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Kinetic study of absorption of chromium (VI) using Canary Bananas Peels in contaminated water

Ricardo Díaz Martín[1], Adib Guardiola Mouhaffel[2], Rubén Contreras Lisperguer[2], and Carlos Mayo del Río[2]

[1]Team leader department building Engineering, CEU San Pablo University, Madrid, Campus de Monte príncipe, Spain

[2]CEU San Pablo University | Madrid. Campus de Monte príncipe, Spain

ABSTRACT: Bananas peel was used as an adsorbent to determine its feasibility for the removal of chromium (VI). Chromium heavy metal released into the environment has caused serious contamination of water and soils with significant environmental and occupational concerns. The removal of the Cr (VI) ions from aqueous solutions is investigated in this study using of banana peels as a low cost biosorbent material. Various parameters such as pH, temperature, contact time, initial metal concentration and adsorbent dosage were investigated to determine the biosorption performance. Equilibrium was attained within 60 minutes and maximum removal of 96% was achieved under the optimum conditions at pH 2. The adsorption phenomenon demonstrated here was monolayer represented by Langmuir isotherm with R^2 value of 0.99 and the Langmuir constants k and q_m was found to be 1,53 (L/mg) and 10,09 (mg/g). The adsorption system obeyed Pseudo second order kinetics with R^2 value of 0.999.

KEYWORDS: Bio-sorption, Cr (VI), Bananas peel, Langmuir, Freundlich.

1 INTRODUCTION

Rapid industrialization and urbanization have resulted in exponential discharge of industrial effluents and toxic heavy metals in to aquatic and terrestrial ecosystem [1] ,Chromium metal, which is currently explored in this research work, is present mainly in leather tanning , precious metal mining and electroplating industrial effluents, according to US EPA, Chromium is considered to be the topmost priority toxic pollutant. Chromium metal in its natural form is found to exist in two states: Cr (III) and Cr(VI). Hexavalent chromium is 100 times more toxic than trivalent chromium and due to its toxicological and carcinogenic consequences, it is likely to cause detrimental health hazards [2]. According to AWWA permissible level of Cr (VI) ion in surface and portable water are 0.1 and 0.05 mg/L respectively [3]. Thus, it becomes top priority to make effluents free from Cr (VI) before releasing into the environment. Common technique involved in the handling of heavy metal remediation includes, precipitation (both physical and chemical), ion exchange (resin based), filtration achieved via physical means, chemical based coagulation, flocculation, and other electrochemical methods [4].

The major hurdles in adapting these techniques includes high operational cost coupled with higher energy requirements, further, generation of huge sludge deposition and finally operational complexities. Thus, the alternative of adsorption as a remediation tool has been considered the best and it is further augmented with it being economical and environmental friendly technique [5]. Many agricultural waste residues had been extensively studied in the past to determine their adsorption efficiency. Bio resource material like agriculture waste residuals, showing maximal adsorption capabilities and metal selectivity had been suggested as suitable bio-sorbent for heavy metal sequestration [4].

Currently locally available agricultural waste residues are an automatic choice for remediation of heavy metals, they are also being considered as an important source of bio sorbents due to the presence of certain functional groups such as hydroxyl, ester, amino, carboxyl, carbonyl, sulphydryl, and phosphor group to which heavy metal bind. In this context, Bananas peel a novel bio sorbent was examined for Cr(VI) binding efficiency. In the present study, various parameters which influence Cr (VI) removal such as pH, initial metal ion concentration, contact time and adsorbent dosage were investigated in a batch mode. Analytical techniques such as FTIR and SEM were employed for bio sorbent characterization. FTIR analysis was employed to determine the active site responsible for bio sorption based on the changes in vibrational frequencies of the functional groups. The surface morphology and the porosity of the bio sorbent were investigated by SEM analysis. Investigations on equilibrium isotherm and adsorption kinetics were also carried out to understand the adsorption mechanism. The present work was carried out at Coimbatore during the period of December 2013 to February 2014.

2 METHODOLOGY

2.1 BIO-SORBENT MATERIAL

Bananas peel were taken from canary island, were washed under running tap water and were subjected to drying in hot air oven at an optimum temperature of 40°C. The finely powdered bio-sorbent was subjected to washing. After washing with distilled water, the mixture was filtered and dried at 50°C for a period of 1 h. The dried powder was stored in an air tight container to prevent moisture. The dried powder was used as a bio-sorbent for the experiment.

2.2 BATCH STUDIES

The maximal adsorption efficiency of biosorbent was determined by varying several parameters which influence the adsorption phenomenon, such as pH, contact time, adsorbent dosage and initial metal concentration by fixing the volume of metal solution to 100ml. After agitating for 30 min in a temperature controlled orbital shaker at 120rpm, the solution was centrifuged. The residual concentration of chromium present in the supernatant was determined spectro-photometrically using 1, 5 Diphenyl carbazide reagent as a complexing agent at 540 nm (APHA method 3500-Cr).

2.3 CHROMIUM REMOVAL ANALYSIS

Chromium removal was estimated using 1,5 Diphenyl carbazide as a complexing agent spectrophotometrically. Different standards containing less than 100 mg/L (20, 40, 60, 80, and 100) were prepared and maintained at pH less than 2. To 10 ml of standard,0.2 ml of diphenyl carbazide was added as a complexing agent. The solution was incubated until red violet color was developed. The absorbance was noted at 540 nm using visible spectrometer (Systronics-106). A blank was prepared for Cr (VI) analysis. The amount of chromium present in the sample was determined from calibrated curve according to the standard method (APHA method 3500- Cr).

2.4 REMOVAL EFFICIENCY

The percentage of Chromium removal (R %) was determined using the below equation:

$$\text{Removal efficiency} \quad (R\ \%) = \frac{\mathrm{Ci-Co}}{\mathrm{Co}} \times 100 \qquad (1)$$

Ci and Co represents the initial and final concentration of chromium metal in mg/L.

Adsorption isotherm

Adsorption isotherm aids in the evaluation of adsorption efficiency of any adsorbent and also facilitates in quantifying the correlation of equilibrium with the amount of adsorbate present in the solution and relates the quantum of adsorbate adsorbed in to any bio-resource material at a given temperature.

Adsorption capacity is given by the empirical relation:

$$\mathrm{qe} = \frac{\mathrm{Ci-Co}}{\mathrm{m}} \times V \qquad (2)$$

Where qe is the adsorption capacity (mg/g), Ci and C0 are initial and final metal concentration (mg/L), m is the mass of the adsorbent (g) and V is the volume of the metal solution (L). In the present study, adsorption of Cr(VI) with the help of Bananas peel powder was investigated by employing various adsorption isotherms.

2.5 LANGMUIR ADSORPTION ISOTHERM

This model is based on the assumption that metal uptake takes place on the homogeneous surface by monolayer adsorption. It involves uniform energies of adsorption. Langmuir adsorption isotherm is represented by the empirical equation:

Where q is the amount of solute adsorbed per amount of adsorbent (mg/g), K (L/mg) and q0 (mg/g) are the Langmuir constants related to energy of adsorption and maximum monolayer capacity and y is the solute concentration in the solution (mg/L). By plotting 1/q versus 1/y, Langmuir parameters were obtained (Langmuir, 1917).

$$\frac{1}{q} = \frac{K}{q_o\ y} + \frac{1}{q_o} \quad (2)$$

2.6 FREUNDLICH ADSORPTION ISOTHERM

Freundlich adsorption isotherm is theorized, that metal uptake takes place on the heterogeneous surface of an adsorbent by multilayer adsorption. It involves non uniform energies of adsorption. Freundlich adsorption isotherm is given by the empirical equation:

Where qe is the amount of solute adsorbed per amount of adsorbent (mg/g), y is the solute concentration in the solution (mg/L), K and n are the Freundlich constants related to adsorption capacity and intensity. By plotting lnqe versus $\ln_y$, Freundlich constants k and n were obtained. It also determines the heterogeneity of surface pore distribution and the value of n indicates the favorability of adsorption (Freundlich, 1906).

$$\text{Ln } q_e = \text{Ln } q_k + \frac{\ln y}{n} \quad (2)$$

2.7 ADSORPTION KINETICS

Studies on adsorption kinetics had been carried out to describe adsorption mechanism and diffusion process. The generated data were tested using Pseudo first order and second order kinetics equation.

3 RESULTS AND DISCUSSION

3.1 RESULTS

The plot reveals that the rate of chromium ion removal is rapid in the beginning, with Cr (VI) uptake of 77.3% and 55.3% for 20 and 50mg/l concentrations in just 1 minute (Figure 1). This was then followed by a slow increase and thereafter the rate of Cr (VI) removal tends to become relatively constant. This is probably due to the availability of large number of active binding sites initially in the banana peel adsorbent and consequently large numbers of Cr (VI) are bound onto the banana peel. The equilibrium time of Cr (VI) was observed to have been obtained within 20 min. Similar trends of equilibrium time were also observed in studies conducted by Memonet al., [11] in Cr (III) removal.Results also showed that low initial concentrations of 20 mg/l indicated higher Cr (VI) removal rates than at initial concentrations of 50 mg/l. Cr (VI) uptake of 80.6 %(1.6mg/g) and 57.3% (2.9mg/g) was attained at 20min.This Cr (VI) uptake showed similar trends to previous studies conducted using banana peels (Al-Azzawiet al.,[2]; Memonet al.,[11]; Memonet al.,[10]). Banana peels uptake of Cr (III) of 60-79% at higher adsorbate concentrations (10-100 mg L-1) and 80-99% at lower adsorbate concentrations (0.5-8 mg L-1) have been observed (Memonet al.,[11]). Hence, with uptake rates of 58%, banana peels is reflected as an efficient adsorbent material for the removal Cr (VI) from aqueous solution.

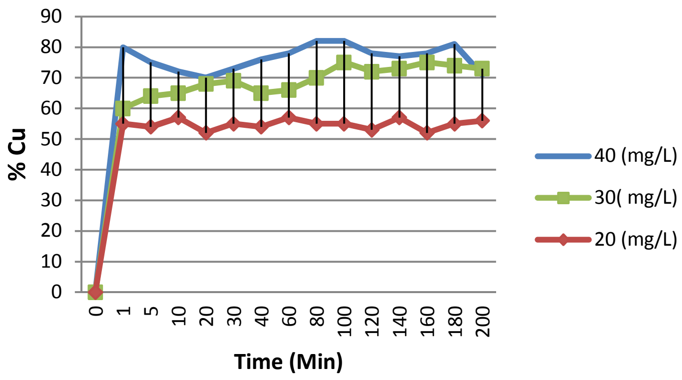

Fig. 1: Effect of contact time on % Cr (VI) removal by acacia charcoal at 20 ,30 and 50 mg/l.

Similar results were obtained by Muthukumaran and Beulah, (2010), where stretching of O-H group was responsible for the adsorption of Cr(VI) using chemically activated *Syzygium jambolanum* nut carbon.

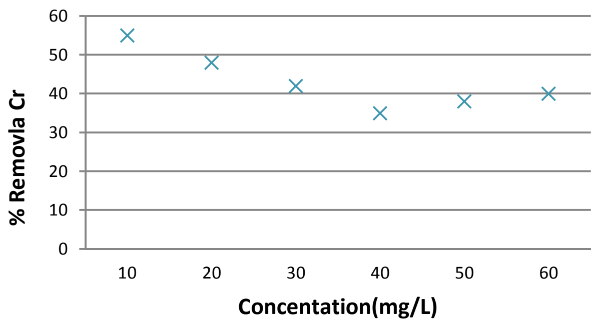

Fig. 2: Effect of Initial concentration on Cr (VI)removal (adsorbent: 0.01g/ml, Initial Concentration: 40 mg/l.

3.2 EFFECT OF ADSORBENT DOSAGE

Adsorbent dosage plays a major role in adsorption process. From the result, as shown in the Fig. 4, it is understood that, with an increase in adsorbent dosage from 0.1 to 0.5 g, there exists an increase in percentage removal from 51 to 92% and the maximum removal was attained at the adsorbent dosage of 0.5 g. The observed trend may be due to greater availability of surface area and functional groups at higher adsorbent dosage (Suresh and Babu, 2008). As a result, electrostatic interaction occurs between the functional groups present in the active site of the adsorbent and the metal ions present in the solution, similar trends were reportedby Devi et al., (2012).

3.3 EFFECT OF CONTACT TIME

The effect of initial concentration on removal of Cr (VI)ion on the adsorption efficiency by banana peels was investigated as shown in Figure 2. It was observed that the percentage removal of Cr (VI) decreased with the increase in initial Cr (VI) concentration. At initial concentrations of 5 mg/l the maximum Cr (VI)removal efficiency was found to be 53 %, while at levels of 50 mg/l the removal efficiency was at 35%.This indicates that the removal of Cr (VI)is dependent on the initial concentration of Cr (VI)present in the solution.

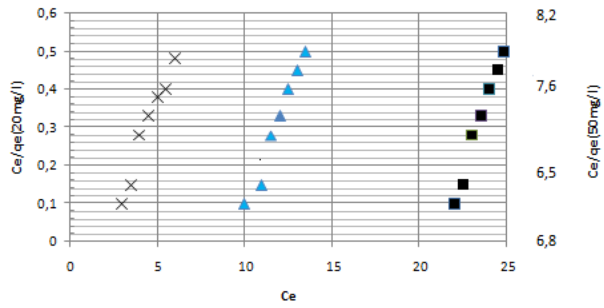

Fig. 3: Langmuir Isotherm of Cr (VI) adsorption onto banana peels at 20 ,30 and 40 mg/l concentrations.

3.4 EFFECT OF INITIAL METAL CONCENTRATION

The experiments were performed by varying the initial metal concentration from 20 to 100 mg/L, while the contact time was varied from 15 to 60 minutes at a constant adsorbent dosage of 0.5 g/100 ml at pH 2 and an agitation speed of 120 rpm. Cr (VI) removal as a function of contact time and initial metal concentration is given in the Fig. 6. From the Fig. 6, it is clear that with an increase in metal concentration from 20 to 100 mg/L, removal percentage decreases from 97 to 88 with an increase in adsorption capacity. The maximum removal was obtained within 15 minutes, after which there was negligible removal since the surface of the sorbent gets exhausted after the formation of one layer thickness of metal ions and then metal uptake rate is controlled due to the transport of ions from exterior to interior site of the adsorbent. Similar trend was observed with ternary bio polymeric microspheres [5]. The data generated due to effect of initial metal concentration help sin determining he equilibrium concentration (Ce), adsorption capacity(qe), metal uptake rate and kinetic characteristics.

3.5 EQUILIBRIUM ISOTHERMS

Isotherms have been used to describe the equilibrium relationship between the amount of solute that is present in the solution and adsorbent [7]. In the present study, Langmuir, Freundlich and Temkin models were employed. The best equilibrium model was determined based on correlation coefficient. represents the investigations over various adsorption isotherms on Cr(VI) removal. Under the optimal conditions, the metal adsorption equilibrium was very well represented by Langmuir isotherm which accounts for existence of monolayer adsorption on homogeneous surface.

Langmuir constants q0 and k evaluated from the slope and intercept are 19.23 (mg/g) and 0.0061 (L/mg) respectively with the correlation coefficient of 0.992. Higher R2 value indicates the strong binding of Cr(VI) ions to the adsorbent. Bananas peel powder was found to have better adsorption capacity which indicates the favorability of Langmuir isotherm.

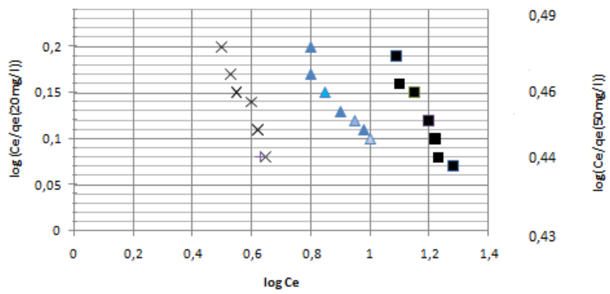

Fig. 4: Freundlich Isotherm of Cr (VI)adsorption onto banana peels at 20 ,30 and 40 mg/l concentrations.

3.6 ADSORPTION KINETICS

Studies on adsorption kinetics were carried out in order to determine the metal uptake rate. The effect of initial metal concentration was investigated to determine the best kinetic model. Pseudo first order kinetics model were applied by plotting log (qe-qt) versus time as shown in the table 1 and 2. The equilibrium adsorption capacity qe and the second-order rate constant K2 were calculated from the slope and intercept of the plot of t/qt against t as shown in Figure 3. The calculate parameters for the data of second-order-kinetic model were summarized in Table 1. Results indicated a good fit (R2>0.998) of the experimental data with the second-order kinetic equation. The linear plots also show a good agreement between the experimental (qe, exp) and calculated (qe,cal) values. This finding indicates that the adsorption of Cr (VI) onto banana peels follows the pseudo-second-order kinetic model. Results also shows that as the initial Cr (VI)concentration increases, adsorption capacity at equilibrium (qe), initial sorption rate (h) and the adsorption rate (K) also increased.

Table 1: Parameters of the pseudo-first-order kinetics.

Parametre	First –order Kinetic Model		
Initial Cr(VI)	K1 (1/min)	qe,cal (mg/g)	R^2
40 (mg/L)	0,002	0,022	0,676
30 (mg/L)	0,002	0,018	0,643
20 (mg/L)	0,002	0,034	0,785

Table 2: Parameters of the pseudo-first-order kinetics

Parametre	Second-order Kinetic Model			
Initial Cr(VI)	K2 (mg min)	qe,cal (mg/g)	h	R^2
40 (mg/L)	96,810	0,019	0,082	1,000
30 (mg/L)	45,870	0,015	0,076	1,000
20 (mg/L)	33,480	0,014	0,006	0,998

Table 3: Parameters of the Langmuir and Freundlich isotherm

Model	Langmuir isoherm				Freundlich isotherm		
Parametre	qm	Kl	Rl	R2	Kf	n	R2
50 (mg/L)	1,626	0,180	0,004	0,980	28,700	13,28	0,980
30 (mg/L)	5,890	0,345	0,010	0,975	13,450	4,30	0,954
20 (mg/L)	11,120	0,760	0,290	0,970	2,540	2,20	0,940

observed to decrease as the initial concentrations of chromium increased. The adsorption Cr (VI) onto banana peels follows a pseudo- second-order kinetics and shows good fits with both the Langmuir (R2> 0.997,qm>1.626) and Freundlich (R2>0.988) isotherm models. This study can conclude that banana peels provide a low cost favorable option from chromium removal in aqueous solution. However, recommendations are made to study the effect of the amount of adsorbate and temperature on the removal efficiency in order realize a good decontamination of leather wastewater.

4 CONCLUSION

The research presents batch studies investigations on the use of banana peels (Musa Sapientumbiomass)to adsorb Cr (VI) from aqueous solutions. In batch mode studies the adsorption was dependent on initial metals ion concentration, and agitation time. Cr (VI) uptake equilibrium was attained in 20 minutes, and banana peels was observed to be able to absorb 2.2 mg/g of Cr (VI)at concentrations of 50 mg/L. Cr (VI)adsorption onto banana peels was also observed to decrease as the initial concentrations of chromium increased. The adsorption Cr (VI) onto banana peels follows a pseudo- second-order kinetics and shows good fits with both the Langmuir (R2> 0.997,qm>1.626) and Freundlich (R2>0.988) isotherm models. This study can conclude that banana peels provide a low cost favorable option from chromium removal in aqueous solution. However, recommendations are made to study the effect of the amount of adsorbate and temperature on the removal efficiency in order realize a good decontamination of leather wastewater.

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