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ADSORPTION OF CR(VI) ION FROM AQUEOUS SOLUTIONS BY SOLID WASTE OF POTATO PEELS

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ABSTRACT:
Pollution of wastewater with heavy metal has always been a serious problem to the environment. Chromium is considered one of the most noxious heavy metals. Adsorption is now reorganized as an alternative technology of defence for chromium removal due to local availability, technical efficiency and cost effectiveness. Potato peel powder can be used as a low cost biosorbent to remove hexavalent chromium from aqueous solutions under various experimental conditions. Different parameters including equilibrium contact time, initial metal ion concentration, potato peel dose, pH and temperature were studied through a number of batch sorption experiments. Both the Langmuir and Freundlich were found to fit the adsorption isotherm of Cr (VI) ion onto potato peel. The Langmuir adsorption capacity was found to be 1.97 mg/g while Freundlich constants including Kf and n were 1.57 and 2.5, respectively. The adsorption kinetic was found to be more fit with the pseudo-first order model. This study showed a high efficiency of potato peel for the biosorption of Cr (VI) ion from aqueous solutions.

KEYWORDS: Adsorption; Chromium (VI); Isotherm; Potato Peel; Wastewater.

1. INTRODUCTION

Pollution of wastewater with heavy metals is considered a serious environmental issue, because these metals are not biodegradable and can be accumulated in living tissues (Deng et al., 2006). These metals can be present with high concentrations in waste water that discharges from electroplating industries and most mining activities. Chromium (Cr) is considered one of the most noxious heavy metals. Hexavalent chromium compounds have high toxicity and they can be carcinogenic, mutagenic and often reason for lung cancer (Sikaily et al., 2007; Li et al., 2008). The united states environmental protection agency limits for chromium in discharge into inland surface water to be 0.1 mg/L (EPA, 1990).

There are various methods have been employed in wastewater treatment technology to remove heavy metals from aqueous solutions including electrochemical treatment, membrane separation, precipitation, reverse osmosis, evaporative recovery, ionic exchange and adsorption (MonserandAdhoum, 2002; AnirudhanandRadhakrishnan, 2008). Most of these procedures are ineffective at low Cr(VI) concentrations and costly. However, adsorption is now reorganized as an alternative technology of defence for chromium removal due to local availability, technical efficiency and cost effectiveness (Li et al., 2008). Recently, considerable attention has been given to removal of Cr(VI) from aqueous solution using a number of materials such as activated carbons (Mohan andPittman, 2006), mineral oxides, biological materials (Bailey, et al., 1998; Sallau et al., 2012), agroindustry waste residues (Hasan et al., 2008), fruit peelings (Krishna andSwamy, 2012) and leaves (Prasad et al., 2012).

To the potato industry, management of potato peel as waste product causes a considerable problem. Therefore, it needs to find an integrated, environmentally-friendly solution. Potato peel (PP) can be used as a low-cost biosorbent and alternative for more costly wastewater treatment processes (GuechiandHamdaoui, 2011).

The present study investigated adsorption efficiency of chromium (VI) ions from aqueous solutions on potato peels as solid waste and low cost biosorbent. Different parameters including equilibrium contact time, initial metal ion concentration, potato peel dose, pH and temperature were studied through a number of batch sorption experiments to optimize the adsorption equilibrium, adsorption capacity, adsorption isotherms and adsorption kinetic.

2. MATERIALS AND METHODS

2.1 Materials

An analytical reagent grade of potassium dichromate (K2Cr2O7) was taken to prepare (1000 mg/L) stock solution of Cr (VI) in deionized water and stored in a dark place. This solution was used to prepare working solutions by appropriate dilutions. 1,5-Diphenylcarbazide solution was prepared by dissolving 250mg in 50 mL acetone and stored in a brown volumetric flask. Hydrochloric acid and sodium hydroxide (Fisher-Scientific, UK) were used for pH adjustment. 1 M HCl was used to clean all glassware followed by rinsing in deionised water.

2.2 Biosorbent preparation

Potato peels (PP) were brought from local restaurants (Duhok/Kurdistan Region-Iraq) and washed thoroughly and soaked for 2–3 hrs in deionized water. Then, PP were rinsed with 0.1MHCl to make the surface of PP more protonated and extent the strength of attraction of Cr (VI) ions in the solution (Mutongoet al., 2014). The biosorbent was dried in an oven at 100 oC for 3 hrs then burned for 2 hrs at 750 oC in the furnace. The burned potato peels were then ground to 100% and sieved passing 40 μm and stored in desiccators for further use. Approximately 10 kg from fresh potato peel can give 100 g peel powder. Table 1 shows analysis of the charcoal of potato peels.

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Table 1. Characteristics of the adsorbent" (Aman*et al.*, 2008)

Characteristics	Values
Ash (%)	6.96
Carbon (%)	27.85
Moisture (%)	1.6
Volatile Matter (%)	60.85
Bulk density (%)	0.37
Iodine number (mg/ g)	725

2.3 Adsorption studies

All experiments were carried out using a known weight of charcoal of potato peel contacted with 200 mL of Cr(VI) solution of different concentrations (2 – 10 mg/L) using 250 mL volumetric flasks. The flasks were gently agitated for a specific time at different temperature in an incubator shaker at 150 rpm. Samples of solutions were taken out at each time and centrifuged for 10min at 2500 rpm. The supernatant was separated using a syringe and filter discs (0.20 μm) and analyzed colometeriy by adding 1,5- diphenylcarbohydrazide in acidic solution. The product of purple complex of Cr(VI) was analysed using a Jenway 6700 UV spectrophotometer (Clesceriet al., 1998). The molar absorptivity of this reaction at 540 nm is approximately 40 000 Lg–1cm–1. Adsorption of Cr (VI) ion to the wall of the glassware was examined under operating conditions showing no adsorption.
The percentage removal of $K_2Cr_2O_7$ and equilibrium adsorption capacity (qe) were calculated using the following equations:

$$\%\ Removal = \frac{C_o - C_t}{C_o} * 100\ \% \qquad (1)$$

$$qe = (C_0 - C_e)V/\ M(2)$$

Where C_0 is the initial concentration (mg/ L) of the Cr(VI) ions in solution, C_t and C_e are the concentrations at a specific time and equilibrium respectively, V is the volume of solution by L and M is the weight of the potato peel by g, the unite of qe is mg/g.
The effect of several parameters on the adsorption efficiency of chromium (VI) ions onto potato peels was investigated including contact time, adsorption equilibrium, adsorbent dose, pH, temperature and adsorption isotherm and kinetic.

3. RESULTS AND DISCUSSION

3.1 Effect of contact time

Study the effect of contact time showed increasing in the adsorption percentage of Cr(VI) on potato peels with increasing the contact time (Fig. 1). The adsorption% was 94% after 35 min then it becomes constant attaining equilibrium with increase in contact time. It is clear that, at the beginning a large number of vacant surface sites on potato peel are available for adsorption of Cr(VI) ions but these surface sites become exhausted with passage of time (Zhan *et al.*, 2000). A 35 min of contact time was chosen for all further work.

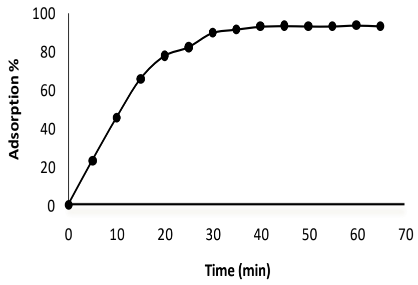

Figure1. Effect of contact time on adsorption of Cr(VI) ions on PP

3.2 Effect of initial concentration of Cr(VI)

Fig. 2 shows the effect of initial concentration of Cr(VI) (2 to 10 ppm) on the removal of metal ions by PP. The removal percentage was found to decrease with increase in initial metal concentration. However, the quantity adsorbed per mass unit of PP (Qe) showed increasing with increasing in the concentration of Cr(VI) (Fig. 3). A possible explanation for this might be attributed that no sufficient surface sites available to adsorb more chromium ions from the solution (Mutongo et al., 2014). The ratio of available active sites to the total Cr(VI) ions in the solution is high at low concentration, therefore, all ions can interact with PP and are adsorbed rapidly from the solution. However, at high concentration, the quantity adsorbed of Cr(VI) ions per mass unit of PP (Qe) is higher (Abdel Wanees et al., 2012). At initial chromium concentration of 10 ppm, the adsorption percentage is 87.6%, whilst 2 ppm showed a removal of 98.5%.

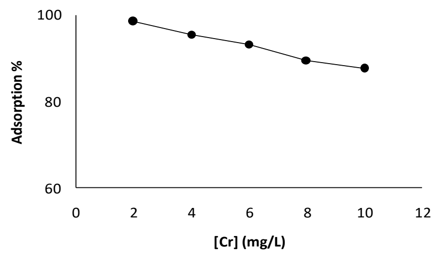

Figure 2. Effect of initial concentration on adsorption of Cr(VI) ions on PP

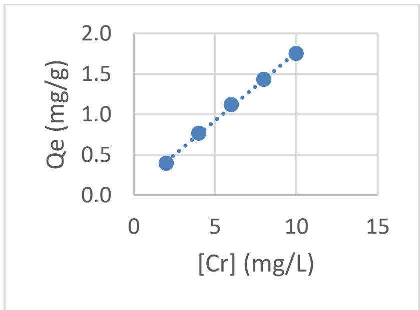

Figure 3. Effect of initial concentration on quantity adsorbed of Cr(VI) ions on PP

3.3 Effect of adsorbent dose

Adsorption experiments were also performed at different weights (namely 0.2, 0.4, 0.6, 0.8, 1, 2 and 3 g) of potato peels. The adsorption percentage increased with an increasing in PP dosage (Fig. 4). This might be attributed to high surface area of the adsorbent are available for adsorption (Namasivayam et al., 1998; Garg et al., 2007). Maximum removal (97%) was observed with PP weight of 2 and 3 g.

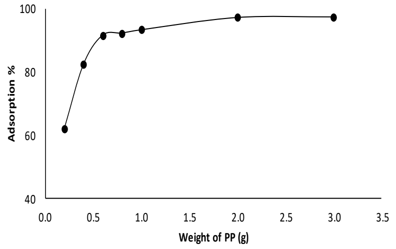

Figure 4. Effect of variant potato peels adsorbent dosage on the adsorption of Cr(VI) ions

3.4 Effect of pH

The effect of pH on process of adsorption movement on potato peels was investigated at different pH ranging from 2 to 12 (Fig. 5). No big pH effect was found, the removal efficiency was close values (approximately 92%, RSD%=1) at all pH.

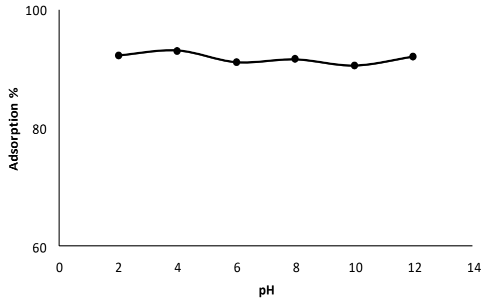

Figure 5. Effect of pH on adsorption of Cr(VI) ions on PP

Table 2. The optimum conditions of adsorption Cr(VI) ions on potato peels powder.

Contact time	Initial conc.	Adsorbent dose	pH	Temperature	Agitation speed
35 min	6 mg/L	1 g	6	25 ºC	450 rpm

3.7 Adsorption isotherm

Adsorption isotherm was investigated selecting fixed PP dosage at 1 g and various concentrations of $K_2Cr_2O_7$ (2-10 mg/L). A number of models are described adsorption isotherms but Langmuir and Freundlich are more familiar models used (Malik, 2004; Gupta andBabu, 2006; Saradhi*et al.,* 2010).
The Langmuir model can be expressed in a nonlinear form as following equation (Langmuir, 1918):

$$q_e = \frac{Q_m b C_e}{1 + bC_e} \qquad (3)$$

Where C_e is the concentration of sorbent (mg/L) at equilibrium, Q_m represents to the maximum adsorption capacity (mg/g), q_e is the mass of metal ion adsorbed per unit dose of adsorbent at equilibrium (mg/g), b refers to Langmuir isotherm constant (L/mg). Q_m and b values can be obtained by rearranging the equation 3:

$$\frac{C_e}{q_e} = \frac{1}{bQ_m} + \frac{C_e}{Q_m} \qquad (4)$$

Plotting of C_e/q_e versus C_e suggests the applicability of Langmuir model shown in Fig.7. Q_m and b values were determined from the slope and intercept of the liner plot to be 1.97 and 4.2 respectively. The maximum adsorption capacity in present work is lower than that mentioned in previous studies (Abdullah andPrasad 2009; Mutongo*et al.,* 2014).

3.5 Effect of temperature

Temperature is an important parameter that determines the thermodynamic of adsorption process. Six different temperatures were investigated (namely 25, 30, 35, 40, 45 and 50 o C). As presented in Fig. 6, the adsorption percentage was the same (92% approximate, RSD% = 0.8) at all temperatures. This can be explained to saturation of available binding sites on PP hence no more ions can be adsorbed particularly the number of active sites on the adsorbent surface is constant.

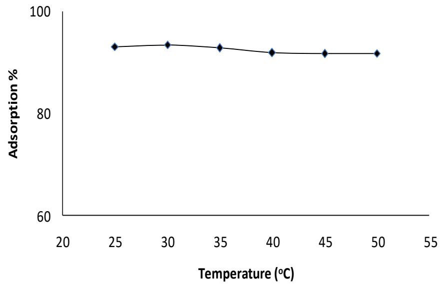

Figure 6. Effect of temperature on adsorption of Cr(VI) ions on PP

3.6 Optimum conditions

The optimum conditions in this study can be summarized as shown in Table 2.

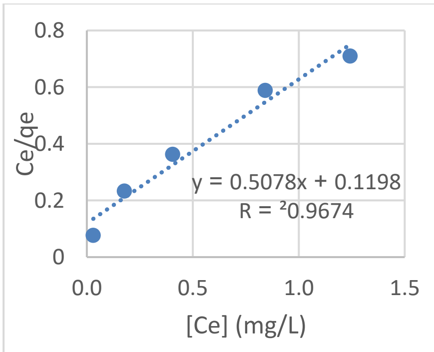

Figure 7. Langmiur isotherm

On the other hand, Freundlich isotherm can be written as equation 5:

$$q_e = K_f C_e^{1/n_f} \qquad (5)$$

Freunlidh model can be applied for heterogeneous surfaces or non-ideal adsorption (Riveroet al., 2004). Where nf and Kf are Freundlich constants and determined by equation 6:

$$\ln q_e = \ln K_f + \frac{1}{n_f}\ln C_e \qquad (6)$$

Plotting of lnqe versus lnCe obeys the Freundlich isotherm (Fig. 8). kf and nf values were determined from the plot to be 1.57 and 2.5 respectively.

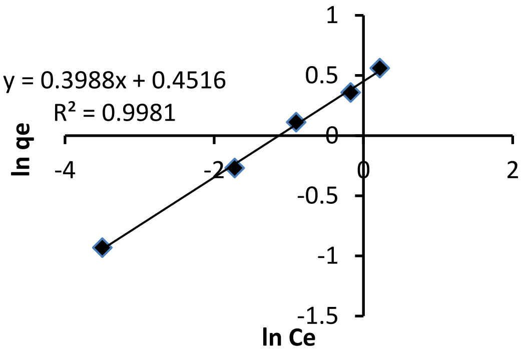

Figure 8. Freundlich isotherm

3.8 Adsorption Kinetic

An adsorption kinetic process was investigated applying pseudo first-order and pseudo second-order models. The pseudo first-order model can be described in the following equation (Chiou and Li, 2003):

$$\ln (q_e - q_t) = \ln q_e - k_1 t \quad (7)$$

Where q_e is the quantity adsorbed (mg/g) at equilibrium, q_t is the quantity adsorbed at specific time t, k_1 is constant (min^{-1}) which can be calculated from the linear plot of $\ln(q_e - q_t)$ versus t (Fig. 9) .

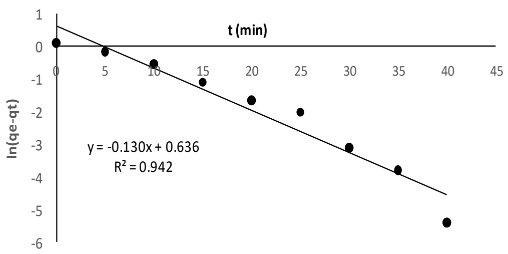

Figure 9. Pseudo first-order kinetic plot

In pseudo-second order model, the adsorption rate depends on the adsorbent capacity and adsorbate concentration (McKay and Ho, 1999). This model is written as:

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (8)$$

Where k_2 is constant (g mg^{-1} min^{-1}) and determined from the intercept of the plot of t/q_t versus t, and q_e can be calculated from the slope (Fig. 10).

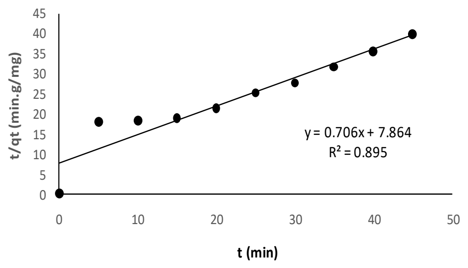

Figure 10. Pseudo second-order kinetic plot

Table 3 shows kinetic parameters of both models. Based on R^2 values, the adsorption of Cr(VI) ions on potato peel was found to be more fit with the pseudo first-order than the pseudo second order model suggesting that the rate limiting step might not be chemisorptions.

Table 3. Kinetic parameters

Pseudo first order			Pseudo second order		
k_1 (min^{-1})	R^2	q_e(mg/g)	k_2 (g mg^{-1} min^{-1})	R^2	q_e(mg/g)
0.130	0.942	1.730	0.063	0.895	1.410

4. CONCLUSION

The potential of using a solid waste of potato peel as a good adsorbent for the removal of Cr (VI) from aqueous solutions was investigated. The results of batch adsorption experiments elucidate the removal percentage of metal ion from its solution. The adsorption capacity strongly depends on initial concentration of metal ions, contact time with PP, and adsorbent dosage. However, no big pH and temperature effects were observed giving removal efficiency close to 92%. The chromium adsorption follows the Langmuir and Freundlich isotherm models suggesting that both monolayer and heterogeneous surface adsorption affect the biosorption. The adsorption kinetic was found to be more fit with the pseudo first-order than the pseudo second order model.

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