Study Of Removing Of The Hexavalent Chromium Ion From Aqueous Solutions Using Coal And Ficus Modified

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ABSTRACT

This paper concludes the utilization of coal and ficus for removing chromium (VI) from aqueous solution. For this purpose, coal was without further purification processes. On the other hand, ficus modified was prepared after cleaning, drying, grinding. Results were analyzed and parameters were calculated for the pH, biosorbent doses, initial Cr (VI) concentration, and contact time by batch systems. The optimum removal of chromium was found at pH equal to 2 and 3 using coal and ficus modified, respectively with the removal efficiency of chromium from aqueous solutions 98.2% and 91.5%, respectively. The efficiencies were calculated using 0.2 g and 0.4 g and initial chromium concentration 20 mg L-1 and 25 mg.L-1 under a contact times of 30 min and 60 min using coal and ficus modified, respectively. FTIR spectra were conducted for adsorbent before and after chromium (VI) removal to discover the number of active sites and the functional groups on the adsorbent. The results of FTIR spectra were conducted for adsorbent before and after chromium (VI) removal to discover the number of active sites and the functional groups on the adsorbent. The results indicated the adsorption isotherm and kinetics are more compatible with Freundlich isotherm and pseudo-second-order consecutive.

Keywords: Chromium (VI), Coal, modified ficus.

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INTRODUCTION

Heavy metal pollution is one of the main reasons for environmental problems. The existence of toxic heavy metals such as chromium pollutants in aqueous streams resulting from the discharge of not treated minerals containing effluents in water bodies is a major environmental issue. Chromium in nature can be under many forms According to the degree of oxidation and there are two more stable forms which are chromium (III) trivalent and Hexavalent chromium (VI), but chromium (VI) represents the greatest threat to the environment and human health, due to its high solubility in water, its toxicity and potential for cancer, it may also cause nausea, diarrhea, liver and kidney damage, dermatitis, internal bleeding, and respiratory problems, and is categorized seventh among the 20 most dangerous pollutants by Environmental Protection. Agency Acute, United States of America (EPA, US) [1,2,3,4,5,6,7,8].

Pollution and deposition of chromium ions in soil and water will negatively affect the life and healthy environment of humans, animals and plants [9,10]. However, these treatment procedures are limited by some factors such as high energy and chemical requirement, incomplete removal, generation of toxic sludge [11]. Cr(VI) has been Widely use in a variety of industries like photograph, tannery, ceramic, glass industries, dyes, paints, fungicides chrome alloys and Metal industries. The wastewater from these industries is found to contain a large amount of chromium ^[12,13]. Various methods of removing chromium from aqueous environmental systems and improving wastewater treatment method is urgently needed. Several techniques ,including Ion exchange ^[14,15], reduction ^[16], chemical precipitation ^[17], polymer-based filtration, membrane separation ^[18,19], adsorption ^[20,21,22], electrochemical precipitation ^[23,24], solvent extraction ^[25,26], cementation ^[27], electrokinetic emediation ^[28], evaporation, reverse osmosis and bio-sorption ^[29] and emulsion per traction ^[30]. Therefore there is a need to develop low-cost and available absorbents to remove heavy metal ions from the aqueous environment. The different biomasses previously tested include sugarcane bagasse ^[31]. Nymphaea rubra ^[32], Ried water hyacinth roots ^[33], acid treated cashew nut shell ^[34]. modified corn stalk ^[35], Echornia crassipes ^[36] and activated carbon from Tamarind wood ^[37].

The eco-friendly green method by use coal and ficus modified can be utilization as economical, a low-cost, available alternative absorbent material and efficient adsorbents to remove of Cr (VI) from aqueous solutions.

Experimental

Productions the surface of absorbent

Ficus modified used in the study were get from local garden, wash it with water well, then with distilled water and put it in an oven at a temperature of 80 $^{\circ}$ C until it dries almost for 12 hours, then grind the leaves and the dry stem and place it on an watch class and spread it, the samples were treated with drops of concentrated H₂SO₄, turn it by the glass motor and leave for a period of time for the purpose is to draw in water molecules and to get carbonized at 120 $^{\circ}$ C oven for 24 h. It is then drenched with deionized water until any remaining acid is remove., the sample was dried by oven at 115 $^{\circ}$ C, Chilled, grinded and sifted to a volume of 300 m and stored in well sealed containers then utilize it as a surface.

Curve calibration of Chromium ions

 K_2CrO_4 (obtained from Merck) 0.25 g was dissolved in distilled water 100 mL volumetric flask, thereafter, drawing 1.5 mL from it, the volume was completed to 100 mL to prepared Cr(VI) then stored at room temperature. All working solutions were prepared by diluting the chromium (VI) stock solution with D.W at different concentrations. (5, 10, 15, 20, 25, 30 and 35 mg.L⁻¹) in 20 mL. Determination of Cr (VI) concentration at wave

length 370 nm by atomic absorption spectrophotometer (Shimadzu 1700, Japan).



Fig.1: The absorption spectrum of hex chromium shows the highest absorption peak at λ max 370 nm. Batch Adsorption Studies

20 mL test tubes were used for testing in batches performed at different pH (2-9), absorbent dose (0.05-0.4 g), were used different concentrations of Cr (VI) (5,10,15,20,25,30,35 mg.L⁻¹) and contact time was (10-60 min.) for coal and ficus modified. After adding surfaces of adsorbents pH was modify to required value by (1:1 HCl and 0.1N NaOH) and Measured using pH meter (Model pHep), Hanna Instruments, the tubes were shaken for (10-60 min.) at temperature 25 °C. After that the mixture was filtered by filter paper to separate the adsorbent from solution at 25 °C. The residual amount of Cr (VI) ions in water was determined using UV/Vis. spectrophotometer (Shimadzu, UV-1700) at the maximum wavelength 370 nm.^[38].

Calculation of adsorbed amount.

The amount of Cr (VI) absorbed on both surfaces was calculated from the difference between the primary and remaining Cr (VI) concentrations at various test time as follows equations (1,2) ^[44]:

Where

 q_t = Cr(VI)adsorbed (mg Cr(VI) g⁻¹ sorbent) at a given time.

 V_{s} = Volume of sample solution (L).

 C_i = Initial concentration (mg.L⁻¹).

 C_t = concentration at a given time (mg.L⁻¹).

m = Weight of sorbent (g).

%R= Removal efficiency of adsorption.

RESULTS AND DISCUSSION

Effect of initial pH

The impact of the pH on adsorption conduct was evaluated over a pH range from (2- 9) with making all other parameters constant, contact time (30,60 min), adsorbent dose (0.2,0.4 g), at temperature 25 °C and initial chromium concentrations are (20, 25mg.L⁻¹) for both coal and ficus modified. The results figure 2 showed that the maximum of Cr(VI) elimination efficiency of adsorption was (98.2%) for coal at pH = 2 and (91.5%) for ficus modified at pH = 3.

At acidic condition, the dominant species of Cr(VI) ions in solution are HCrO₄, Cr₂O₇⁻², CrO₄⁻², Cr₃O₁₀⁻² and Cr₄O₁₃⁻² ^[39]. These anionic species can absorb on the proton active sites of adsorbents, although they are very acidic Cr(VI) anions are towards lower pH ^[40]. This result is probably due to the positively charged surface at the acidic value since there is no competition to chromium ions in solution leading to this significant adsorption capacity through electrostatic forces of attraction. With increasing pH, hydroxyl ion (OH⁻) concentration increases. A competition occurs with the anionic species Cr (VI), causing a decrease in the amount of chromium absorbed and the number of active sites has decreased significantly ^[22]. It can be inferred from figure 2 that in neutral solution the surface charge of the adsorbents is negative at pH< 7, neutral at pH 7 and positive at pH > 7.

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Fig.2: Effect of pH on chromium removal by coal and ficus modified, adsorbent dose 0.2,04 g, Cr(VI) concentration 20,25 mg L^{-1} , contact time 30,60 min at 25^oC.

Effects of the amount of dosage

The effect of adsorbent dose on the adsorption capacity of the Cr(VI), was studied via different the initial amount of the adsorbents (0.05, 0.1, 0.2, 0.3, 0.4 g) by make all other parameters constant, pH 2, 3, while initial chromium concentrations were 20, 25mg.L⁻¹contact time 30, 60 min at 25° C for both adsorbent.

The impact of coal and ficus mass on the adsorbed amounts of Cr(VI) is appeared in figure 3. An increase in adsorbent dosage leads to an increase of removal efficiency from 55.3% to 85.9% when changing adsorbent amount for 0.2 g in coal case. However, the chromium adsorption efficiency increase from 35.8% to 81.6% for dosage at 0.4 g of ficus modified, which is probably Because the higher number of active sites at higher adsorbent concentration ^[22].



Fig.3: The effect of the adsorbent dosage on chromium (VI) elimination by coal and ficus modified, pH 2,3, contact time 30,60 min and Cr(VI) concentration 20,25 mg L^{-1} at 25^oC.

The effect of the concentration Cr(VI) of solutions

The effect of the initial concentration of Cr(VI) were studied via performance the experiments at different initial concentrations (5, 10,15, 20, 25, 30 and 35 mg.L⁻¹) with keeping whole other parameters constant, pH 2,3, adsorbent dose 0.2, 0.4 g, contact time 30, 60 min. at 25° C for both on adsorbents surfaces. The results of this

study are display in figure 4 showed that the maximum of Cr(VI) removal efficiency was 91.2% for coal at concentration 20 mg L⁻¹ and 71.5% for ficus modified at 25mg.L⁻¹. This diagram referred to the removal efficiency was decreases with increases the initial of Cr(VI) it is obvious that the surfaces adsorbents had a finite number of active sites, and these sites were saturated in a certain concentration, and therefore the filled adsorbent would not be able to utilization more Cr(VI) molecules ^[38].



Fig.4: Effect of initial Cr (VI) concentration on Cr(VI) removal by coal and ficus modified, pH 2,3 adsorbent dose 0.2,0,4 g and contact time 30,60 min at 25^oC.

Effect of contact time

The removal of Cr(VI) by adsorbents was investigated as a function of contact time from (10-60 min) with keeping all other parameters constant, pH 2, 3, adsorbent dose 0.2,0.4 g and initial chromium concentrations are

20,25mg.L⁻¹ at 25° C for both adsorbent. Maximum Cr(VI) removal was about 92.6, 79.8% at 30, 60 min. for coal and ficus modified are offered in figure 5. This may be because this verity that initially all adsorbent sites were vacant and the solute concentration gradient were high. However, later, with a gradual decrease in the number of active sites in the bulk solution^[41], and therefore no Important increases Event between 40-60 min. and 30-50 min for both absorbent.



Fig.5: Effect of contact time on Cr(VI) removal by coal and ficus modified, pH 2,3, adsorbent dose 0.2,04 g and Cr(VI) concentration $20,25 \text{ mgL}^{-1}$ at 25° C.

Characterization of adsorbent

FT-IR analysis has been done on the coal and ficus modified before and after the sorption process. To determine the types of functional groups responsible for the removal of chromium (figures 6 and 7) offers the FT-IR spectra for both on surfaces adsorbents before and after adsorption of process.

In both absorbent there is remarkable shift in positions of -OH and C -O group peaks Pointing Cr(VI) binding essentially with -OH and C- O groups Similarly the bending modes of aromatics have also shifted, indicative of association with the aromatic ring. The changes in FTIR spectra confirm the complexation of Cr(VI) with functional groups exists in the adsorbents. Table 1 shows the functional groups and their respective wavelengths identified in the spectra.



Fig.6: Fourier transform infrared (FTIR) spectra investigation of Cr(VI) onto coal before (A) and after (B) Cr(VI) adsorption.



Fig.7: Fourier transform infrared (FTIR) spectra investigation of Cr(VI) onto ficus modified before (A) and after (B) Cr(VI) adsorption.

Table 1: shows the functional groups and their respective wavelengths identified in the spectra.

	soi puon.		respective wavelengths identified in the spectra.			
Coal Wavelength	Cr /coal	Ficus	Cr/Ficus	Functional Groups	Ref.	
(cm ⁻¹) before	Wavelength (cm ⁻	Wavelength (cm ⁻	Wavelength (cm ⁻			
	¹) after	¹) before	¹) after			
3099	3149	3100	3200	-0H	42	
2357	2897 and 2943	2350	2375	СНЗ	22	
1685 and 1699	1764	1600	1700	-C=0	43	
1394	1506	1150	1225	Aromatic rings	44	
808 and 798	862	700	800	N-H	46	
663	684	750	810	aromatic	35	
				compounds		

Kinetic modeling for Chromium (VI)

There were two kinetic models verified so as to prognosticate data of Chromium (VI) absorption as a function of time by a pseudo-first-order and pseudo-second-order kinetic models at various concentrations. The first-order-model equation may be expressed as shown (3) ^[45].

$$\ln (q_e - q_t) = \ln q_e - k_1 t_{.....}(3)$$

Where q_e (mg.g⁻¹) is the quantity of Cr(VI) biosorbed at equilibrium, qt (mg.g⁻¹) the mass of Cr(VI) at any time and k_1 (min⁻¹) is the equilibrium rate constant of pseudo-first-order adsorption. The value of k_1 is determined from the slope of the plot of ln (qe –qt) versus t, respectively figure 8. The pseudo-second-order model, which leads to the following equation (4) ^[45]:

$$\frac{t}{qt} = \frac{1}{k_{2qe^2}} + \frac{t}{qe} \dots (4)$$

Where k_2 is the rate constant of pseudo-second-order (mg.g⁻¹.min). The values of k_2 and qe are determined from the slope and intercept, respectively of the plot of t/qt versus t (figure 9). The correlation coefficients R^2 of the second pseudo-order was greater and nearer to unity than the first-order pseudo-models. The calculated qe value from the pseudo-second-order model is in good approval with experimental qe value. This Indicates that a pseudo second-order regression coefficient can well describe depict the kinetics of chromium adsorption on coal and ficus modified. Kinematic parameters were recorded in Table 2 Cr(VI) sorption onto coal and ficus modified.



Fig. 8: Pseudo-first-order model kinetic for removal Cr(VI) from aqueous solutions by coal and ficus modified.



Fig. 9: pseudo-second-order model kinetic for removal Cr(VI) from aqueous solutions by coal and ficus modified.

Table 2: Evaluated parameters of pseudo-first-order and pseudo-second-order and and intra- particle diffusion for Cr (VI) metal ion sorption onto coal and ficus modified.

	incus incument				
Model	Adsorbent	qe (mg g ⁻¹)	$k_1 (min^{-1})$	R ²	
Pseudo-first-order	Coal	1.19	0.0292	0.9849	
	Ficus	0.028	0.0105	0.9837	
		qe (mg g ⁻¹)	k ₂ (g mg ⁻¹ min ⁻¹)	R ²	
Pseudo-second-order	Coal	0.0494	0.0533	0.997	
	Ficus	0.1081	0.4933	0.9992	
intra-particle diffusion		kp(mg.g ⁻¹ .min ^{1/2)}	С	R ²	
	Coal	0.0438	1.1707	0.9572	
	Ficus	0.0392	1.1889	0.862	

Intra-particle diffusion model

The intra-particle diffusion model advanced by Weber and Morris equation (5) ^[47,48] was used to forecast the actual rate-controlling step incloded in the adsorption process.

$qt = KP t^{1/2} + C.....(5)$

where qt is the Quantity of Cr (VI) adsorbed per unit mass of sorbent (mg.g⁻¹) at time t, kp is the rate constant of intra-particle (mg.g⁻¹ min^{-1/2}) and the value of C (mg.g⁻¹) represents proceed the thickness of the boundary layer, is intraparticle diffusion coefficient it shown in Figure 10

and Table 2. KP which was calculated from the slope of the linear portion of curves and C is intercept of the line, It is supposed that the greater the intercept, the greater the contribution of the surface adsorption. In the rate-controlling step intraparticle diffusion works important role in controlling the kinetics of the adsorption operation. The plot of qt against $t^{1/2}$ produces a straight line do not passing through the origin, this shows that the intraparticle diffusion is not the only rate limiting step, but other kinetic models may so control the rate of adsorption [49].



Fig.10: Intraparticle diffusion curve for adsorption of Cr (VI) onto coal and ficus modified. Adsorption isotherms

Study of the sorption equilibrium data information is significant for layout of a biosorption system ^[13]. Hence the data, gained from isothermal study, were tested examined with Langmuir and Freundlich models. The Langmuir isotherm was applied to estimation the adsorption capacity of adsorbents utilized and proposition that uptake of happens on a homogeneous surface by monolayer sorption without interplay contact between adsorbed molecules. In adding, the model suppose orderly energies of adsorption onto the surface and no trans immigration of the adsorbate. The linear form of the Langmuir adsorption isotherm is represented as equation (6) ^[47]:

$$\frac{1}{qe} = \frac{1}{bq^{0}Ce} + \frac{1}{q^{0}} \dots (6)$$

Where Ce is the equilibrium concentration of adsorbate (mg.L⁻¹), and qe is the amount of chromium adsorbed per gram at equilibrium (mg.g⁻¹), q⁰ (mg.g⁻¹) and b (L.mg⁻¹) are Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The values of q0 and

b were calculated from the slope and intercept of of the linear plot of 1/qe versus 1/Ce, respectively.

The most suitable adsorption system is the Freundlich adsorption model. Freundlich demonstrates that the absorption on occurred in several layers with a differentiated distribution of the effective sites, the Freundlich equation (7)^[47] is expressed linearly is presented as:

$$\log qe = \log k + \frac{1}{n} \log Ce \dots (7)$$

Where qe is the amount of Cr(VI) adsorbed at equilibrium (mg g^{-1}) and Ce is the residual concentration of chromium in solution (mg L^{-1}). The values of K and n were affect the adsorption isotherm. The greater these values, the greater the adsorption capacity. The values of K and n were obtained from the slope and intercept of a plot of log qe versus log Ce.

The results of the experimental data of the Langmuir and Freundlich models are recorded in Table 3. Based on the correlation coefficient that was calculated, it was found the Langmuir is more suitable than Freundlich model removal of the Cr(VI) from aqueous solutions on both adsorbents of surfaces. As ficus modified is adsorption capacities considered more than coal (Figure 11 and 12) [47].



Fig. 11: Freundlich plot of chromium (VI) loded on coal, ficus.



Fig. 12: Langmuir plot of chromium (VI) loded on coal , ficus modified.



Adsorbents									
Freundlich isotherms			Langmuir isother						
	Kf (mg g^{-1})	n(Lmg ⁻¹)	R ²	$q0 (mg g^{-1})$	b(Lmg ⁻¹)	R ²			
Coal	2.9302	1.273074	0.9831	4.8852	8.354	0.9512			
Ficus	3.555	0.73	0.9983	1.725	0.175	0.9781			

CONCLUSION

Chromium was eliminated from solution by coal and ficus modified via an electrostatic attraction mechanism coal and ficus modified could be fitting adsorbents for the elimination of chromium noxious from aqueous solutions. The adsorption was found to be intensely reliant on pH, adsorbent dose, contact time and Cr(VI) concentration. Highest elimination Cr(VI) was noticed at pH 2,3. The competencies of coal, ficus modified for chromium (VI) elimination from aqueous solutions were 98.2%, 91.5% consecutive.

FTIR characterization of the adsorbents has shown a clear difference in the initial state and Cr(VI)-loaded stated onto adsorbents. The kinetic data were very suit by a pseudo-second order model of both adsorbents. The Freundlich isotherm delivered the best correlation for adsorption of Cr(VI) on to coal and ficus modified.

The experimental statistics too displayed that intraparticle diffusion did not follow to express the mechanism for the adsorption of Cr(VI) onto coal and ficus modified adsorbents, respectively.

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