LOW –COST ADSORBENT FOR HEAVY METALS UPTAKE FROM AQUEOUS METAL ION SOLUTION: A REVIEW

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ABSTRACT
In this research, adsorption of chromium (VI) ions on Eihhornea Crassipies has been studied through using batch adsorption techniques. The main objectives of this study are to 1) To investigate the chromium adsorption from aqueous solution by Eihhornea Crassipies, 2) To determine appropriate kinetics parameters of chromium (VI) adsorption on Eihhornea Crassipies. The results of this study showed that adsorption of chromium by Eihhornea Crassipies reached to equilibrium after 180 mts and the change of chromium removal efficiency was observed. The Pseudo – first order kinetic model over the other model rendered it best in adsorption of Cr (VI) on Eihhornea Crassipies

INTRODUCTION

One of the heavy metals that have been a major focus in water and wastewater treatment is chromium and the hexavalent form of it has been considered to be more hazardous due to its carcinogenic properties. Chromium has been considered as one of the top 16th. toxic pollutants and because of its carcinogenic and teratogenic characteristics on the public, it has become a serious health concern (Torresdey *et al.,* 2000).Chromium can be released to the environment through a large number of industrial operations, including metal finishing industry, iron and steel industries and inorganic chemicals production (Gao *et al.,* 2007). Eucalyptus bark (Sarin and Pant, 2006), maize bran (Singh *et al.,* 2006), coconut shell, waste tea, rice straw, tree leaves, peanut and walnut husks. The obtained results showed that the adsorption of chromium (VI) by Eihhornea Crassipies. The obtained results showed that the adsorption of chromium (VI) by Eihhornea Crassipies. The aims of this study are to 1) investigate the chromium adsorption from aqueous solution by Eihhornea Crassipies 2) To find optimum adsorption isotherm as well as the rate of adsorption kinetics.

MATERIAL AND METHODS
Preparation of adsorbent
The Eihhornea Crassipies was ground and particle sizes between 75 and 300 microns were obtained by passing the milled material through standard steel sieves. Then, they used for experiments without washing or any other physical or chemical treatments.

Batch sorption experiments
The sorption studies were carried out at 30 ±1°C. Solution pH was adjusted with H_2SO_4 or NaOH. A known amount of adsorbent was added to samples and was agitated by jar test at 250 rpm agitation speed, allowing sufficient time for adsorption equilibrium. Then, the mixtures were filtered through filter paper, and the Cr (VI) ions concentration were determined in the filtrate using spectrophotometer

Adsorption kinetics
Pseudo – first order and second order models were applied to test experimental, data and thus elucidated the kinetic adsorption process. Lagergren proposed a method for adsorption analysis which is pseudo – first order kinetic equation in the form

$$\text{Log } (q_e - q_t) = \log q_e - K_1/2.303 \, t$$

The value of K_1 for Cr (VI) adsorption by Eihhornea Crassipies was determined from the

plot log (q_e – q_t) against t (fig.1). The parameter of pseudo – first –order model are summarized in table 1.Although the correlation coefficient (R^2) is generally greater than 0.923 for all initial concentrations under the limit of the experimental q_e for the pseudo – first order kinetic model. As such, the adsorption of Cr (VI) on Eihhornea Crassipies cannot be best described by the equation of Lagergren does not fit well to the whole range of contact time and is generally applicable over the initial stages of the adsorption processes. Therefore the pseudo – second order kinetic model as shown in Eq was used to study the adsorption kinetic of the present system

$t/q_t = 1/ k_2 q^2 e + (1/ q_e) t$ where k_2 (g/mg min) is the second –order rate constant the q_e and K_2 can be calculated from the slope and intercept of the plots t/q_t versus t (Fig 2)

The high correlations and coefficients and high agreement that exist between the calculated and experimental q_e values of the pseudo – first order kinetic model over the other model rendered it best in adsorption of Cr (VI) on Eihhornea Crassipies. This confirms that the sorption data are well represented by the pseudo – first order kinetics for the entire sorption period.
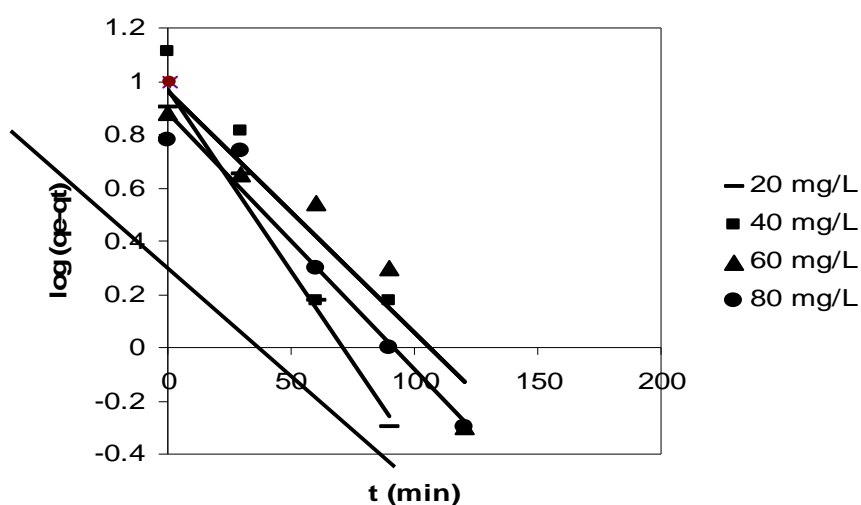

Fig. 1: Pseudo- first- order kinetics for adsorption of chromium (VI) on Eihhornea Crassipies
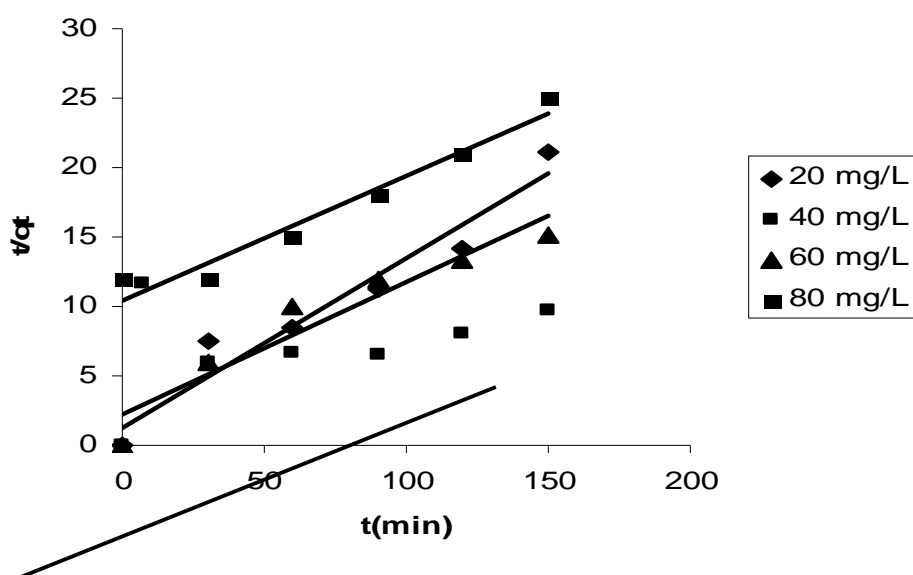

Fig. 2: Pseudo-second-order kinetics for adsorption of chromium (VI) on Eihhornea Crassipies

Table 1: Comparison of the pseudo first order, pseudo – second order adsorption rate constant and calculated and experiment q_e value obtained at different initial chromium (VI) concentrations

Co	Pseudo first order model				Pseudo second order		
	Qe.exp (mg/g)	qe.cal (mg/g)	K_1 (1/min)	R^2	qe.cal (mg/g)	K_2 mg min	R^2
20	17	7	0.9718	0.923	10	1.24	0.933
40	31	25	1.088	0.975	28	2.24	0.956
60	9.5	6	0.960	0.986	9	2.36	0.978
80	7	6	0.883	0.954	4	4.10	0.967

The kinetic results were further analyzed by the intra particle diffusion model to elucidate the diffusion mechanism

$$Q_t = K_{id} t^{1/2} + C$$

Where C is the intercept and K_{id} is the intraparticle diffusion lkrate constant (mg/g min $^{0.5}$) which can be evaluated from the slope of the linear plot q_t versus $t^{1/2}$ (fig. 3) If the regression of q_t versus $t^{1/2}$ is linear and possesses through the origin then intra particle diffusion is the sole rate- limiting step for intraparticle diffusion plots the first, sharper region is the instantaneous adsorption or external surface adsorption. The second region is the gradual adsorption stage where intra particle diffusion is the rate limiting. In some cases the third region exists, which is the final equilibrium stage where intraparticle diffusion starts to slow due to the extremely low adsorb ate concentrations left in the solution. As seen from fig 3 the plots were not linear over the whole time range implying that more than process affected the adsorption
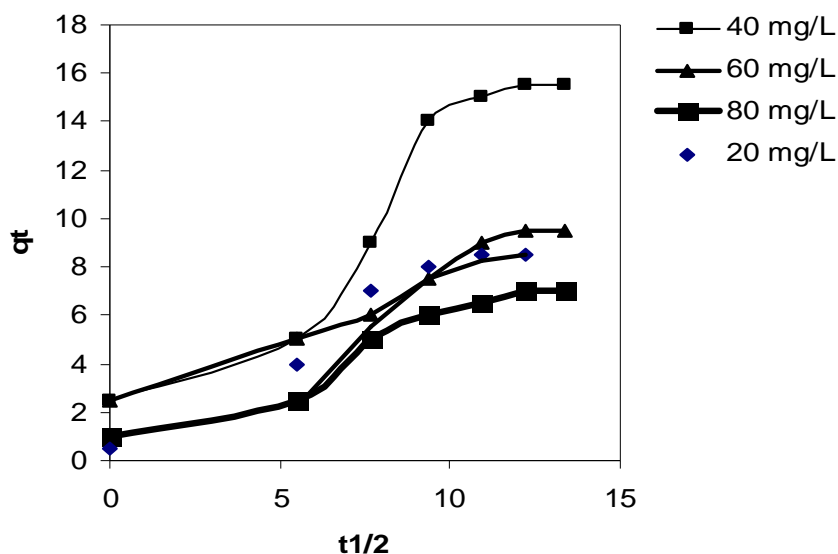
Determination of the thermodynamic parameters
From the kinetics adsorption experiments, the thermodynamic parameters such as ΔG, Δ H and Δ S were obtained from the following equation

$$K_c = C\ Ae/\ Ce$$
$$Log\ kc = \Delta S/\ 2.303\ R - \Delta H/2.303\ RT$$
$$\Delta G = -\ RT\ ln\ K_c$$

Where C_e and C A e are the equilibrium concentration in solution (mg/L) and the solid phase concentration at equilibrium (mg/L) respectively Kc is the partion coefficients of each temperature. R is the gas constant (8.314 j/mole k), and T is the temperature in Kelvin. From the slope and y- intercept of the linear plot of lnKc versus 1/T the changes of enthalpy and entropy could be obtained. This result was consistent with the above mentioned case that the adsorption capacities of Cr (VI) ion increased with the increasing of temperature, the negative value of ΔG (-2.6 & -

2.4 kJmol^{-1}) indicated that the adsorption process was spontaneous and the negative values of ∆S (-1.72& -1.05 kJmol^{-1}) suggest an increase in the randomness at the solid / solution interface during the adsorption process

Thermodynamic Parameters					
	T (K)	∆G (kJmol^{-1})	∆H (kJmol^{-1})	∆S (Jmol^{-1}k^{-1})	r^2
Cr^{6+}	303	-2.6	-205	-1.72	0.986
	313	-2.4	-109	-1.05	0.945

CONCLUSION
The results revealed the potential of Eihhornea Crassipies agricultural waste material is low cost adsorbent for removing metal ion solutions. The suitability of Pseudo first order kinetic and pseudo second order models for the sorption of Cr(VI) onto Eihhornea Crassipies was also discussed The kinetic modeling study has shown that the experimental data were found to follow the pseudo – first order model suggesting a chemisorptions process.

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