

Removal of Toxic Hexavalent Chromium from Aqueous Solutions by adsorption onto treated rice waste

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Abstract

Treated rice wastewas obtained by pyrolysis of Egyptian rice waste (straw,husk and hull). It was characterized using chemical analysis,FTIR, SEM, XRF, and surface area analysis by BET. Treated rice waste(TRW)was used as an adsorbent to remove (Cr (VI)) from aqueous solution. Experiments were done in batch mode with the variables such as temperature, pH, initial Cr (VI) concentration, contact time, agitation speed and adsorbent dose. The adsorption kinetics well fitted using a pseudo second order kinetic model. The adsorption isotherm data were fitted to Langmuir as well as Freundlich adsorption model. The adsorption capacity of 22.22 mgg^{-1} was obtained. Thermodynamic studies revealed that the overall adsorption process was spontaneous, exothermic in nature. TRW could be used as low cost adsorbent for Cr (VI) removal from an industrial wastewater.

Keywords: rice waste, Adsorption,Cr(VI),Wastewater treatment, Batch processing, Kinetic parameters

1. Introduction

Hexavalent chromium is a very hazardous toxic metal to the aquatic environment and it is recognized as carcinogenic and mutagenic agent. Cr (VI) is produced in a variety of industries such as wood preservation, tanning and dyes, pigments for plastic, textiles and paints. (Yu et al., 2000). Many treatment techniques have been studied for Cr (VI) removal from industrial wastewater. These include chemical precipitation, membrane separation, ion exchange, reverse osmosis and solvent extraction (Jayakumar et al., 2014). New technique for removing chromium from wastewaters using bacteria (Sahin and öztürk, 2004; Chan et al., 2003; Xu et al., 2005), fungi (Goyal et al., 2003; Dursun et al., 2003), algae (Park et al., 2005) and various kinds of plants (Nakano et al., 2001; Cervantes et al., 2001) have been reported. Among all these, adsorption is the most commonly technique and a feasible alternative (Das et al., 2000).

By-products of agriculture are an innovative and promising technology for heavy metal ions removal from the aqueous environment. Many research has already been done on the different types of biosorbents for the removal of metal ions such as Hg, Ni, Cr, Cu, Pb, Cd, etc. The adsorbents are used in the natural form, or after modifying by chemical or thermal processes for increasing their sorption capabilities. Extensive work has been done for the removal of chromium employing waste agriculture materials (Sud et al., 2008).

A number of agriculture wastes like, modified coconut shell charcoal (CSC), saw dust, Maple sawdust, Hazelnut shell, Almond shell (Kurniawan et al., 2006), peanut shells and jatropha wood (Gueye et al., 2014) and wheat bran (Kaya et al., 2014) have been examined and showed a high efficiency in removing Cr(VI).

Rice waste in natural form as well as activated rice waste carbon was used as adsorbent for chromium (VI) removal and results were also compared with other adsorbents and commercial activated carbon (Srinivasan et al., 1988; Roy et al., 1993; Munaf and Zein, 1997; Guo et al., 2002; Ajmal et al., 2003; Bishnoi et al., 2004; Oliveira et al., 2005; Agrafioti et al., 2014). In the traditional production of rice a considerable portion of the rice waste is discarded by burning or dumped into the aqueous streams. This can create serious environmental problems. Searching for new ways of obtaining useful-adsorbent from rice waste in order to contribute to the conservation of a valuable natural environment is concerned.

The aims of this study are to evaluate the biosorption capacity of treated rice waste for removal of Cr(VI) from aqueous solutions and wastewater. Characterization of adsorbent was concerned. The effect of various parameters including pH, initial Cr(VI) concentrations, contact time, temperature, adsorbent dose and speed of agitation were investigated. Emphasis was also given on evolution of chromium adsorption isotherms, kinetics and thermodynamics about Cr(VI) adsorption by (TRW) in this work.

2. Experimental

2.1 Adsorbent

Treated rice waste (straw, husk, hull) used in the present study was obtained from a company for treatment of environmental residual, Alexandria. According to the manufacture, the treated rice waste was obtained by using physical reactor through destructive distillation

process in an inert atmosphere to avoid contamination of the environment with the gases rising from burning rice waste and take advantage of these waste. The treated rice waste (TRW) was used without further treatment.

2.2 Cr (VI) ions solution

1000 mg l⁻¹ stock solution of Cr (VI) was prepared. Solutions of diluted HNO₃ acid or NaOH (0.1 M) were used to adjust initial pH. All chemicals were AR grade reagents. To ensure the reliability, accuracy, and reproducibility of the data all the isotherm tests were replicated twice and the experimental blanks were run in parallel. Only the average values are reported. The maximum deviation observed is less than 5 %.

2.3 Characterization

IR spectra were obtained for (TRW) from 4000 to 400 cm⁻¹ in KBr disk (Perkin – Elmer). XRF analysis was performed using analytical Axios Advanced XRF & Electric muffle furnaces & Thermal Dryer. The Quantachrome Nova Automated Gas Sorption surface area analyzer was used to determine specific surface area (S_{BET}). The chemical analysis of (TRW) was performed using an energy-dispersive X-ray spectrometer attached to SEM(JEOL, JSM - 5300 SEM, OXFORD instrument).

2.4 Adsorption

Adsorption of Cr (VI) onto TRW was done in batch mode. In order to get the optimum conditions for Cr (VI) removal many parameters were investigated. The parameters studied were contact time, adsorbent dose (1-4 g/100 ml), pH(1-10), agitation speed (50-200 rpm), initial concentrations (25-100 mg l⁻¹) and temperature (25-40 °C). The experiments were out at room temperature (25±1°C) in Erlenmeyer flask (250 ml) and the total volume of the reaction mixture was kept at 100 ml. The mixture was shaken on mechanical shaker for 60 min. After that the mixture was filtered through 0.45 μm filter paper. The equilibrium concentration of Cr (VI) in the solution was determined by reacting with 1,5-diphenylcarbazide and the absorbance was measured in SPEKOL 1300UV – visible Spectrophotometer at wave length 540 nm.

3. Results and discussion

3.1 Adsorbent characterization

Chemical composition of TRW was determined by XRF. The results of XRF analysis are shown in Table (1). FTIR spectra of TRW before and after sorption of chromium (VI) are shown in Fig.1. The spectra showed the presence of many good functional groups for Cr(VI) adsorption such as OH at 3431.82 cm⁻¹, Si-H at 2351.42 cm⁻¹, Si-O at 1092.96 cm⁻¹, Si-C at 794.60 cm⁻¹ and Si-O-Si at 465.59 cm⁻¹. After Cr (VI) adsorption, noticeable broad band at 3625.53 cm⁻¹ and broad slight shift band from 1092.96 to 1036.95 cm⁻¹ and from 794.60 to 686.15 cm⁻¹ for OH, Si-O-Si and SiC were observed. This indicated that these functional groups participate in the adsorption of Cr (VI). Scanning electron microscope of TRW (Fig. 2) showed a system of complicated pore networks as a result of the presence of small cavities, cracks and attached fine particles over the surface. The brightness in some parts is probably due to the presence of silica. The TRW show a small particle (3 – 198.6 nm) which provides a larger surface area contaminant adsorption. The specific surface area of the adsorbent was 360 m²/g, as measured by BET.

Table 1. XRF Chemical analysis of TRW

Compound	Concentration (wt%)	Compound	Concentration (wt%)	Compound	Concentration (wt%)
CaO	3.72	K ₂ O	2.81	SiO ₂	49.02
ZrO ₂	0.006	P ₂ O ₅	0.32	TiO ₂	0.09
MgO	0.40	SO ₃	0.04	Al ₂ O ₃	0.42
Co ₃ O ₄	0.01	Cl	0.03	Fe ₂ O ₃	1.76
ZnO	0.02	SrO	0.03	MnO	0.08
Cr ₂ O ₃	0.063	NiO	0.019	LOI	40.99

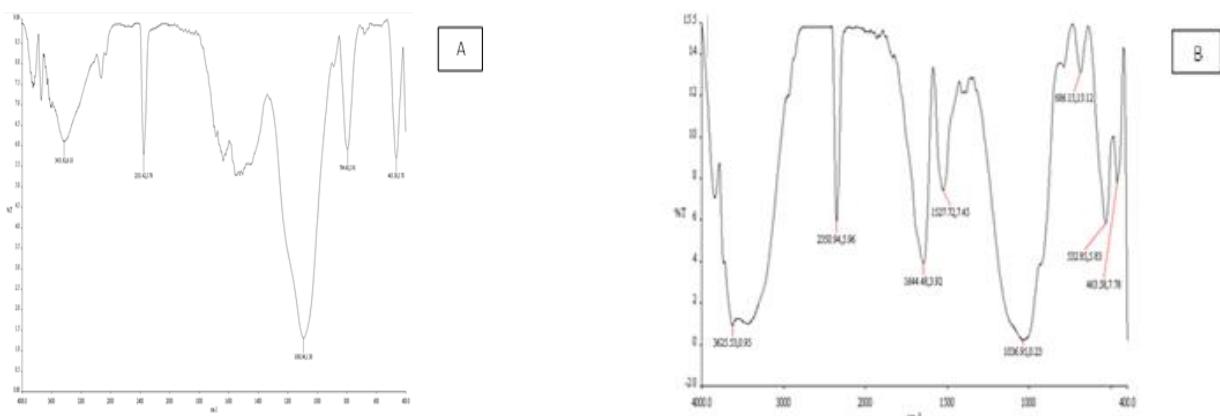


Figure 1. FTIR spectra of TRW (A) before adsorption, (B) after adsorption.

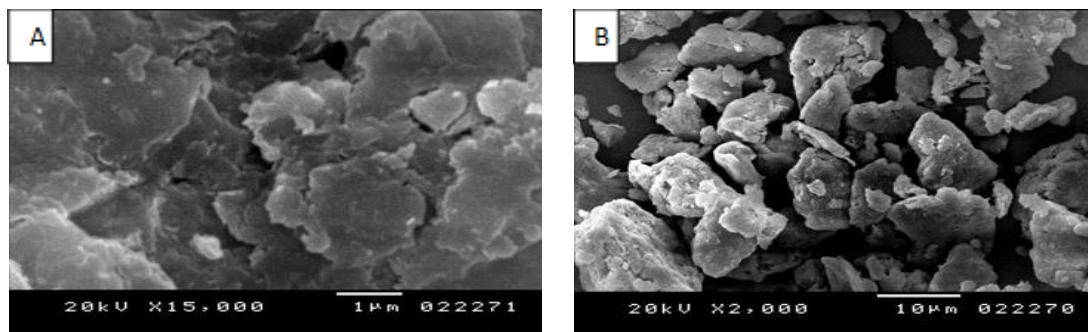


Figure 2. SEM of TRW A) before adsorption, (B) after adsorption

3.2 Effect of pH on adsorption process

The pH of the aqueous solution is an important factor affecting on the adsorbent surface charge, ionization degree, dissociation of functional groups on the active sites of the adsorbent and the solution solute chemistry. Fig.3 shows the dependence of different Cr (VI) species(CrO_4^{2-} , HCrO_4^- or $\text{Cr}_2\text{O}_7^{2-}$) on pH.(Sperling et al. 1992). At pH>1 deprotonated forms of Cr(VI) is noticed. Above pH 7 only CrO_4^{2-} ions exist in solution throughout the concentration range. In the pH between 1 and 6, HCrO_4^- is predominant (Greenwood and Earnshaw 1984, Nieboer and Jusys 1988). In this study,pH was varied from 1 to 10. The results presented in Fig. 4 indicate that the maximum adsorption of Cr(VI) ions was observed at pH 1. As mentioned by Rao et al., 2002, favorable effect of low pH can be attributed to presence of excess hydrogen ions that neutralization of negatives charges on surface of the

adsorbents, thereby facilitating the diffusion of hydrogenchromate ions (HCrO_4^-) and their subsequent adsorption.

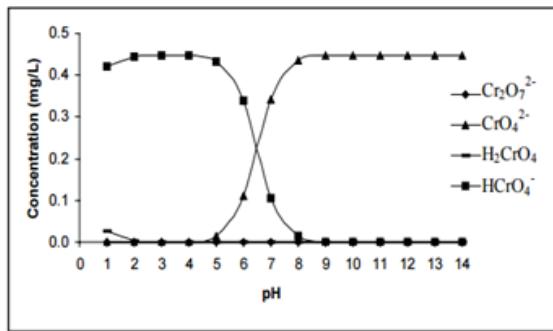


Figure 3. Cr (VI) speciation as a function of pH (Source: visual MINTEQ program)

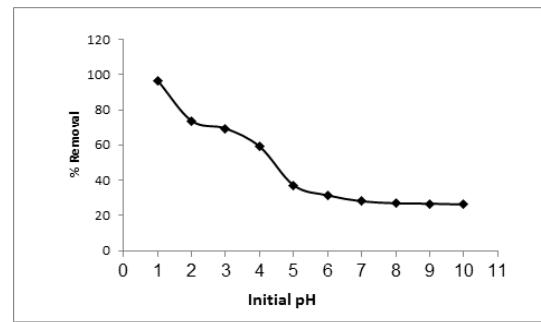


Figure 4. Effect of pH on removal of Cr(VI)

3.3 Effect of initial concentration and contact time

An enough contact time between adsorbate and adsorbent is required to achieve an equilibrium state. Fig.5 shows the removal percentage for $25\text{-}100 \text{ mg l}^{-1}$ Cr (VI) with contact times up to one hour. It is cleared that removal percentage of Cr (VI) was increasing with increasing contact time.

Fig.6 indicates Cr(VI) adsorbed per unit weight of adsorbent (q_t). At high concentrations (100 mg l^{-1} and 70 mg l^{-1}), a rapid uptake of Cr (VI) occurred in the first 10 min of contact and was followed by a more gradual uptake rate until equilibrium was reached. However, lower concentrations needed less time to reach equilibrium.

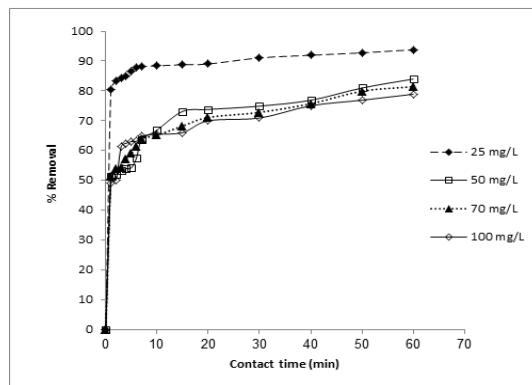


Figure 5. Effect of contact time and initial Cr (VI) concentration on the removal percentage of Cr from aqueous solutions ; pH, 1 ; volume, 100 ml; agitation speed, 200 rpm; adsorbent dosage, 4g/100 ml and temperature, 25°C

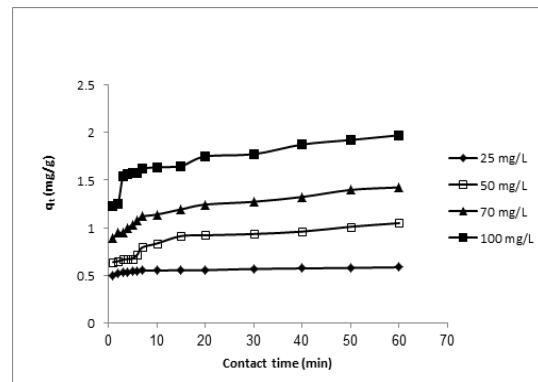


Figure 6. Effect of contact time and initial Cr(VI) concentration on the uptake of Cr per unit weight of adsorbent ; pH, 1; volume, 100 ml; agitation speed, 200 rpm; adsorbent dosage , 4g/100 ml and temperature, 25°C

3.4 Effect of adsorbent dosage

To investigate the effects of adsorbent dose on the adsorption of Cr(VI) was carried out using 100 mg l⁻¹ of Cr(VI) solutions. Fig.7explains that while the amount of Cr(VI) adsorbed (mg g⁻¹ adsorbent)by TRW decreased with increasing amount of adsorbent (g l⁻¹), the removal percentage increased from 46.55% to 78.89%.These results well agree withthe results recorded by Lee et al.(1995)for adsorption of Cr(VI) and Cr(III) on copper- coated moss, which suggested that the relationship between amounts of adsorbed and Cr adsorbed was close to a hyperboliccurve. The agitation speed was varied from 50 to 200 rpm to observe the effect of agitation on Cr(VI) sorption.Itwas found thatthe removal percentageincrease with increasing the speed which facilitates proper contact between the metal ions in solution and sorbent.

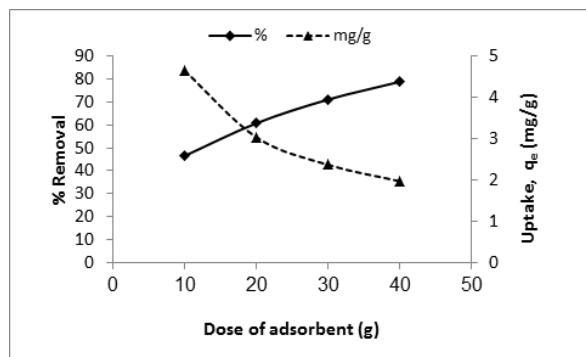


Figure 7. Effect of adsorbent dosage variation on the removal percentage and uptake of Cr(VI); pH,1; volume,100 ml; agitation speed, 200 rpm; [Cr(VI)] , 100 mg l⁻¹ and temperature, 25 °C

3.5 Adsorption kinetics

The kinetics of adsorption describes the rate of chromium ions uptake on TRWwhich controls the equilibrium time. To explain the mechanism of solute adsorption onto sorbents, three kinetics models, pseudo first order, pseudo second order andintra-particle diffusion modelmodels are used.

3.5.1 The pseudo-first order kinetic mode

The integral form of the pseudo first-order model generally expressed as follows:

$$\log (q_e - q_t) = \log q_e - k_1 t \quad (1)$$

where q_e and q_t are the values of amount adsorbed per unit mass at equilibrium and at any time t . k_1 is the equilibrium rate constant for pseudo-first order adsorption.The first order rate constant k_1 can be calculated from the slope of the plot of $\log (q_e - q_t)$ versus time fig (8). Table (2) shows that the theoretical values of q_e are not in good agreement with the experimental values calculated from Eq. (1). Therefore, the pseudo-first-order model is not appropriate for modeling the adsorption of Cr (VI) onto TRW.

3.5.2 The pseudo-second order kinetic model

The linearized form of the equation is expressed as:

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

Plotting of t/q_t versus t show a linear relation for the pseudo – second order kinetics model, the value of q_e is easily calculated from the slope, and the second order rate constant k_2 can be obtained from the intercept.

Table (2) and Fig.8 indicate that the adsorption data were well fit by a pseudo-second-order kinetic model as compared to a fit by a pseudofirst-order kinetic rate model.

Table 2. Rate adsorption constants for three kinetic models at different initial concentrations of Cr (VI).

C _o (mg/L)	Pseudo first-order model					Pseudo- second order model					Intra- particle diffusion		C	R ²	
	q _e (Exp.)	K ₁ (min ⁻¹)	R ²			ARE	K ₂ (g/mg min)	q _e (Cal)	R ²			AR E	K _i (mg g ⁻¹ min ^{-1/2})		
			q _e (Cal)	R ²	ARE				R ²	AR E					
25	0.58 6	0.044	0.09 5	0.95 2	20.94 7		3.529	0.58 5	0.99 9	0.0 43		0.01	0.5 12	0.87 6	
50	1.04 9	0.044	0.39 9	0.93 3	15.49 1		0.421	1.05 5	0.99 7	0.1 43		0.064	0.5 82	0.92 2	
70	1.42 4	0.051	0.51 8	0.94 0	15.90 6		0.349	1.43 5	0.99 7	0.1 93		0.077	0.8 61	0.96 4	
100	1.97 2	0.046	0.58 3	0.93 5	17.60 9		0.317	1.97 6	0.99 7	0.0 51		0.092	1.2 98	0.85 2	

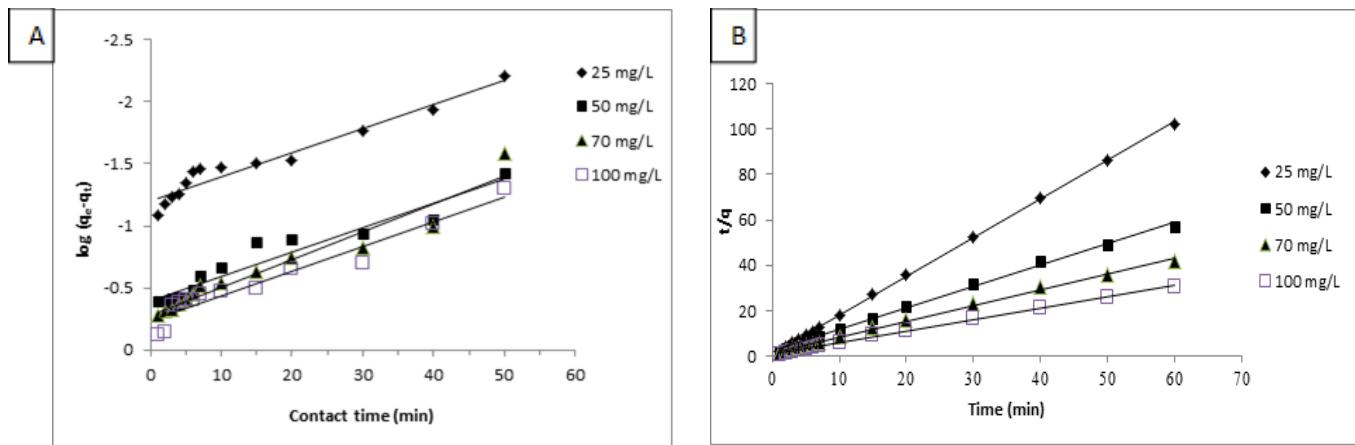


Figure 8. Pseudo first order (A) and Pseudo second order (B) kinetics plot for Cr(VI) adsorption at different initial concentration; pH, 1; volume, 100 ml; agitation speed, 200 rpm; adsorbent dosage, 40 g l⁻¹ and temperature, 25 °C

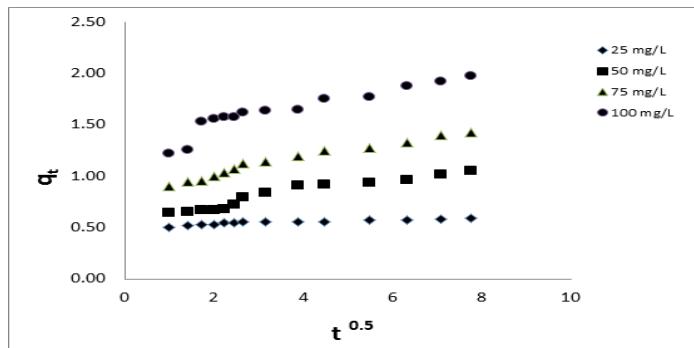


Figure 9. Intra- particle diffusion plots for adsorption of Cr(VI) on TRW

3.5.4. Test of kinetic validity

The goodness of fitting of the kinetic data was evaluated by the average relative error (ARE) function calculated by the following equation:

$$ARE = \frac{100}{n} \sum_{i=1}^n \left[\frac{q_{e\text{ cal}} - q_{e\text{ exp}}}{q_{e\text{ exp}}} \right] (4)$$

Where n is the number of observations. Based on the values of ARE presented in Table 2, the data fit better to the pseudo-second order kinetic model at all initial concentrations of Cr(VI), suggesting that the adsorption rate is dependent more on the availability of the adsorption sites rather than the concentration of metal ion in solution.

3.6 Adsorption isotherm

Adsorption of Cr(VI) by TRW was modeled using the Freundlich and Langmuir isotherms.

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_{0,b}} \frac{1}{C_e} \text{Langmiurequation(5)}$$

$$\ln q_e = \frac{1}{n} \ln C_e + \ln k \text{Freundlich equation} \quad (6)$$

where q_e is the amount of metal adsorbed per unit mass of adsorbent (mg g⁻¹), C_e the equilibrium concentration of solute in the bulk solution (mg L⁻¹), Q_0 the solid phase concentration corresponding to the complete monolayer coverage of adsorption sites (Huang and Smith, 1981). The Freundlich isotherm constants k_f and n are determined from the intercept and slope of a plot of $\ln q_e$ versus $\ln C_e$ (Fig.10). The slope $1/n$ is measure of the sorption intensity or surface heterogeneity (Benjamin, 1978). For $1/n = 1$, the partition between the two phases is independent of the concentration. The situation $1/n < 1$ is the most common and corresponds to a normal an L-type Langmuir isotherm (Reed, and Matsumoto, 1993), while $1/n > 1$ is indicative of a cooperative sorption (Haghresht and Lu, 1998) which involves strong interactions between the molecules of adsobrate. In this study the constant were found to be $k_f = 0.108$ and $n = 1.07$. Value of n is greater than unity indicating beneficial sorption and is classified as L-type isotherms reflecting a high affinity between adsorbate and adsorbent.

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:

$$R_L = \frac{1}{1+bC_0} \quad (7)$$

Where C_0 is the initial concentration of Cr(VI). Thus R_L is a positive number whose magnitude determines the feasibility of the sorption process. The process is irreversible if $R_L = 0$, favorable if $R_L < 1$, linear if $R_L = 1$ and unfavorable if $R_L > 1$. The dimensionless separation factor, R_L was determined at different adsorbent doses. The value of R_L was found to be less than 1 and greater than 0 indicating the favorable adsorption of Cr (VI) on TRW. From Langmuir sorption isotherm Q_0 and b were calculated from the intercept and slope of plots of $1/q_e$ versus $1/C_e$ at different doses (Fig. 10). The Cr(VI) adsorption capacity on TRW was 22.22 mgg^{-1} .

The adsorption isotherm data were fitted to Langmuir as well as Freundlich adsorption model.

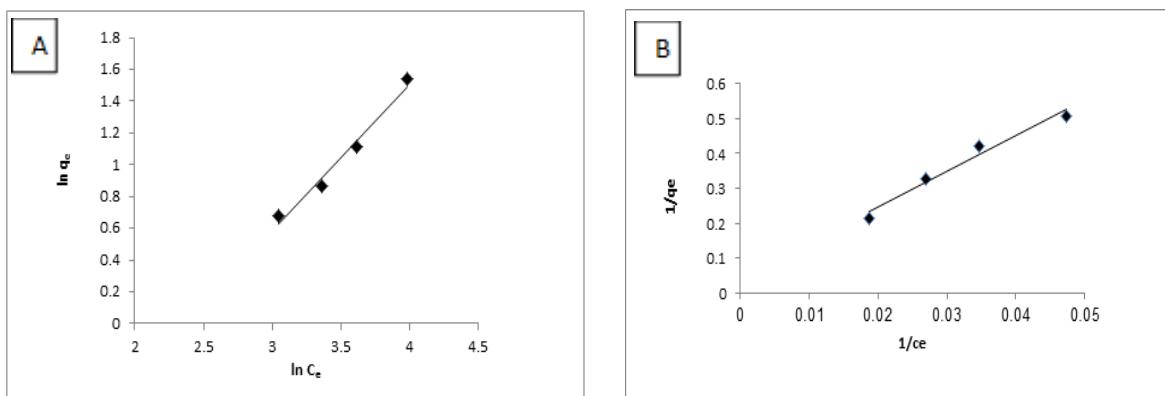


Figure 10. Freundlich (A) and Langmuir (B) isotherm for Cr(VI) adsorption; pH, 1; [Cr (VI)] = 100 mg l^{-1} ; volume, 100 ml; agitation speed, 200 rpm; and temperature, 25°C

Table 3 shows a comparison between the adsorption efficiency of TRW, with different adsorbents for the Cr(VI). It is clear that the TRW used in the present study has a significant adsorption capacity in comparison to other adsorbents: rice husk (0.6 mg g^{-1}), groundnut husk (11.4 mg g^{-1}), riverbed sand (0.79 mg g^{-1}) and wheat bran (5.28 mg g^{-1}). These results indicate that the TRW applied in this study is a better alternative to other low cost adsorbents. However, higher adsorption capacities of 140, 131 and 59.88 mg/g were respectively reported for activated carbons derived from jatropha wood and peanut shells modified by KOH, Modified groundnut shell and treated waste newspaper.

3.7 Thermodynamics

The effect of temperature on adsorption process was investigated by changing temp from 25°C to 40°C at C_0 ; 100 mg l^{-1} , pH 1, adsorbent dose; 4 g/ 100ml, v; 100 ml, agitation speed; 200 rpm and 60 min of contact time.

The results show that the adsorption capacities (q_e) and removal percentage of Cr(VI) decrease with rise in temperature. The Gibb's free energy change (ΔG°) can be evaluated from the flowing equation (Hamadi et al., 2001; Karthikeyan et al., 2005):

$$\Delta G^\circ = -RT \ln k_0 \quad (8)$$

$$K_0 = C A_e / C_e \quad (9)$$

Where k_0 is the equilibrium constant ($m^3 mol^{-1}$), $C A_e$ is the concentration of Cr(VI) adsorbed on TRW at equilibrium ($mg l^{-1}$), C_e is the Cr(VI) concentration in solution at equilibrium ($mg l^{-1}$), R is the universal gas constant ($8.314 J mol^{-1} K^{-1}$) and T is temperature(K) (Rojas et al., 2005; Zakaria et al., 2009).The Gibb's free energy change is also related to enthalpy change(ΔH°) and entropy change (ΔS°) at constant temperature (Fan et al., 2008) :

$$\ln k_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

The values of ΔH° and ΔS° were calculated from the slope and intercept of the Van't Hoff plot ($\ln k_0$ vs. $1/T$) (Sarin and Pant, 2006). The calculated values are given in Table (4). The results show that sorption of Cr(VI) on TRW is an exothermic process. The value of Gibb's free energy change (ΔG°) for these processes becomes less negative with increasing temperature, which shows that sorption is less favored at high temperatures. Negative values indicated the feasibility and spontaneity of the adsorption. Enthalpy change was $-63.610 kJ mol^{-1}$, which indicated the exothermic nature of adsorption process. The negative entropy change (ΔS°) for the process was caused by the decrease in degree of freedom of the adsorbed species (Rojas et al., 2005; Sari and Tuzen, 2008; Gasser et al., 2007).

Table 3. Comparison of adsorption capacity of different sorbents for Cr (VI) removal.

Adsorbent	$Q_{max} (mg g^{-1})$	Reference
Mixed waste tea	94.34	Cherdchoo et al., 2019
Manufacture-grade Fe_2O_3 -carbon foam	33	Chang-Gu et al., 2017
Magnetic magnetite (Fe_3O_4) nanoparticles	34.87	Shalini et al., 2016
Rice husk carbon	47.61	Khan et al., 2016
Treated waste newspaper	59.88	Dehghani et al., 2016
Peels of pea (<i>Pisum sativum</i>) pod	4.33	Sharma et al., 2016
Modified groundnut shell	131	Samson et al., 2016
Rice husks	0.6	Sumathi et al., 2005
Modified Groundnut husk by Sulfuric acid followed by silver impregnation	11.4	Dubey and Gopal, 2007
Riverbed sand modified by H_2SO_4 (40%)	0.79	Yadav et al., 2013
Wheat bran modified by tartaric acid	5.28	Kaya et al., 2014
Biochar produced solid wastes	44.05	Agrafioti et al., 2014
Marine green algae <i>Halimedagracilis</i>	55.55	Jayakumar et al., 2014
Activated carbons derived from jatropha wood and peanut shells modified by KOH	140.84 and 106.38	Gueye et al., 2014
Treated Rice waste(TRW)	22.22	Present study

Table 4. Thermodynamic parameters for Cr (VI) adsorption on TRW

T (K)	k_o	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (J/mol K)
298	3.74	-3.266		
303	2.3	-2.098		
308	1.5	-1.038	-63.610	-202.778
313	1.1	-0.248		

3.8 Removal of Cr(VI) from wastewater

Real wastewater was used to study its effect on capability of TRW to adsorb Cr(VI). Sample was collected from El-Umoum drain (contains several industrial effluents and agriculture drain from Alexandria Governorate) near lake Maruit, Alexandria, Egypt in polyethylene bottle. pH and salinity were measured in situ. The sample was filtered through Whatman no 0.42 filter paper and spiked with standard solution of Cr (VI).

Wastewater sample was transferred into an Erlenmeyer flask into the incubator shaker, optimum conditions were applied based on present study (dose: 4g, pH: 1, speed of rotation: 200 rpm, temperature: 25 °C). After 60 min, the suspensions were filtered then Cr (VI) concentration was measured by Spectrophotometer at wave length 540 nm. The results show that salinity and pH were 4.9 and 8.15 respectively, 81% removal of toxic chromium from real wastewater was detected. The difference between the percent removal of Cr(VI) from aqueous solution (96.75%) and wastewater is attributed to the presence of other ions and impurities in the wastewater, in which a slight hindrance to Cr(VI) adsorption may occur compared to the prepared solution.

4. Conclusion

The results of the present studies indicated that TRW prepared by thermal treatment of Egyptian rice wastewater was an efficient adsorbent for chromium (VI) removal ions from aqueous solutions and wastewater. Experiments were performed as a function of initial pH, metal ion concentration, temperature, agitation speed and adsorbent dosage. At optimum adsorption conditions, the predicted removal efficiency of Cr(VI) by TRW reached 96.75% and 81% for aqueous and wastewater respectively. The adsorption was found to follow the pseudo-second-order model from the kinetic studies. The equilibrium data fitted well to Langmuir model with the maximum adsorption capacity of 22.22 mg/g. The calculated thermodynamic parameters indicated the exothermic and spontaneous nature of the adsorption process.

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