6) is more used in order to improve the fit of the sum of the square of the errors method at low concentration values [17].

$$HYBRID = \frac{100}{n-p}\sum_{i=1}^{n}\frac{(q_{e,exp} - q_{e,cal})^2}{q_{e,exp}} \tag{6}$$

3. RESULTS AND DISCUSSION

Characterization of AC-TiO₂ composite adsorbent
Table 1 presents the values of pH_{zpc}, Iodine number and the Methylene blue (MB) index as characteristics of AC-TiO₂ composite. pH value of 2 obtained for the porous composite as shown in Figure 1. Point of zero charge is a pH value at which the sum of the negative charges are equal to those of the positive charges and, the net charge on the surface is zero. The surface of the composite is positively charged at pH less than 2 and negatively charged at pH greater than 2 [10]. The Iodine number values and Methylene blue (MB) index showed that our porous

composite is primarily made up of micro and mesopores, suggesting that the surface of the composite had high oxygen functional groups consisting with lone pair electrons which could serve as Lewis base.

Table 1: Characteristics of AC-TiO₂ composite.

Parameters	Values
Iodine Number (mg g^{-1})	492.38
MB Index (mg g^{-1})	3232.48
pHzpc	2
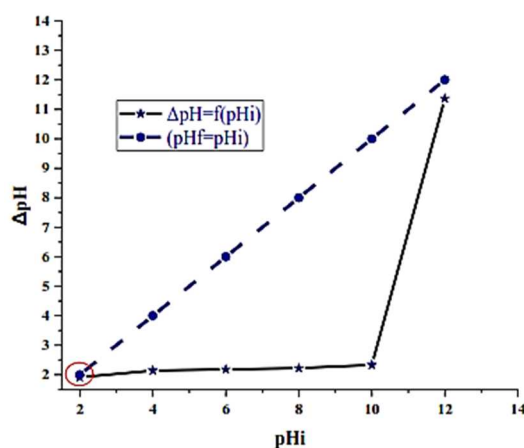
Figure 1: pH$_{pzc}$ of AC-TiO₂ composite

The FT-IR spectrum of porous composite is shown in Figure 2. Several peaks are shown by this spectra indicating that our porous composite is composed of various functional groups which can be used to bind Cr (IV) ions. The broad absorption band at 3240 cm^{-1} is characteristic of the stretching vibration of hydroxyl group OH of Ti(OH)₂. The band at 2338 cm^{-1} indicate the presence of C≡C of alkyne. The peaks observed at 1617 cm^{-1} represents the C=O in the Quinone structured of lignin whereas peaks appearing at 951 cm^{-1} is due to Ti-O formation while the peaks at 614 cm^{-1}, 477 cm^{-1}, and 415 cm^{-1} can be ascribed to the OH out of plane bending modes CH of AC bonding [11, 26].
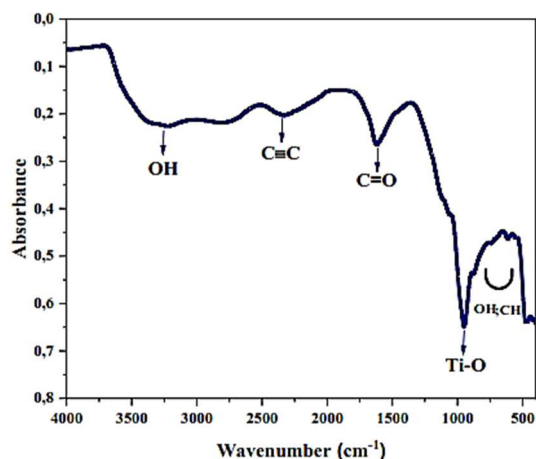
Figure 2: FTIR spectra of AC-TiO₂ composite

Adsorption experiments

Effect of contact time
The effect of contact time on Cr (VI) ions adsorption is presented in Figure 3. As can be observed, the adsorption capacity of Cr (VI) ions increases with increasing of contact time, and reach the maximum and remained constant after 15 min for the various original concentrations, and the maximum adsorbed quantities were 4.53 mg g^{-1}, 7.12 mg g^{-1} and 9.01 mg g^{-1} of original concentrations of 10, 20 and 30 mg L^{-1}, respectively. The fast adsorption at

initial stage is probably due to the availability of many active sites on the composite material surfaces. In the other hand, the pH$_{zpc}$ was found to be 2, consequently there were strong electrostatic attractions between the positive charge surface of composite and the anionic solution of $[HCrO_4]^-$ ions. This can also be explained by the penetration of Cr (VI) ions in the inner active sites of the composite [12]. Higher adsorption with high initial concentrations is due to the presence of important driving force by increased concentration necessary to overcome all the mass transfer resistances of the pollutant between the aqueous and solid phases thus increasing the adsorption capacity. This trend agrees with the report of other investigators [13].
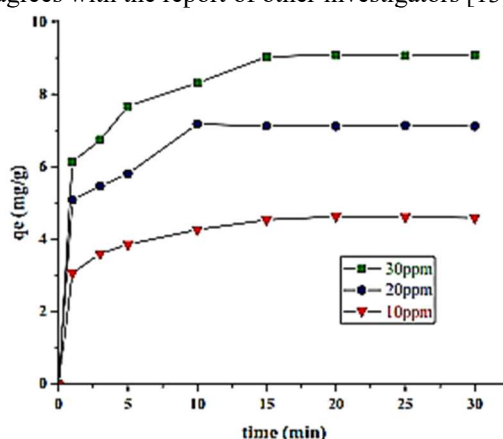

Figure 3: Effect of the contact time on Cr(VI) ions adsorption at different initial concentrations (conditions: adsorbent dose = 0.05 g, pH of solution = 4.8, temperature = 30 °C, agitation speed =120 rpm, and volume of Cr(VI) ions solution = 20 mL)

Effect of adsorbent dosage
The studies are carried out with a adsorbent quantity ranging from 0.01 g to 0.09 g; other experimental conditions were contact time (15 min), total volume of the reactional solution (20 mL), initial Cr(VI) concentrations (10, 20, and 30 mg L^{-1}). The result is presented in Figure 4 which reveal that the adsorbed quantities of Cr(VI) ions increase with increasing of initial metal ions concentration ((q_e(30 mg L^{-1}) > q_e(20 mg L^{-1}) > q_e(10 mg L^{-1})), and decrease with increasing of adsorbent quantity and tend to be constant for high TiO$_2$-AC composite mass. This can be explained by the fact that, the increase of adsorbent mass involves a growth of the electrostatic interactions between the particles of the composite which leads to desorption of the hexavalent chromium (VI) ions on the adsorbent sites, thus led an agglomeration of TiO$_2$-AC composite particles forming aggregates; reducing contact surface by the fact that active sites on the porous composite become recovered. Consequently, there is an increasing in diffusion phenomenon Cr(VI) ions through the active sites. These results agree with those observed by Joana et *al*. [14]. TiO$_2$-AC composite mass of 0.01 g were retained for further experiments.
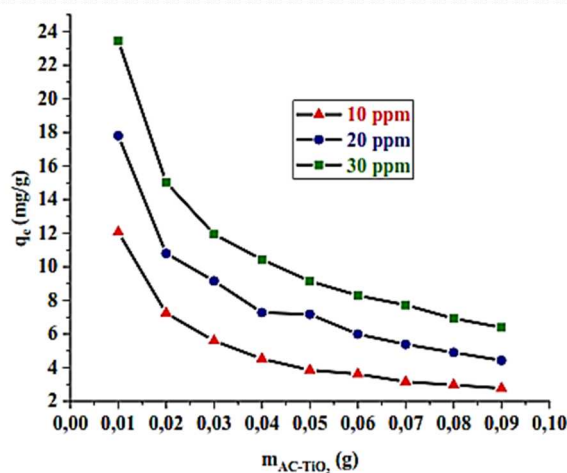
Figure 4: Effect of TiO₂-AC composite dose on Cr(VI) ions adsorption at different initial concentrations (conditions: contact time = 15 min, pH of solution = 4.8, temperature = 30 °C, agitation speed =120 rpm, and volume of Cr(VI) ions solution = 20 mL)

Effect of pH

Initial pH of the solution plays an important role in adsorption process, particularly on the adsorption capacity [15]. It is evident to observe that Cr(VI) ions adsorbed quantity decreases with increasing of initial solution pH values (Figure 5). Point of zero charge value ($pH_{pzc} = 2$) can explain the observed effect of pH on the Cr(VI) adsorption capacity onto TiO₂-AC composite that revealed the positively charged surface and the form of hexavalent chromium(VI) ion at pH= 2 which is $[HCrO_4]^-$. The decrease of the adsorption capacity can be due to the fact that the surface of porous composite would be negatively charged with values of weak acid pH, which unsupported the adsorption of the hexavalent chromium (VI) ions. On the other hand, for values of pH < 2, porous composite surface is positively charged and would have multiples gap due to the presence of titanium, and thus likely supported the hexavalent chromium (VI) ion adsorption. In addition, higher adsorption of Cr(VI) ions at strength acidic pH on porous composite might be due to the lack of HO^- ions competing with anions for the available adsorption sites. Similar results were observed in previous work [16]. Furthermore, it is also noted that the adsorbed quantity is maximum with pH equal to 1.0 (17.27, 22.92 and 41.86 mg g⁻¹, respectively for initial Cr(VI) ions concentrations of 10, 20 and 30 mg L⁻¹). This can be explained by the fact that in strength acid zone, load of porous composite surface is positive as shown by the pH_{pzc} value and the presence of many functional group on FT-IR spectra.
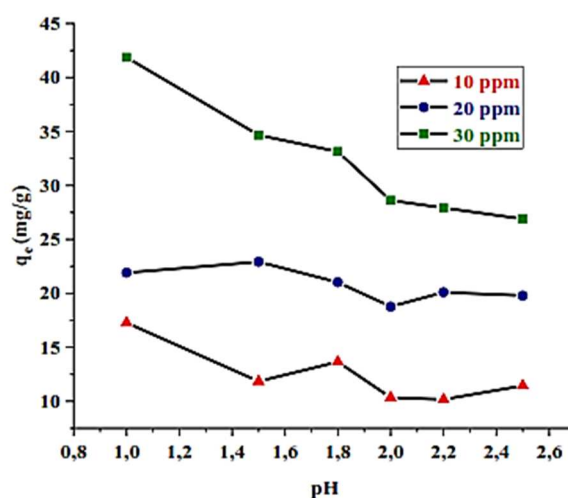

Figure 5: The effect of initial pH values on Cr(VI) ions adsorption on TiO₂-AC composite at different initial concentrations (conditions: adsorbent dose = 0.01 g, temperature = 25±2 °C, agitation speed = 150 rpm).

Effect of ionic strength

The effect of ionic strength on Cr(VI) ions adsorption is presented in Figure 6 which shows that, the adsorption capacity of Cr(VI) ions decreased slightly and tend to remain constant despite the addition of *NaCl* solution. This means that efficiency of TiO_2-AC composite materials on removal of hexavalent chromium (VI) ions in aqueous solution is not influenced by the presence of electrolytic strength. Existing of molecular interactions were suggested to explain this decrease on uptake capacity, these interactions included van der Waals interactions [17, 25]; dipole-ion and dipole-dipole interactions which occur between hexavalent chromium (VI) ions in solution.
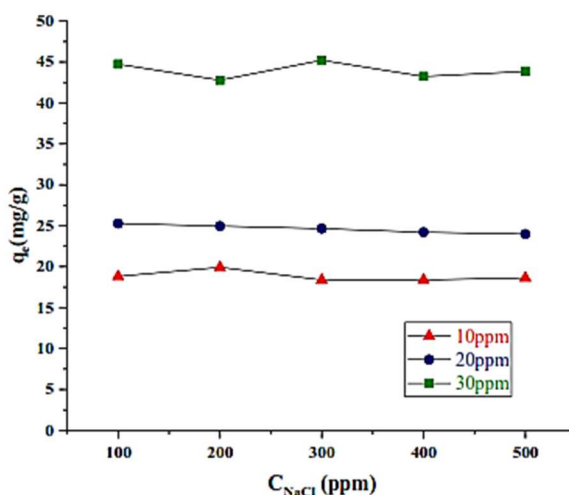

Figure 6: Effect of ionic strength on Cr(VI) ions Adsorption onto TiO₂-AC composite at different initial concentrations (conditions: adsorbent dose = 0.01 g, initial solution pH = 2, temperature = 25±2 °C, agitation speed = 150 rpm).

Kinetic modelling analysis

Examination of controlling mechanism of Cr(VI) ions adsorption process onto TiO_2-AC composite (namely, chemical reaction and mass transfer) was carried by applying pseudo-first- and pseudo-second-order, and intra-particle diffusion kinetic models to the experimental data. The best fitting model was chosen base on correlation coefficients R^2 of the linear regression form of the three kinetics models.

The linear form of pseudo-first-order expressed by the Lagergren equation [18] is given as:

$$ln\,(q_e - q_t) = ln\,q_e - k_1 \qquad\qquad (7)$$

where q_t (mg g^{-1}) is the amount of adsorbed Cr(VI) ions at time t, k_1 (min^{-1}) is the pseudo-first-order rate constant, and q_e the amount adsorbed at equilibrium of adsorption, derived from extrapolation of experimental data at time t = infinity. A straight line of $ln(q_e - q_t)$ versus t suggests the applicability of this kinetic model (Figure 7). q_e and k_1 (Table 2) were determined from the intercept and slope of the plot, respectively. The equilibrium fitted data shows low R^2 values, different for each initial concentration. However calculated q_e values (1.98 mg g^{-1}, 3.75 mg g^{-1}, and 3.74 mg g^{-1}) did not matched with the experimental values (4.88, 7.71, and 9.22 mg g^{-1}) for the three initial concentrations showed that the liquid-phase adsorption of hexavalent chromium (VI) ion onto porous composite did not fit well to pseudo-first-order.
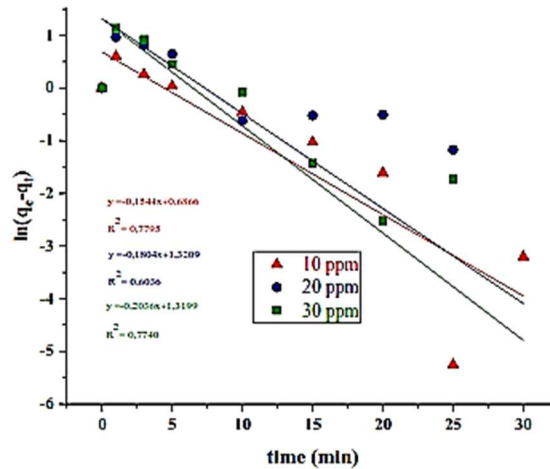
Figure 7: Plot of the pseudo-first-order kinetic model for Cr(VI) ions adsorption onto TiO₂-AC composite

The linearized form of pseudo-second-order kinetic model [26,27] is expressed as follow:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \qquad (8)$$

Plot of t/q_t *vs* t is presented in Figure 8 and the kinetic model parameters are presented in table 2. The values of determination coefficient R^2 for all experiments with initial Cr(VI) ions concentrations were higher than other models and closed to 1. The calculated values of adsorption capacity $q_{e, cal}$ (4.96; 7.71, and 9.40 mg g^{-1}) agree with experimental values $q_{e, exp}$ (4.88, 7.71, and 9.22 mg g^{-1}). These results suggested that adsorption mechanism of Cr(VI) ions onto TiO₂-AC composite occurred by chemisorption process and the pseudo-second-order kinetic model was the best fit. It is also observed that the k_2 value is highest for the concentration of 10 mg L^{-1} showing fastest adsorption, however q_e (adsorption capacity) is highest for 30 mg L^{-1}. This observation supports the fact that higher adsorption at higher initial concentrations is due to the influence of an important driving force from increased necessary concentrations to overcome all mass transfer resistances of the pollutant between aqueous and solid phases thus increasing the rate of hexavalent chromium (VI) ion adsorption onto porous composite [12].

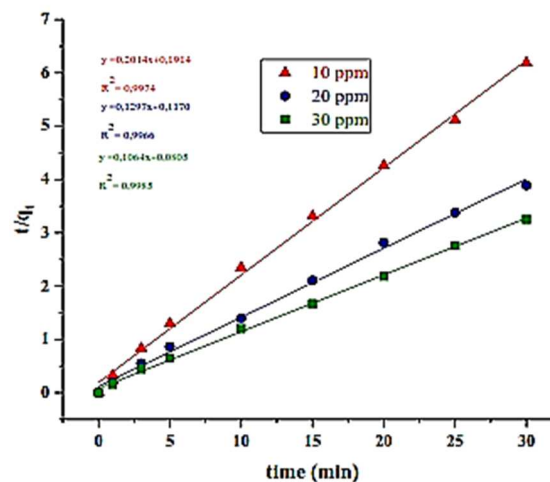*Figure 8: Plot of the pseudo-second-order kinetic model for Cr(VI) ions adsorption on TiO₂-AC composite*

To evaluate the limiting rate of the hexavalent chromium (VI) ions adsorption on porous composite, the possible contribution of intraparticle diffusion on Cr(VI) ions adsorption process was explored using Weber-Morris model [26]:

$$q_t = k_{int}\sqrt{t} + c \qquad (9)$$

where k_{int} was calculated from the slope of the plot of q_t versus $\sqrt{t}$. As shown in Figure 9, the linear portion of plot is not passing through the origin at each of the tested initial Cr(VI) ions concentrations, which indicates hexavalent chromium (VI) ions adsorption onTiO$_2$-AC composite is a complex process. Both the surface adsorption as well as intraparticle diffusion contributes to the rate determining step [20]. The constant K_{int} increases with the increasing of initial concentrations (table 3), indicating that the rate adsorption is limited by the diffusion of adsorbed hexavalent chromium (VI) ions within the composite pores at short time period. It is postulated that hexavalent chromium (VI) ion transported to the external composite surface through film diffusion and its rate is very high. After the saturation of surface the hexavalent chromium (VI) ions enter into the composite by intraparticle diffusion through pore and interior surface diffusion until the equilibrium is reached which is represented by the second straight [15].
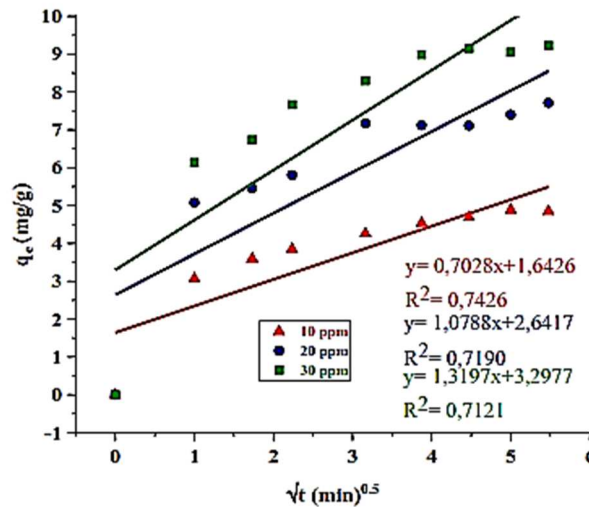

Figure 9: Plot of intraparticle diffusion kinetic model for Cr (VI) ions adsorption onto TiO$_2$-AC composite.
Table 2: Kinetics parameters of pseudo-first- and pseudo-second-order models for adsorption of Cr (VI) ion onto TiO$_2$-AC composite

C_i (ppm)	$q_{e,exp}$ mg g^{-1}	Pseudo-first order			Pseudo-second order		
		k_1 (L min^{-1})	$q_{e,cal}$ (mg g^{-1})	R^2	K_2 [g (mg min)$^{-1}$]	$q_{e,cal}$ (mg g^{-1})	R^2
10	4.85	-0.15	1.98	0.77	0.21	4.96	0.99
20	7.71	-0.18	3.75	0.60	0.14	7.71	0.99
30	9.23	-0.20	3.74	0.77	0.14	9.40	0.99

Table 3: Kinetic parameters of intraparticle diffusion model for adsorption of Cr(VI) onto TiO$_2$-AC composite

Intraparticle diffusion		
a (m^2 s^{-1})	K_{int} (mg L min$^{-1/2}$)	R^2
1.64	0.70	0.74
2.64	1.08	0.72
3.30	1.32	0.71

Modelling of adsorption isotherms

Non-linear adsorption isotherm models
The fundamental goal of equilibrium isotherm analysis is to describe the interactions established between adsorbate and adsorbent surfaces. In order to better describe the adsorption mechanism of Cr(VI) ions onto TiO$_2$-AC composite of the present work, four commonly-used adsorption isotherm models, namely the Langmuir, Freundlich, Dubinin Radushkevich (D-R-K), Temkin models in their non-leaner forms were applied to the

RESEARCHERID

THOMSON REUTERS

[Tcheka *et al.*, 10(1): January, 2021]
IC™ Value: 3.00

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

equilibrium data of Cr(VI) ions onto TiO$_2$-AC. non-linear regression analysis using the four isotherm models (Table 4).

Table 4 Equilibrium models equations used to investigate Cr(VI) adsorption on TiO₂-AC composite

Isotherm models	Equations	References
Langmuir	$q_e = \dfrac{q_{max}.K_L.C_e}{1 + K_L.C_e}$	[29]
Freundlich	$q_e = K_F.C_e^{1/n}$	[30]
Dubinin-Radushkevich	$q_e = q_S.exp(-k_{ad}.\varepsilon^2)$	[31]
Temkin	$q_e = \dfrac{RT}{b_T}\ln A_T.C_e$	[32]

The Langmuir model supposes that the adsorption takes place at specific surface sites as a monolayer on the surface [29]. q_{max} and K_L are the Langmuir constants which are related to the adsorption capacity. K_F and n are the Freundlich constants which are related to adsorption capacity and intensity, respectively.
The Dubinin-Radushkevich assumes a heterogeneous surface [*31*].
$\varepsilon = RT\ln(1 + \frac{1}{C_e})$, represent the Polanyi potential) q_S (mg g^{-1}) is the amount adsorbed per unit weight of adsorbent. The significance of applying Dubinin Radushkevich model is to determine apparent adsorption energy, E (kJ mol^{-1}) which is given by: $E = \frac{1}{\sqrt{2K_{ad}}}$.

The Timken isotherm contains a factor that explicitly taking into account of adsorbent-adsorbate interactions. The model assumes that heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage [22]. Conversely complex adsorption systems including the liquid-phase adsorption. b_T is the constant of adsorption energy, T is the temperature (K), A_T binding constant at equilibrium (L g^{-1}). To show the ability of different isotherms to correlate with experimental results, the theoretical plots from each isotherm have been fitted with the experimental data for adsorption of hexavalent chromium (VI) ions onto TiO$_2$-AC composite (Figures 10).

From Figure 10 and correlation coefficient values in table 5, Freundlich model present the highest R^2 value. The adsorption data fitted well with Freundlich isotherm model indicating the heterogeneous distribution of active sites on porous composite [21]. The values of the correlation coefficient is 1, indicating a good mathematical fit. The error function values were also agree with these observations. Freundlich model present the lowest error values. Based on these observed results, the useful error statistic functions should point out the Freundlich as best-fitting model after non-linear analysis.

To predict the adsorption efficiency of the adsorption process, the dimensionless Langmuir equilibrium parameters were determined by using the following equation:
$$R_L = \frac{1}{1+K_L C_0} \tag{10}$$
where C_0 is the initial concentration and K$_L$ is the Langmuir isotherm constant. The values of R_L were 1 (table 5) for the three initial concentrations (10, 20, and 30 ppm). These values equal to 1, indicating the favorable adsorption of hexavalent chromium (VI) ions on porous composite [23]. Moreover, the values of E are 282.22, 309.62, and 274.01 kJ mol^{-1} respectively (> 16 kJ mol^{-1}) of Dubinin Radushkevich indicating the chemisorption process. In addition, the R$_L$ values showed that the isotherm were linear (R$_L$ = 1). The variation of adsorption energy from Timken model were positives (19.37, 16.32, and 21.50 kJ mol^{-1}). That means the adsorption reaction is endothermic and spontaneous [24].
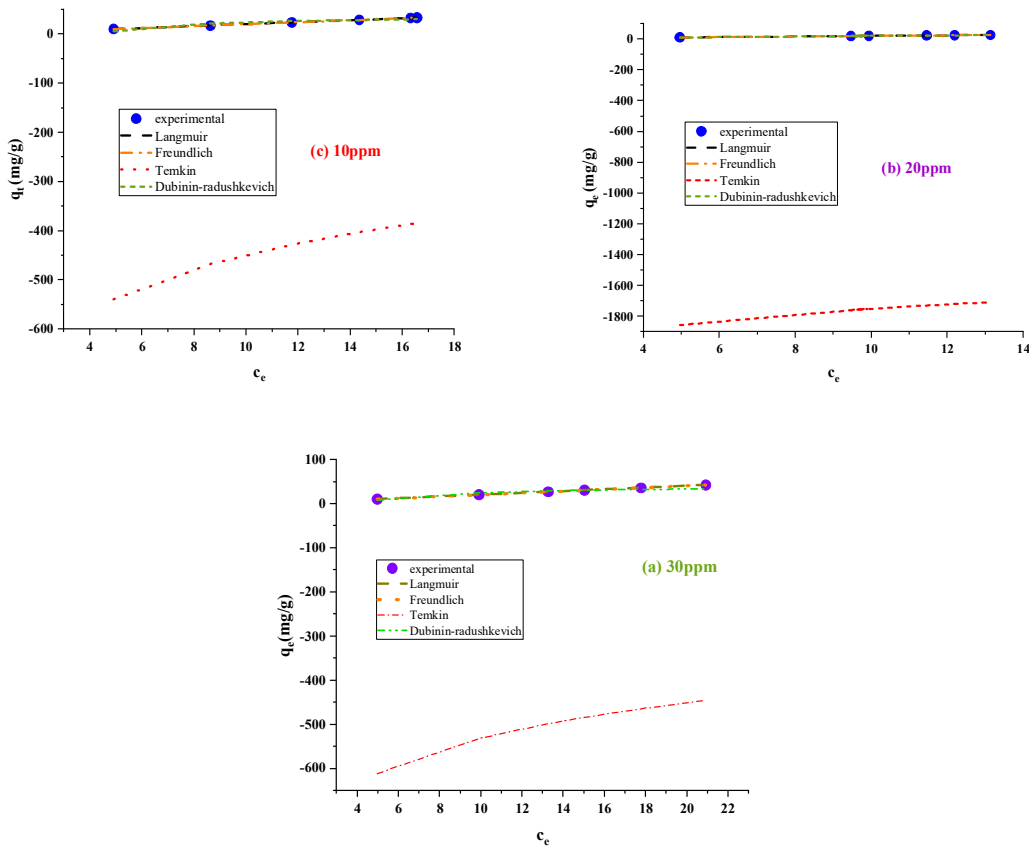
Figure 10: Adsorption isotherms modeling of Cr(VI) ion removal on TiO₂-AC composite (conditions: (adsorbent dose = 0.01 g, pH of solution = 1, temperature = 30 °C, agitation speed = 150 rpm, and volume of Cr(VI) solution = 20 mL)

Table 5: Adsorption isotherm parameters calculated using nonlinear analysis for Cr(VI) adsorption on TiO₂-AC composite

Isotherm	C_i (ppm)	q_{max} (mg L^{-1})	K_L
Langmuir	10	2.06×10^{16}	9.71×10^{-17}
	20	2.40×10^{15}	8.33×10^{-16}
	30	2.1×10^{16}	9.71×10^{-17}
	C_i (ppm)	K_f	n
Freundlich	10	2.000	1
	20	2.000	1
	30	2.000	1
	C_i (ppm)	q_s	K_{ad}
Dubinin Radushkevich	10	35.620	91.2×10^{-7}
	20	26.180	5.1×10^{-6}
	30	36.700	7×10^{-6}
	C_i (ppm)	b_T	A_T
Temkin	10	19.376	3×10^{-3}
	20	16.330	10^{-5}
	30	21.528	10^{-3}

Error analysis and best-fitting of the isotherm models
The best-fitting isotherm model was estimated based on the use of four functions to calculate the error deviation between experimental and predicted equilibrium adsorption data, after non-linear analysis. The results presented in Table 6 revealed that the Freundlich model is the most suitable model to satisfactorily describe the studied adsorption phenomenon. In fact, the highest R^2 value and the lowest RMSE, ARE, EABS and HYBRID values (as written in bold) were found when modelling the equilibrium data using the Freundlich model for non-linear regression analysis. Statistical analysis by χ^2 –test gave the same observations as those obtained by the error calculations, in which Freundlich model lowest values. From these results and those presented in previous work [12,32], the use of statistical tests (χ^2 –test, for example) and calculations of deviation errors between the experimental and predicted values allows to decide without ambiguity on the adsorption isotherm model which best describes the adsorption mechanisms.

Table 6: Non-linear approach of error analysis of the Isotherm models for adsorption of Cr (VI) ion on TiO₂-AC composite using six error functions and χ² as statistical tool

Isotherm	C(ppm)	R^2	χ^2	RMSE	ARE	EABS	HYBRID
Langmuir	10	0.999	2.5×10^{-6}	0.0047	0.0195	0.0188	6.130×10^{-5}
	20	0.999	1.9×10^{-5}	0.012	0.060	0.048	4×10^{-4}
	30	0997	6.2×10^{-2}	0.801	2.933	3.204	1.566
Freundlich	10	**1.000**	5.2×10^{-17}	2.1×10^{-8}	8.4×10^{-8}	8.6×10^{-8}	1.3×10^{-16}
	20	**1.000**	3.7×10^{-17}	1.7×10^{-8}	7.9×10^{-8}	6.7×10^{-8}	9.4×10^{-16}
	30	**1.000**	**2×10^{-18}**	**3.9×10^{-9}**	**1.6×10^{-8}**	**1.5×10^{-8}**	**6.4×10^{-17}**
Dubinin Radushkevich	10	0.880	3.549	0.489	23.548	1.956	88.721
	20	0.909	0.764	0.009	8.907	0.038	19.102
	30	0.740	3.629	1.660	20.225	6.639	90.924
Temkin	10	459.507	70295.2	689.2	3595.1	2757.04	1757380.04
	20	1777.236	1050074	2662.8	14634.5	10651.4	26251855.1
	30	533.563	86044.3	800.3	3820.2	3201.4	2151106.3

4. CONCLUSION

Adsorption of hexavalent chromium (VI) ions onto TiO₂-AC composite derived from mixture biomass of *Bauhinia Reticula* from Mayo-Oulo (Cameroon) and TiO₂ has been studied in the present work. Kinetic studies reveal that equilibrium is attained within 15 minute at pH=1. The maximum adsorbed hexavalent chromium (VI) ions in saline aqueous solution are 19.92 mg g⁻¹; 25.26 mg g⁻¹ and 45.21 mg g⁻¹ respectively for the initial concentrations of 10, 20 and 30 mg L⁻¹, respectively, at a stirring speed of 120 rpm. Adsorption follows pseudo-second-order and both the surface adsorption and intraparticle diffusion contribute to the rate determining step. χ^2-test and some errors calculated revealed that Freundlich isotherm fits the adsorption data adequately. The effect of ionic strength has a significant effect on hexavalent chromium (VI) ions adsorption. Being a useless and abundantly available material, *Bauhinia Reticula* seed hulls and TiO₂ which is not toxic can be used for synthesis of porous composite for industrial application for Cr(VI) ions removal from contaminated water.

REFERENCES
[1] C. Quantin, V. Ettler, J. Garnier, and O. Šebek, ''Sources and extractibility of chromium and nickel in soil profiles developed on Czech serpentinites,'' C. R. Geosci. 340, 872–882, 2008.
[2] A. Ashraf, I. Bibi, N. K. Niazi, Y. S. Ok, G. Murtaza, M. Shahid, A. Kunhikrishnan, D. Li, and T. Mahmood, ''Chromium (VI) sorption e_ciency of acid-activated banana peel over organo-montmorillonite in aqueous solutions,'' Int. J. Phytoremediat., 19, 605–613, 2017.
[3] S. Butera, S. Trapp, T. F. Astrup, and T. H. Christensen, ''Soil retention of hexavalent chromium released from construction and demolition waste in a road-base-application scenario,'' J. Hazard. Mater., 298, 361–367, 2015.

[4] X. Chen, C. Liu, Z. Xu, Y. Pan, J. Liu, and L. Du, ''An effective PDMS microfluidic chip for chemiluminescence detection of cobalt (II) in water,'' Microsyst. Technol., 19, 99–103, 2012.

[5] Y. Gao, and J. Xia, ''Chromium Contamination Accident in China: Viewing Environment Policy of China,'' Environ. Sci. Technol., 45, 8605–8606, 2011.

[6] WHO, ''Chromium in Drinking-Water. Background Document for Development of WHO Guidelines for Drinking-Water Quality,'' World Health Organization: Geneva, Switzerland, 1996.

[7] A. Sheikhmohammadi, Z. Dahaghin, S. M. Mohseni, M. Sarkhosh, H. Azarpira, Z. Atafar, M. Abtahi, S. Rezaei, M. Sardar, H. Masoudi, Journal of Molecular Liquids 255, 313 p., 2018.

[8] A. Sheikhmohammadi, B. Hashemzadeh, and A. Alinejad, ''Application of grapheme oxide modified with the phenopyridine and 2-mercaptobenzothiazole for the adsorption of Cr (VI) from wastewater: Optimization, kinetic, thermodynamic and equilibrium studies,'' Journal of Molecular Liquids, 2019.

[9] M. Sharma, M. Joshi, S. Nigam, S. Shree, D.K. Avasthi, R. Adelung, S.K. Srivastava, and Y. Kumar Mishra, ''ZnO tetrapods and activated carbon based hybrid composite: Adsorbents for enhanced decontamination of hexavalent chromium from aqueous solution,'' Chemical Engineering Journal, 2018.

[10] S. El-Nahas, H. M. A. Salman, and W. A. M Seleem. ''A new and successful utilization of Egypt alum company solid waste in Adsorptive removal of nitrates from water supplies,'' International Research Journal of Pure & Applied Chemistry, 15(3):1-17, 2017.

[11] M. Harouna, R. Djakba, and S. Mouhamadou, ''Adsorption of Copper Ions (Cu++) in Aqueous Solution Using Activated Carbon and Biosorbent from Indian Jujube (*Ziziphus mauritiana*) Seed Hulls,'' *Chemical Science International Journal,* 29(5): 13-24, 2020.

[12] N. Boldizsar, M. Andrada, I. Ceracella, M. Carmen, S. Luminita, and M. Cornelia, Comparative study of Cd(II) biosorption of cultivated *agaricus bisporus* and wild *lactarius piperatus* based biocomposites. Linear and nonlinear equilibrium modelling and kinetics. *Journal of the Taiwan institute of chemical engineers,* 2013.

[13] B. Aurelien, R. T. T. Donald,G. N. Nche, and D.Giscard, ''Anagho, Nonlinear equilibrium and kinetic study of the adsorption of 2,4-dinitrophenol from aqueous solution using activated carbon derived from a olives stones and cotton cake,'' African journal of environmental science and technology 13(9):365-480, 2019.

[14] J. Y. Kim, M. S. Balathanigaimani, and H. Moon, ''Adsorptive removal of nitrate and phosphate using MCM-48, SBA-15, Chitosan and Vulcanic Pumice,'' Water Air and Soil Pollution, 226 (431), 1-10, 2015.

[15] M. A. Hossain, H. H. Ngo, and W. Guo, ''Introduction of Microsoft Excel SOLVER function-spreadsheet method for isotherm and kinetic modeling of metals biosorption in water and wastewater,'' Journal of Water Sustainability, 3(4), 223- 237, 2013.

[16] O. Amrhar, H. Nassali, and M. S. Elyoubi, ''Application of nonlinear regression analysis to select the optimum adsorption isotherm for methylene blue adsorption onto natural Illite clay,''. Bulletin de la Société Royale des Sciences de Liège, 84, 116-130, 2015.

[17] N. Ayawei, A. N. Ebelegi, and D. Wankasi, ''Modelling and Interpretation of Adsorption Isotherms,'' Journal of Chemistry, ID 3039817, 2017.

[18] W. T. Tsa, C. Y. Chang, M. C. Lin, S. F. Chien, H. F. Sun, and M. F. Hsieh MF, ''Adsorption of acid dye onto activated carbon prepared from agricultural waste by $ZnCl_2$ activation,'' Chemosphere, 45(1):51-58, 2004.

[19] I. Mobasherpour, E. Salahi, and A. Asjodi. ''Research on the batch and fixed-bed column performance of red mud adsorbents for lead removal,'' Canadian Chemical Transactions, 2(1):83-96, 2014.

[20] L. Mouni, D. Merabet, A. Bouazaza, and L. Belkhiri, ''Desalination,'' 276, 148, 2011.

[21] C. Joana, Almeida, E. D. Celso Cardoso, S. Daniela, Tavares, Rosa Freitas, Tito Trindade, Carlos Vale, and E. Pereira. ''Chromium removal from contaminated waters using nanomaterials,'' Trends in Analytical Chemistry 118 277-291, 2019.

[22] M. Abbas, S. Kaddour, and M. Trari, ''Kinetic and equilibrium studies of cobalt adsorption on apricot stone activated carbon,'' Journal of Industrial and Engineering Chemistry, 20, 745–751, 2014.

[23] E. Demirbas, N. Dizge, M.T. Sulak, and M. Kobya, ''Chem. Eng. J.,'' 148, 480, 2009.

[24] G. Alberghina, R. Bianghini, M. Fichera, and S. Fisichella, "Dimerization of cibacron Blue F3GA and other dyes influence of salts and temperature," Dye and pigment. 46(3), pp. 129-137, 2000.

[25] Y. S. Ho and McKay, "The adsorption of lead (II) ion on peat. Reponse to comment," Water Research, vol. 33, pp. 578–584, 1999.

[26] W. J. Weber Jr, and J. C. Morris, "Kinetics of adsorption on carbon from solution," Journal of the Sanitary Engineering Division, vol. 40, pp. 31–60, 1963.

[27] Y. S. Ho, and G. McKay, G. ''Pseudo- second order model for sorption process,''. *Process Biochemistry,* 34, 451-465, 1999.

[28] V. K. Gupta, I. Ali, and V. K. Saini, "Defluoridation of wastewaters using waste carbon slurry," *Water Research*, vol. 41, no. 15, pp. 3307–3316, 2007.

[29] I. Langmuir, ''The adsorption of gases on plane surfaces of glass, mica and platinum,''. Journal of the American Chemical Society, 40, 1361-1403, 1918.

[30] H. M. F. Freundlich, ''Über die adsorption in lösungen, zeitschrift für physikalische,'' Chemie (Leipzig), 57, 385–470, 1906.

[31] M. M. Dubinin, and L. V. Radushkevich, ''The equation of the characteristic curve of the activated charcoal'', proc Acad Sci USSR Phys Chem sect 55: 331-7, 1947.

[32] M. C. Ncibi, Applicability of some statistical tools to predict optimum adsorption isotherm after linear and non-linear regression analysis, Journal of Hazardous Materials 153, 207–212, 2008.