PRETREATED POMELO PEEL AS BIOSORBENT OF CADMIUM ION FROM AQUEOUS SOLUTION

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INTRODUCTION

Cadmium is a metal widely used in industries. The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining and refining processes [1]. Its toxic effects are well documented. The kidneys are the critical target organ after ingestion (renal dysfunction, hypertension and anaemia) [2-4]. Cadmium has been well recognized for its negative effect on the environment. Therefore, the removal of cadmium ions from process or waste effluents becomes environmentally important. Traditional technologies for the removal of heavy metals, such as precipitation, ion exchange, filtration, solvent extraction and separation by membranes, are often ineffective and/or very expensive in the reduction of heavy metal ions at very low concentrations [5].

Biosorption has been successfully used in the treatment of cadmium contaminated water using low cost materials. Biosorbents for the removal of metals mainly come under the following categories: bacteria, fungi, algae, industrial wastes, agricultural wastes and other polysaccharide materials. In general, all types of biosorbents have shown good biosorption capacities towards all types of metal ions. Agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewable, low in cost and more efficient are seem to be viable option for heavy metal remediation. Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups. These groups have ability to some extent to bind heavy metal ions by donation of an electron pair from these groups to form complexes with the metal ions in solution [6]. In several papers, It has been found that by modifying agricultural by-products, their capacity can be increased. Common chemical pretreatments include acid, alkaline, ethanol and acetone treatments of the biomass. The success of a chemical pretreatment strongly depends on the cellular components of the biomass itself. In many instances, acidic pretreatment has proved successful; this is because some of the impurities and ions blocking the binding sites can easily be eliminated [7].

Pomelo peel is one of the valuable biosorbent wastes. It has been used to remove cadmium ion from aqueous solution [8]. Therefore, this paper examines pretreated pomelo peel as biosorbent of cadmium ion from aqueous solution. Effects of different chemical modifications were investigated. Influences of solution pH, initial cadmium ion concentration and contact time were also studied.

MATERIALS AND METHODS

Biosorbents preparation

Pomelo peel was collected as solid wastes. The collected materials were then washed with deionized water which was prepared by the technique of reverse osmosis for several times to remove the surface adhered particles and water soluble materials. The washed material were cut into small pieces (1-2 cm) then dried in a hot air oven (Memmert Model 600) at 60°C until they reached a constant weight. In the final stage these materials were dried, ground and screened with sieves of the cut of size of 150-212 µm. It was washed with isopropyl alcohol (PPI). PPI was washed with sodium hydroxide (PPIS) and citric acid (PPIC). PPIS was washed with citric acid (PPISC).

Batch Biosorption Experiments

The batch biosorption experiments were carried out of Erlenmeyer flasks of 100 ml of $Cd(NO_3)_2.4H_2O$ solution concentration 50 mg/l and 0.1 g of material added to and the mixture agitated for 24 hrs with a constant agitation speed of 150 rpm at 25 °C. The effects of solution pH were different solution pH ranging 2 to 6. In order to continue this work, the pH was fixed throughout the experimental work that were used for the optimization of solution pHs. The equilibrium isotherm was determined with a range of different concentrations of $Cd(NO_3)_2.4H_2O$ solution 25, 50, 75, 100, 150 and 200 mg/l. and The kinetic studied at different contact time ranging 0 to 240 min. The contact times were varied at 5, 10, 15, 20, 25, 30, 40, 50, 60, 90, 120, 150, 180, 210, and 240 min.

Cadmium Analysis

After biosorption, biosorbents were separated from the solution by passing through a Watman 0.45 µm GF/C filter and the filtrate was subjected to residual cadmium concentration determination. The initial concentration and the residual concentrations of the cadmium ions were analyzed by Flame Atomic Absorption Spectrophotometer (Perkin Elmer AAnalyst 200).

The cadmium ions capacity per gram of biosorbents was determined by employing the mass balance. The equilibrium cadmium ions capacity could be calculated as

$$q_e = V(C_i - C_e)/m \qquad (1)$$

Where;
q_e = the equilibrium cadmium ions capacity (mg/g);
V = the suspension volume (l);
m = the mass of biosorbent (g);
C_e = cadmium ions concentration at equilibrium (mg/l);
C_i = initial cadmium ions concentration (mg/l)

All experiments were performed in triplicate and mean values were presented. Standard deviation and analytical errors were calculated and the results were shown as the means with relative standard deviations of less than 8%.

RESULTS AND DISCUSSION

Effect of Solution pH

The variation of the solution pH is the one of the most important factors in the biosorption of the metal ions [9]. This factor is capable of influencing not only the binding site dissociation state, but also the solution chemistry of the target metal in terms of hydrolysis, complexation by organic and/or inorganic ligands and redox potentials [10]. Most research conducted on heavy metal biosorption indicates that the decrease in ion biosorption at acid pH may be due to the increase in competition with protons for active sites [11-12]. At alkaline pHs, however, other effects may arise that also alter the process, such as the predominant presence of hydrated species of heavy metal, changes in surface charge or the precipitation of the appropriate salt [13].

The result showed that the effects of pH on the biosorption were shown in Fig 1. Due to proton (H^+) vies with cadmium ions in lower pH, consequently reducing cadmium ions binding on the biosorbent surface. At higher pH, the biosorbent surface takes more negative charges, thus attracting more cadmium ions. However, with further increases in pH the formation of anionic hydroxide complexes decreases the concentration of free cadmium ions; thereby the biosorption capacity of cadmium ions decreases [14]. Based on biosorption capacity effect, PPIS and PPISC were selected as biosorbent in the next experiments.

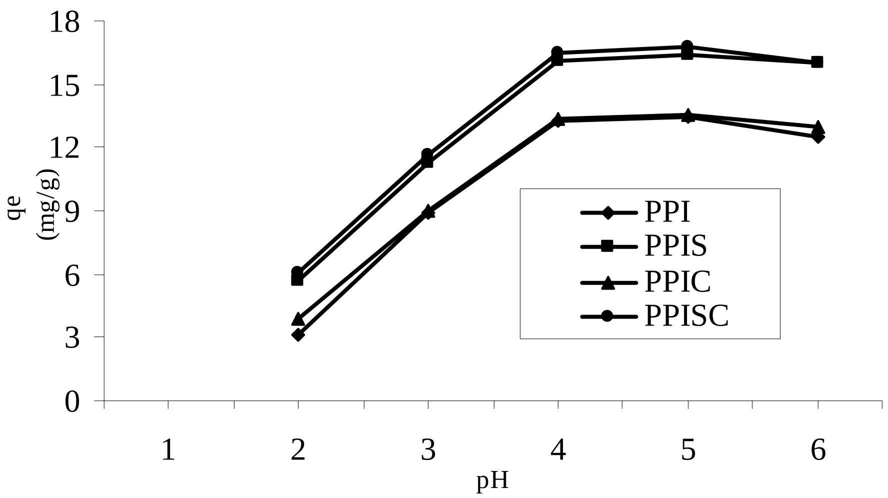

Figure 1 Effect of solution pH on cadmium biosorption by using pretreated pomelo peel

Effect of Initial Cadmium Ion Concentration

Biosorption isotherms can be generated based on numerous theoretical models where Langmuir and Freundlich models are commonly used to fit experimental data when solute uptake occurs by a monolayer biosorption [15-16]. Langmuir isotherm assumes monolayer biosorption, and is presented by the following equation:

$$q_e = q_{max} b\, C_e / (1+b\, C_e) \qquad (2)$$

And the Freundlich isotherm has the form

$$q_e = K_F C_e^{1/n} \quad (3)$$

Where q_e and q_{max} are the equilibrium and maximum uptake capacities (mg/g biosorbent); C_e is the equilibrium concentration (mg/l solution); b is the equilibrium constant; K_F and n are Freudlich constants characteristic of the system.

The influence of initial cadmium ion concentration on biosorption was shown in Fig. 2. The models parameters of Langmuir and Freudlich isotherms were tabulated in Table 1.The experimental data could better be described by the Langmuir isotherm than Freudlich isotherm indicated that monolayer adsorption on the homogenous surface of modified biosorbents. Based on cost effect, PPIS was selected as biosorbent in the next experiment.

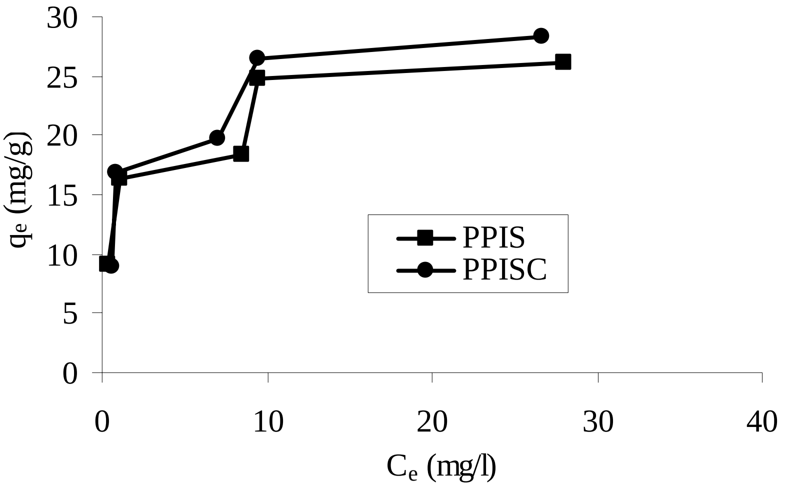

Figure 2 Effect of initial cadmium ion concentration on cadmium biosorption by PPIS and PPISC as biosorbent

Table1 Langmuir and Freundlich isotherm constants for cadmium ions biosorption

Biosorbent	Langmuir model			Freundlich model		
	b (l/g)	q_{max} (mg/g)	R^2	k_f	n	R^2
PPIS	0.71	26.88	0.98	13.14	4.51	0.86
PPISC	0.72	27.10	0.99	13.30	4.02	0.80

Cadmium adsorption capacity attains maximum under this condition with the maximum capacity of 26.88 and 27.10 mg/g for PPIS and PPISC respectively. The results showed that the adsorption capacity for cadmium ion using PPIS and PPISC are greater than that has been found using other adsorbents listed in Table 2.

Table2 Biosorption capacities for cadmium ions using different biosorbents

Biosorbents	Modifying agents	Biosorption capacity (mg/g)	Reference
PPIS	Isopropyl alcohol/ Sodium hydroxide	26.88	This study
PPISC	Isopropyl alcohol/ Sodium hydroxide/Citric acid	27.10	This study
Rice husk	Water washed	8.58	[17]
	Sodium hydroxide	20.24	
	Sodium bicarbonate	16.18	
	Epichlorohydrin	11.12	
Sawdust	Formaldehyde in Sulfuric acid	9.29	[18]
Spent grain	Hydrochloric acid	17.3	[19]
Corncob	Nitric acid	19.3	[20]
Juniper fiber	Sodium hydroxide	29.54	[21]

Effect of Contact Time

Various models can be used to analyze the kinetics of sorption process. The pseudo-first-order rate equation of the Lagergren is one of the most widely used for the biosorption of solutes from a liquid solution [22-23] and is represented as

$$\ln (1-q_t/q_e)= -k_1t \qquad (4)$$

Another model for the analysis of biosorption kinetics is pseudo-second-order. The rate law for this system is expressed as

$$t/q_t = (1/k_2q_e^2) + (t/q_e) \qquad (5)$$

where q_t and q_e are the grams of solute sorbed per gram of biosorbent at any time and at equilibrium, respectively, and k_1 and k_2 are the rate constant of pseudo-first-order sorption and pseudo-second-order sorption, respectively.

The influence of contact time on the biosorption of cadmium was shown in Fig 3. The result that a very fast increase in the biosorption may be observed in the first 20 minutes, a practically constant plateau after 60 minutes.

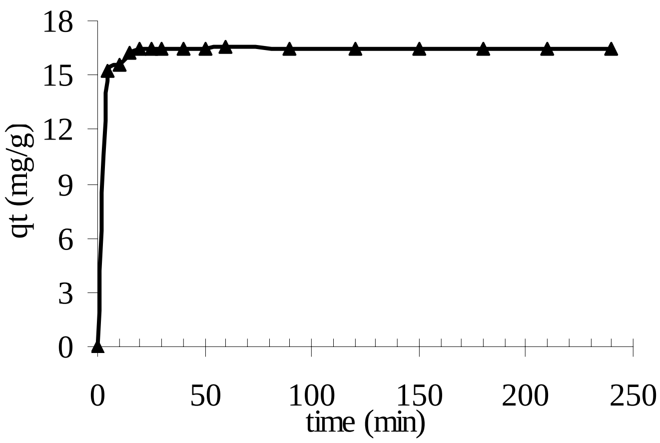

Figure 3 The effect of contact time on cadmium biosorption by PPISC

The biosorption kinetic is given in Fig.4 for the pseudo-second-order and Fig.5 for the pseudo-first-order rate equations. From Figs.4 and 5, it can be concluded that the kinetic of PPISC can be explained with the pseudo-second order equation. The R^2 value for the second-order kinetic model was 1.0, while that for the first-order kinetic model was 0.90. Results using pseudo-first-order and pseudo-second- order model were conducted. The results show that the biosorption kinetics of cadmium ion on biosorbent follows the second order kinetics.

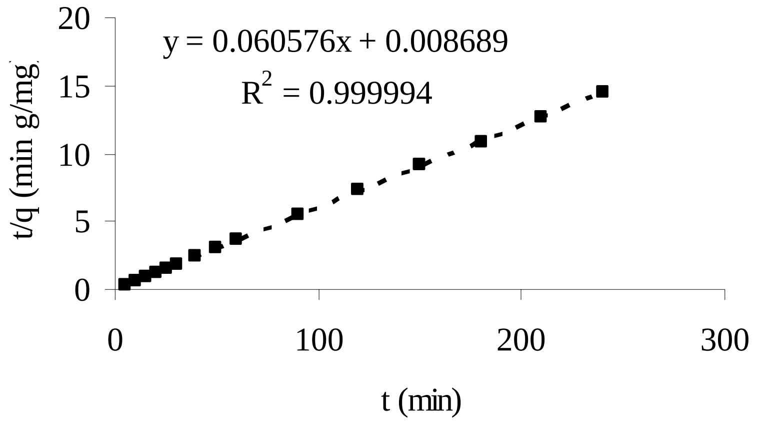

Fig. 4 Biosorption kinetic as descried by pseudo-first-order rate equation

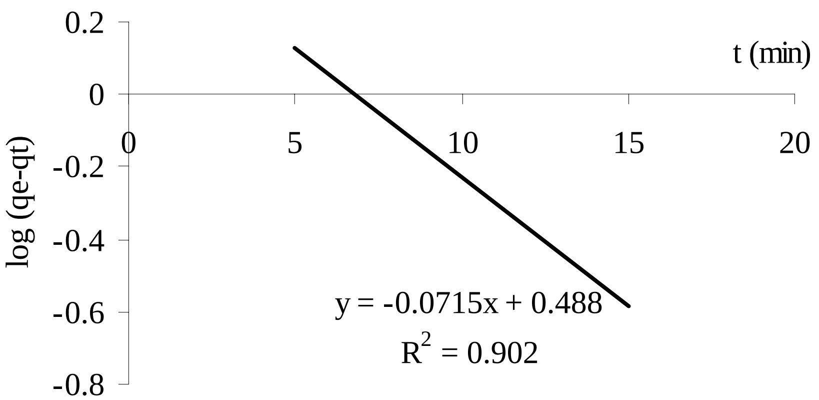

Fig. 5 Biosorption kinetic as descried by pseudo-second-order rate equation

CONCLUSIONS

The biosorption capacity for cadmium ions of pretreated pomelo peel was found to be relatively high when compared with those of many other biosorbents. The results show that the biosorption is solution pH dependent and the order of maximum biosorption capacities was PPISC>PPIS>PPIC>PPI at pH 5. In terms of cadmium capacity and economic efficiency, PPIS appears to be an effective, alternative biosorbent for treatment to cadmium laden effluents. The maximum cadmium uptake is 26.88 mg/l and reaches equilibrium value at about 20 minutes. The pretreated pomelo peel has much potential as biosorbent for the removal of cadmium ion from wastewater.

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