A Comparison between cooking tea-waste and commercial activated carbon for removal of chromium from artificial wastewater

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Abstract

The compare Cr (VI) adsorption characteristics removing from artificial wastewater by using decolorized cooking tea waste (CTW) and commercial activated carbon (AC) were examined. Adsorption experiments were carried out in a batch process and various experimental Parameters such as effect of pH, rpm, temperature, adsorbent dosage, contact time, and initial chromium ion concentration on percentage removal have been studied. Adsorption process was found for two adsorbents to be highly pH dependent. The maximum removal took place at the pH 2. A significant fraction of the total Cr (VI) uptake was achieved within 180 min and initial concentration of 50 mg/L. The maximum efficiency of chromium removal was 99.5% and 99.4% for CTW and AC, respectively and maximum adsorption capacity of chromium ion by using AC and CTW were 42.42, 42.46 mg/g respectively. Studies showed that the Freundlich adsorption model better fitted with the results than Langmuir with R^2 ***equal 0.991 and 0.974 for AC and CTW, respectively. The chromium uptake by the CTW and AC was best described by pseudo-second order rate model. This investigation verifies the possibility of using CTW as a low cost material for the removal of chromium from aqueous solution comparing with AC.***

Key Words: Chromium, Adsorption, activated carbon, cooking tea-waste

المقارنة بين استخدام مخلفات الشاي المطبوخ و الكاربون المنشط التجاري في إزالة الكروم السداسي من المياه المتخلفة المصنعة

الخلاصة:

يهدف البحث الى المقارنة في خواص الامتزاز بين استخدام مخلفات اوراق الشاي المطبوخ والكاربون المنشط. حيث عملية الامتزاز اجريت في منظومة دفعية وتم فيها دراسة المعاملات التالية مثل الرقم الهيدروجيني، سرعة الخلط، درجة الحرارة، وزن المادة المازة، زمن الخلط و تركيز الاكروم الاولي على نسبة الازالة. حيث اثبتت عملية الامتزاز

اعتماد كبير على الرقم الهيدروجيني حيث كانت اعلى نسبة امتزاز عند الرقم الهيدروجيني يساوي (٢). وكان زمن الاتزان بالنسبة الى تركيز الاكروم السداسي البالغ (٥٠) ملغرام/لتر هي ١٨٠ دقيقة. وكانت النسبة العظمى لإزالة الكروم باستخدام مخلفات أوراق الشاي المطبوخ هي ٩٩.٥ % وبالنسبة الى الكاربون المنشط كانت ٩٩.٤ % إما بالنسبة إلى قيمة الامتزاز العظمى لايون الكرم باستخدام الكاربون المنشط ومخلفات أوراق الشاي المطبوخ هي ٤٢.٤٢ و ٤٢.٤٦ ملغرام/غرام على التوالي. بينت الدراسة ان النتائج اكثر انطباقا مع موديل فريندلش منه مع موديل لانكماير. وكذلك انطباق البيانات مع الموديل من الدرجة الثانية من الناحية الكينماتيكية منه مع الموديل من الدرجة الاولى. ومن هذا البحث يتبين انه بامكان استخدام مخلفات الشاي المطبوخ كمادة رخيصة الثمن في عملية ازالة الكروم مقارنة مع الكاربون المنشط التجاري.

1. Introduction:

The presence of toxic heavy metals in water resulting from rapid industrialization and technological advances is a worldwide environmental problem [1]. While hexavalent (CrO_2^{-4} and $Cr_2O_2^{-7}$) and trivalent (Cr^{+3} and $CrOH^{+2}$) species of chromium are prevalent in industrial waste solutions, the hexavalent form has been considered more hazardous to public health due to its mutagenic and carcinogenic properties [2, 3]. Hexavalent chromium is present in the effluents produced during the electroplating, leather tanning, cement, mining, dyeing, fertilizer and photography industries and causes severe environmental and public health problems. Hexavalent chromium has been reported to be toxic to animals and humans and it is known to be carcinogenic [4]. Its concentrations in industrial wastewaters range from 0.5 to 270.000 mg /L [5]. The tolerance limit for Cr (VI) for discharge into surface waters is 0.1 mg/L and in potable water is 0.05 mg /L [6]. In order to comply with this limit, it is essential that industries treat their effluents to reduce the Cr (VI) to acceptable levels.

A wide range of physical and chemical processes are available for the removal of Cr (VI) from waste water such as electro-chemical, precipitation, ultra-filtration, ion exchange, electro-dialysis, reverse osmosis, chemical precipitation, and adsorption [7, 8, 9, 10]. The major drawbacks with these processes are high cost, toxic sludge generation or incomplete metal removal but adsorption has proved to be very effective same commercial activated carbons have been used as received and also after chemical modifications for Cr (VI) adsorption [9, 11].

Several studies are reported using adsorbents such as wool, rice, straw, coconut husks, peat moss [12], walnut skin, coconut fiber [13] and cotton seed hulls [14, 15]. Some studies had also utilized waste products like distillery sludge [16], sawdust, mustard seed cakes [17, 18], and coconut waste [19]. In spite of these developments quest for more techniques that are cost effective is still wanting.

In the present study compare between used AC and CTW, has been investigated for its property to remove Cr (VI) from synthetic aqueous solution.

2. Material and Methods

2.1. Preparation of adsorbent

Commercial granulated activated carbon (AC) was used as an adsorbent in the present work. It was supplied by Unicarbo, Italians to the Iraqi local markets. The physical properties were measured by oil research and development center and were coincided with that supplied by the manufacture. These physical properties are listed in table (1). The cooked tea waste (CTW) was collected from house and teashops in the Baghdad city, Iraq. CTW was decolorized using distilled water, dried at 60^{o}C for 24 hrs. The dried material was ground and sieved to get the particle size of 0.77 mm, which was used for this study. The physical characteristics of the adsorbent are shown in Table (1).

Table (1) Characteristic of AC and CTW

Parameter	AC	CTW
pH	7.84	6.35
Bulk density, g/cm^3	0.5261	0.2051
BET surface area, m^2/g	1100	495.54
Particle porosity	0.5	-----
Ash content	5	4.83
Particle size, mm	0.77	0.77

2.2. Batch adsorption studies

Batch experiments with AC and CTW were conducted to investigate the parametric effects of initial adsorbate concentration on Cr (VI) adsorption. All reagents used were of Abbrev grade (Sigma-Aldrich, Germany). Chromium samples were prepared by dissolving a known quantity of potassium dichromate ($K_2Cr_2O_7$) in distilled water and used as a stock solution and diluted to the required initial concentration (range from 25 to 300 mg /L). 100 ml of Cr(VI) solution of known concentration (Co) and initial pH was taken in a 250 ml of Erlenmeyer flask with a required amount of adsorbent and was agitated at a speed of 200 rpm in a thermostatic shaker at 20ºC for a specified period of contact time. Then the solution was filtered through a 0.45 µm membrane filter. The initial pH of the solution was adjusted by using either 0.1 N NaOH or 0.1 N H_2SO_4. Thermo UV-visible spectrophotometer (model genesys 10 UV, made in USA) was employed with 1,5-diphenylcarbazide in acid medium to determine the remaining concentrations of Cr(VI) in the sample. The filtrate was analysed for the remaining Cr(VI) concentration. The amount of Cr (VI) adsorbed in mg/g at time *t* was computed by using Equation (1).

$$qe = \frac{(Co - Ce) \times V}{m} \qquad (1)$$

Where:

*C*o and *C*e are the Cr (VI) concentrations in mg/L initially and at equilibrium, respectively, *V* is the volume of the Cr (VI) solutions in L, *m* is the weight of activated carbon in g.

The percentage of removed Cr (VI) ions (*R %*) in solution was calculated using Equation (2).

$$R(\%) = \frac{(Co - Ce)}{Co} \times 100 \qquad (2)$$

The effect of pH, temperature, agitation speed, dose of adsorbent, contact time, and initial concentration of Cr (VI), was investigated by varying any one of the process parameters and keeping the other parameters constant.

3. Reslts and Discussion:

3.1. Effect of pH

The initial pH of the metal solution is an important parameter affecting adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the of the adsorbate during reaction [20]. To examine the effect of pH on the Cr removal efficiency, the pH was varied from 2.0 to 12.0. As shown in Figure (1) the uptake of free ionic Cr^{+6} depends on pH, where optimal metal removal efficiency occurs at pH 2 and then declining at higher pH. Removal efficiency reaches 85.6 and 89.24 at PH 2 for AC and CTW, respectively and decreases with increase pH and reaches to 18 and 11 at pH 12 for AC and CTW, respectively.

Chromium exists mostly in two oxidation states which are Cr (VI) and Cr (III) and the stability of these forms is dependent on the pH of the system [21, 22]. It is well known that the dominant form of Cr (VI) at pH 2 is $HCrO_4^-$. Increasing the pH will shift the concentration of $HCrO_4^-$ to other forms, CrO_4^{-2} and $Cr_2O_7^{-2}$. Maximum adsorption at pH 2.0 indicates that it is the HCrO4- form of Cr (VI), which is adsorbed preferentially on the adsorbents.

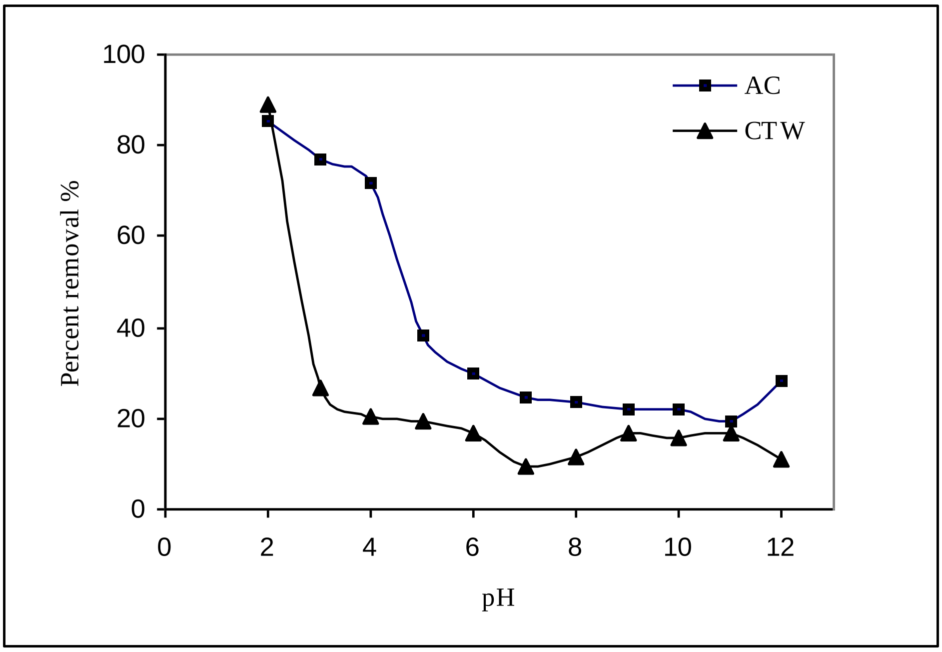

Figure (1) Effect of pH on chromium removal by AC and CTW [Cr (VI) concentration=50mg/L, agitation speed = 200 rpm, adsorbent dose = 0.5 g/L, contact time= 180 min, and temp.20^{o}C]

3.2. Effect of agitation speed

The effect of agitation speed on removal efficiency of Cr (VI) was studied by varying the speed of agitation from 50 to 300 rpm, while keeping the other parameter as constant. As can be seen from Figure (2), the Cr (VI) removal efficient generally increased with increasing agitation speed. The Cr removal efficiency of AC and CTW adsorbent increased from 14.8% to 85.6%, 68% to 89.2%, respectively. When agitation speed increased from 50 rpm to 200 rpm and the adsorption capacity remained constant for agitation rates greater than 200 rpm. These results can be associated to the fact that the increase of the agitation speed, improves the diffusion of Cr ions towards the surface of the adsorbents [23]. This also indicates that a shaking rate in the range 150-200 rpm is sufficient to assure that all the surface binding sites are made readily available for Cr uptake. Then, the effect of external film diffusion on adsorption rate can be assumed not significant. For convenience, agitation speed of 200 rpm was selected as the optimum speed for all the adsorbents.

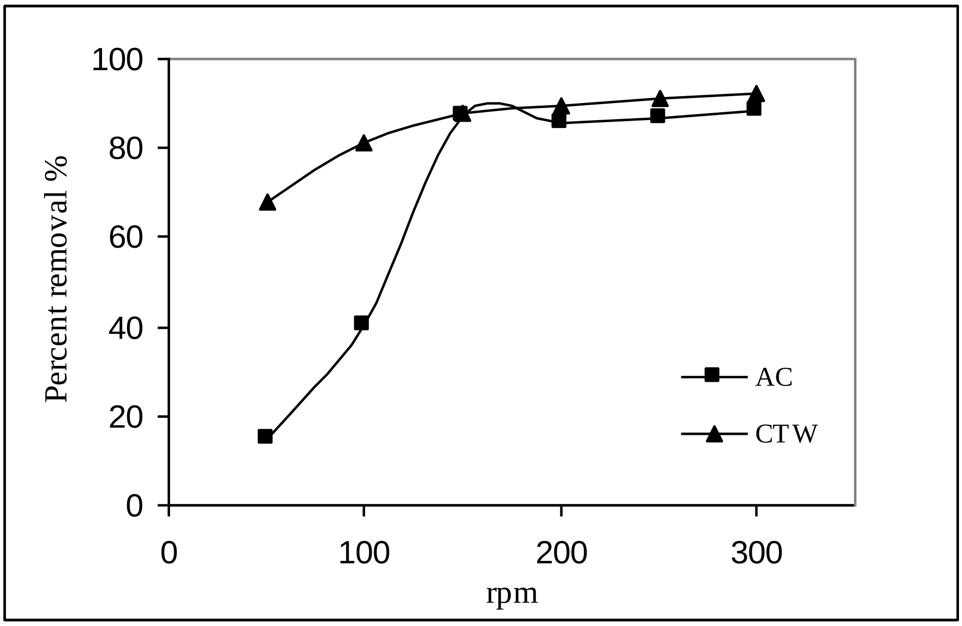

Figure (2) Effect of agitation speed on chromium removal by AC and CTW [Cr (VI) concentration=50mg/L, pH=2, adsorbent dose = 0.5 g/L, contact time= 180 min, and temp. 20^{o}C]

3.3. Effect of temperature

The effect of temperature on removal efficiency of Cr (VI) was studied by varying the temperature from 20 to 40^{o}C, while keeping the other parameter as constant. As can be seen from Figure (3), the Cr (VI) removals efficient generally decrease with increasing temperature for CTW and less effective for AC. The amounts of Cr (VI) removed after treatments at 20, 30, and 40 °C are about 74%, 73%, and 72.9%, for activated carbon and 81.2%, 74.4% and 73%, for cooking tea waste.

3.4. Effect of adsorbent dose

The dependence of Cr sorption on dose was studied by varying the amount of adsorbents from 0.05 to 0.9 g/l. Figure (4) presents the Cr removal efficiency for all the two types of adsorbents used. Form Figure (4) it can be observed that removal efficiency of the adsorbent generally improved with increasing dose. This is expected due to the fact that the higher dose of adsorbents in the solution, the greater availability of exchangeable sites for the ions.

At 50 mg/l concentration of Cr (VI), the maximum Cr (VI) removal efficiency was about 99.4% for AC at the dosage of 0.9 g/l, while for CTW it was 99.5% at the dosage of 0.9 g/l. This suggests that after a certain dose of adsorbent, the maximum adsorption sets in and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent.

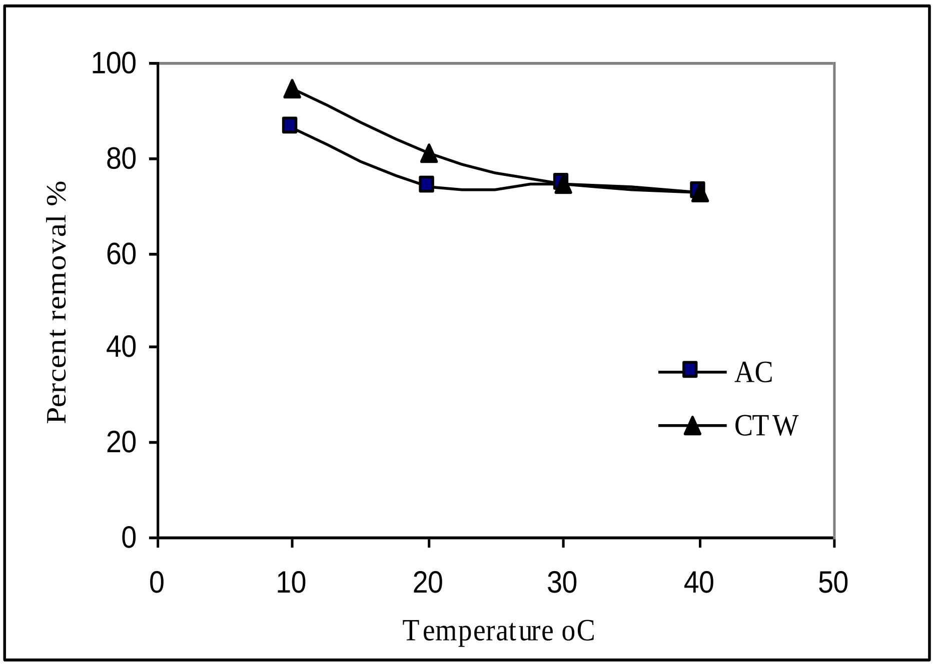

Figure (3) Effect of temperature on chromium removal by AC and CTW [Cr (VI) concentration=50mg/L, pH=2, adsorbent dose = 0.5 g/L, contact time =180 min, and agitation speed 200rpm]

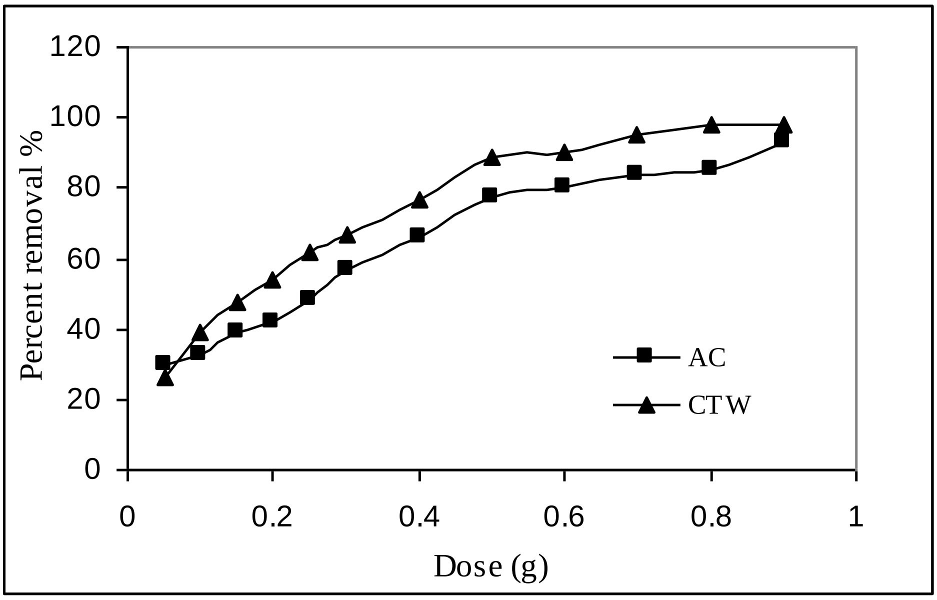

Figure (4) Effect of adsorbent dose on chromium removal by AC and CTW [Cr(VI) concentration=50mg/L, PH=2, temp. 20^{o}C, contact time= 180 min, and agitation speed 200rpm]

3.5. Effect of contact time

Figure (5) indicates that removal efficiency increased with an increase in contact time before equilibrium is reached [24]. It can be seen that Cr removal efficiency of AC and CTW increased from 58.76% to 99.4% and 68% to 99.5% respectively when contact time was increased from 15 to 180 min. Optimum contact time for both AC and CTW adsorbents was found to be 180 min. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

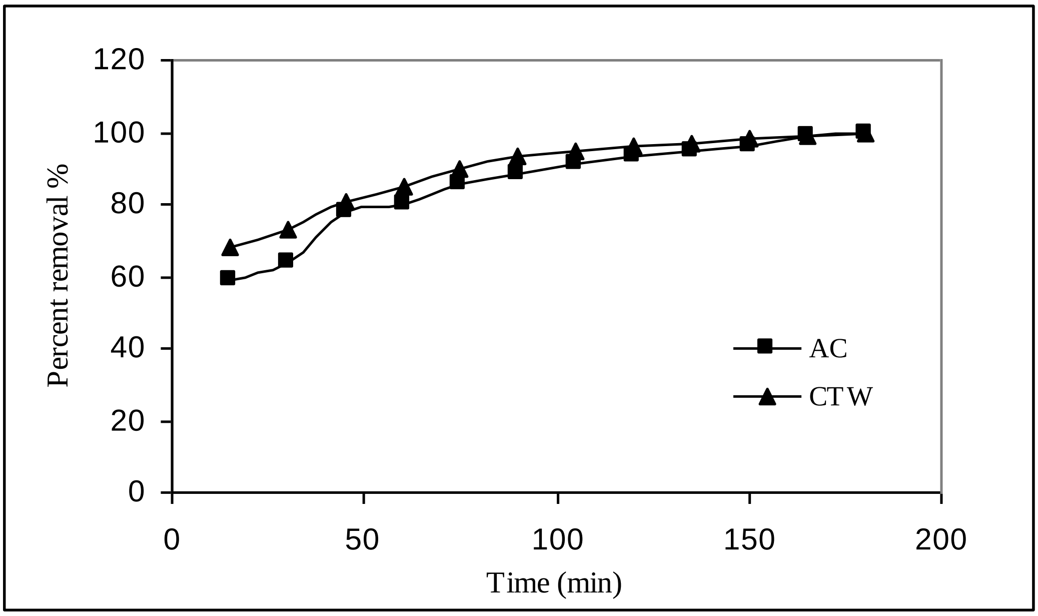

Figure (5) Effect of contact time on chromium removal by AC and CTW [Cr(VI) concentration=50mg/L, pH=2, temp. 20^{o}C, adsorbent dose = 0.9 g/L , and agitation speed 200rpm]

3.6. Effect of initial chromium concentration

The initial concentration provides an important driving force to overcome all mass transfer resistance of metal between the aqueous and solid phases. The effect of initial chromium concentration on the adsorption is shown in Figure (6). It can be seen from the figure that with increased Cr (IV), the percentage removal of chromium decreased. As seen in Figure (6), while the initial Cr (IV) concentration increased from 25 to 300 mg/L, the percent chromium removal by AC and CTW decreased from 90.6 to 50.4 % and 94.8 to 53.6, respectively. But the amount of Cr (VI) ions adsorbed per unit mass of adsorbent increased with the increase of the initial chromium concentrations. For AC and CTW, the adsorption capacity increased from 4.5 to

30.26 mg/g and from 4.74 to 32.16, respectively. This can be attributed to the effective pore diffusivity decrease with increasing initial metal concentration [25,26] and to a more efficient utilization of the sorptive capacities of the sorbent due to greater driving force (by a higher concentration gradient pressure) [27] .

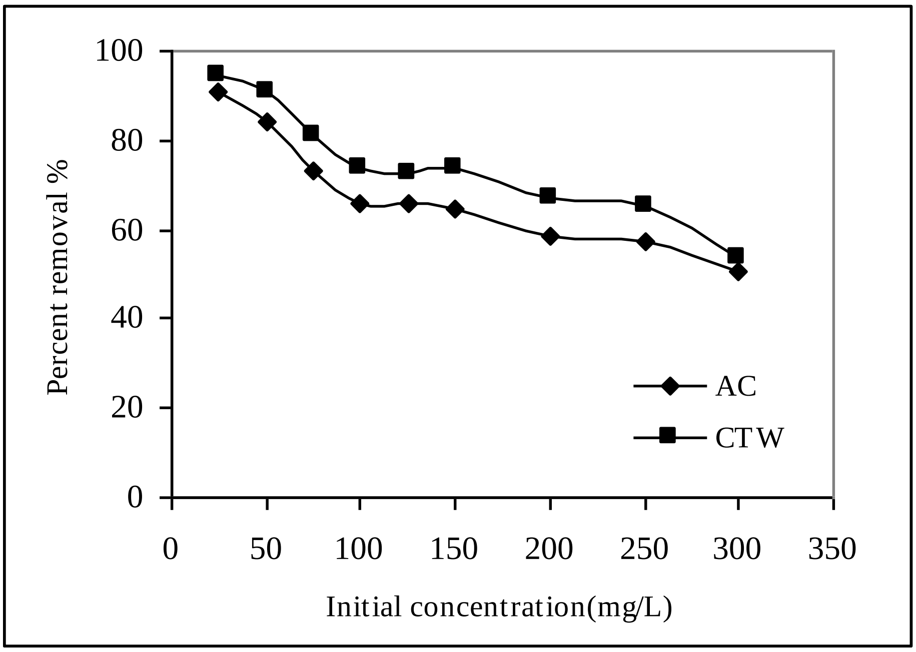

Figure (6) Effect of initial concentration on chromium removal AC and CTW [PH=2, temp. 20^{o}C, adsorbent dose = 0.5 g/L, contact time= 180 min, and agitation speed 200rpm]

3.7. Adsorption isotherm

To examine the relationship between sorbed (qe) and aqueous concentration Ce at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are most widely used. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. To get the equilibrium data, initial chromium concentration were varied while the adsorbent mass in each sample was kept constant. Three hrs of equilibrium periods for sorption experiments were used to ensure equilibrium conditions. The Langmuir isotherm relationship is of a hyperbolic form as shown in Equation (3).

$$qe = Qo\ b\ Ce / (1+b\ Ce) \qquad (3)$$

Where q_e (mg/g) is the amount of metal ions adsorbed onto the unit mass of the adsorbent to form a complete monolayer on the surface, Qo is the Langmuir equilibrium constant which is related to the affinity of binding sites, Ce the solution phase metal ion concentration, and b is the Langmuir constant [28]. The constants Qo and b are the characteristics of the Langmuir equation and can be determined from using statistica program. The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless separation factor (R_L) which describes the type of isotherm and is defined by Equation (4).

$$R_L = 1 / (1+b\ Co) \tag{4}$$

Where: b is a Langmuir constant and Co is the initial concentration [29].

The parameter (R_L) is related to the shape of the isotherm according to the following characteristics: RL > 1 represents unfavorable adsorption; RL = 1 corresponds to a linear relationship; 0 < RL < 1 is favorable adsorption and RL = 0 is irreversible. In the present study, RL remained between 0.169 to 0.709 for activated carbon and for cooking tea waste 0.111 to 0.600 (0 < RL < 1), which indicates that both activated carbon and cooking tea waste are good adsorbents for Cr(VI) ion removal.

The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface. The equation is commonly represented by equation (5):

$$qe = K_f\ Ce^{(1/n)} \tag{5}$$

Where K_f and n are the Freundlich constants that are associated with adsorption capacity and adsorption intensity, respectively[30]. The value of n between 2 and 10 shows good adsorption. The constants K_f and n are the characteristics of the Freundlich equation and can be determined from using statistica program.

The Langmuir and Freundlich equations were used to describe the data derived from the adsorption of Cr^{+6} by each adsorbent over the entire concentration range studied. As shown in Table (2) for this study Freundlich isotherm has a better fitting model than Langmuir.

Table (2) Langmuir and Freundlich constants for adsorption of Cr^{+6} using AC and CTW.

Two-parameter models		AC	CTW
Langmuir	Qo (mg/g)	42.42	42.46
	b (L/mg)	0.0164	0.0266
	R_L	0.709 – 0.169	0.600 – 0.111
	R^2	97.52	96.56
Freundlich	K_f (L/g)	2.660	4.306
	n	2.028	2.350
	R^2	99.10	97.42

3.8. Adsorption dynamics

The study of adsorption dynamics describes the solute uptake rate and evidently this rate controls the residence time of adsorbate uptake at the solid-solution interface. The kinetics of Cr(VI) adsorption on the activated carbons were analysed using pseudo first-order [31], pseudo second-order [32], Elovich [33,34] , and intraparticle diffusion [35, 36] kinetic models. The conformity between experimental data and the model predicted values was expressed by the correlation coefficients (R^2, values close or equal to 1). A relatively high R^2 value indicates that the model successfully describes the kinetics of Cr (VI) adsorption.

3.8.1. pseudo first-order equation

The pseudo first-order equation is generally expressed in Equation (6).

$$\frac{dq_t}{dt} = K_1(q_e - q_t) \qquad (6)$$

where:

q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg/g),

k_1 is the rate constant of pseudo first-order adsorption (L/min).

After integration and applying boundary conditions t = 0 to t = t and qt = 0 to qt = qt, the integrated form of Equation (6) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{K_1}{2.303}t \qquad (7)$$

The values of log (q_e - q_t) were linearly correlated with t. The plot of log (q_e - q_t) vs. t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively. Table (3) and Figure (7) summarizes the values of the corresponding model parameters.

3.8.2. Pseudo second-order equation

The pseudo second-order adsorption kinetic rate equation is expressed in Equation (8).

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \qquad (8)$$

Where:
k_2 is the rate constant of pseudo second-order adsorption (g/mg.min).
For the boundary conditions $t = 0$ to $t = t$ and $qt = 0$ to $qt = qt$, the integrated form of Equation (8) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + kt \qquad (9)$$

Which is the integrated rate law for a pseudo second-order reaction. Equation (9) can be rearranged to obtain Equation (10), which has a linear form:

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2 q_e{}^2} + \frac{1}{q_e}(t) \qquad (10)$$

The plot of (t/qt) and t of Eq. (10) should give a linear relationship from which qe and k_2 can be determined from the slope and intercept of the plot, respectively. Table (3) and Figure (8) summarizes the values of the corresponding model parameters.
The correlation coefficients for the pseudo-second order kinetic model are 0.998 and 0.999 for AC and CTW, respectively. These indicate that the adsorption system is probably best described by the pseudo-second order kinetic model.

3.8.3 Elovich equation

The Elovich model equation is generally expressed in Equation (11).

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \tag{11}$$

where:
α is the initial adsorption rate (mg/g·min)
β is the desorption constant (g /mg) during any one experiment
To simplify the Elovich equation, Chien and Clayton[37] assumed $\alpha\beta t \gg t$ and by applying the boundary conditions $qt = 0$ at $t = 0$ and $qt = qt$ at $t = t$ Equation (11) becomes:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta}\ln(t) \tag{12}$$

If Cr(VI) adsorption fits the Elovich model, a plot of *qt* vs. ln(*t*) should yield a linear relationship with a slope of (1/β) and an intercept of (1/β) ln(αβ). Table (4) and Figure (9) summarizes the values of the corresponding model parameters.

3.8.4 Intraparticle diffusion model

The intraparticle diffusion model is expressed in Equation (13).

$$R = k_{id}(t)^a \tag{13}$$

A linearised form of the equation is followed by

$$\log R = \log k_{id} + a\log(t) \tag{14}$$

Where:
R is the per cent Cr(VI) adsorbed
t is the contact time (h)
a is the gradient of linear plots
k_{id} is the intraparticle diffusion rate constant (h^{-1})
a depicts the adsorption mechanism
k_{id} may be taken as a rate factor, i.e., per cent Cr(VI) adsorbed per unit time.

The values of k_{id} were calculated from the slope and the R^2 values led to the conclusion that the intraparticle diffusion process is the rate-limiting step. Higher values of k_{id} illustrate an enhancement in the rate of adsorption, whereas larger *k*id values illustrate a better adsorption mechanism, which is related to an improved bonding between Cr(VI) ions and the adsorbent particles. Table (4) and Figure (10) summarizes the values of the corresponding model parameters.

Table (3) Langmuir and Freundlich constants for adsorption of Cr^{+6} using AC and CTW.

Adsorption material	First-order kinetic model			Second-order Kinetic model		
	K_1	qe (calculated)	R^2	K_2	qe (calculated)	R^2
Activated carbon	0.022	3.89	0.910	0.009	6.013	0.998
Cooking tea waste	0.033	3.45	0.967	0.013	5.907	0.999

Table (4) Elovich and interparticle diffusion model constants for adsorption of Cr+6 using AC and CTW.

Adsorption material	The Elovich model			The intraparticle diffusion model		
	β	α	R^2	K_{ia}	a	R^2
AC	1.038	1.7004	0.983	3.525	0.9631	0.983
CTW	1.293	6.0775	0.981	43.09	0.1657	0.979

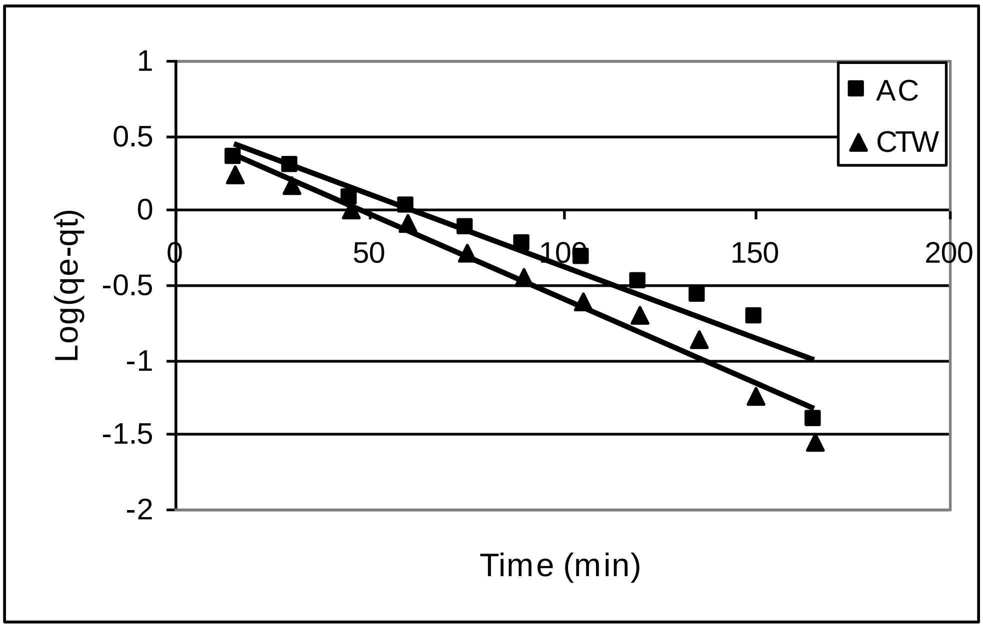

Figure (7) The pseudo first-order equation for chromium (VI) by AC and CTW.

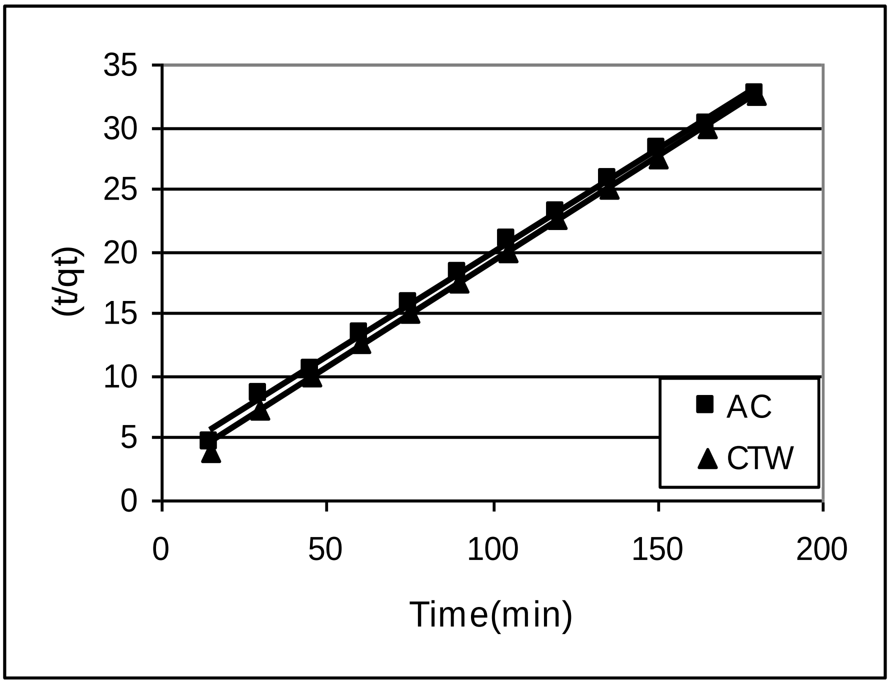

Figure (8) The pseudo second-order equation for chromium (VI) AC and CTW.

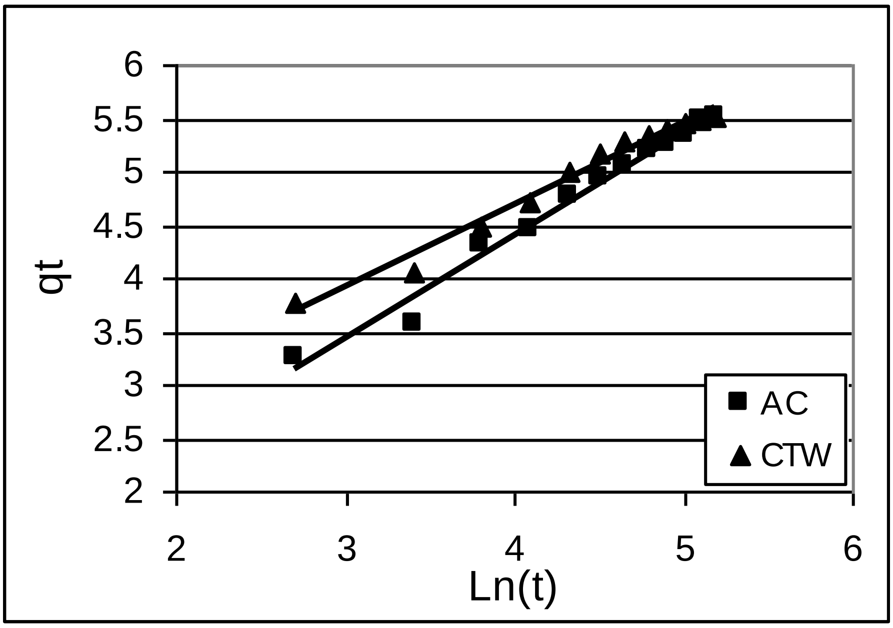

Figure (9) Elovich adsorption for chromium (VI) by AC and CTW.

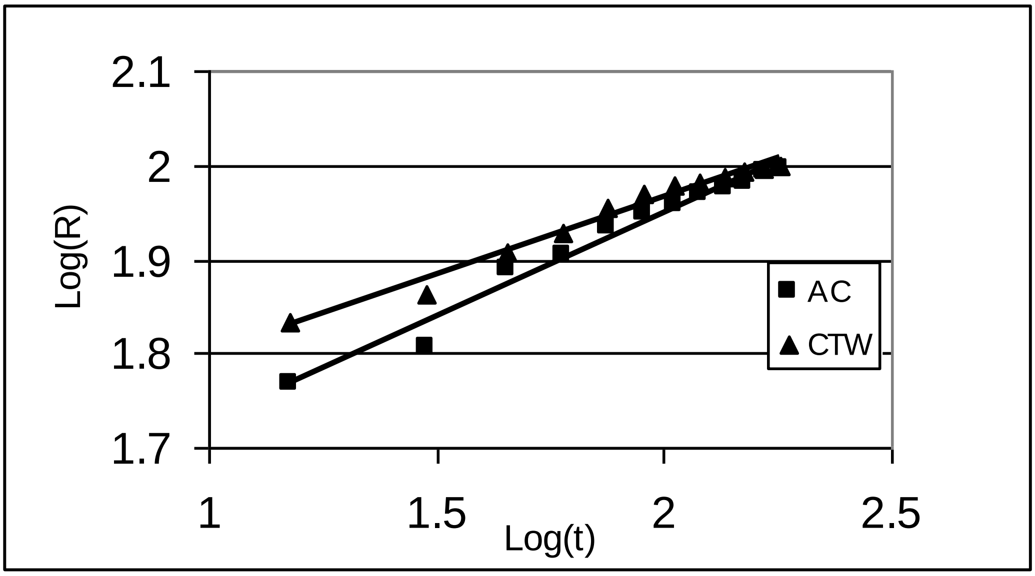

Figure (10) Interparticle diffusion adsorption for chromium (VI) by AC and CTW.

4. Conclusion:

Study shows possibility of using cooking tea waste for removing toxic hexavalent chromium ions from artificial wastewater in batch process in comparison with commercial activated carbon. The chromium uptake was dependent on the equilibrium pH and chromium concentration, with pH = 2.0, being the optimum pH value. Batch equilibrium sorption experiments were carried out in Erlenmeyer flasks for 180 min. (0.05 to 0.9 g of adsorbent, 100 mL of metal solution) in a rotary shaker. These experiments were done from aqueous Cr^{+6} solutions of initial concentrations ranged from 25 to 300 mg/ L. The maximum efficiencies of chromium removal were 99.5% and 99.4% for cooking tea waste and activated carbon, respectively.The experimental adsorption data observed agreed with the Langmuir and Freundlich adsorption model. The chromium (VI) uptake by the cocking tea waste and activated carbon followed pseudo second-order rate model.

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