

Studies of Adsorption of Cadmium Ions by Biowaste Adsorbent from Aqueous Solutions with Ion-Selective Electrodes and ICP-OES

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Abstract

Using environment-friendly and low-cost biowaste adsorbents as toxic metal ion removal substrates from aqueous solutions has a great economic advantage. This work evaluated pumpkin and potato peel biowastes for the adsorption of cadmium ions. The biowastes were treated with acid or base. Batch experiments were carried out by introducing a known concentration of metal ion solution into the biowaste sorbent at various pH levels. The pH and metal ion concentration was monitored with pH and cadmium ion-selective electrode continuously for two hours, and the final concentration for the metal ion after 24 hours was measured with the cadmium electrode and then confirmed with ICP-OES. L-type isotherms were obtained that fit to Freundlich model. Adsorption isotherms showed chemical adsorption and the kinetics following the second order model. Equilibrium adsorption capacity is higher than 29 mg/g at pH 5.6 when the initial concentration is 220 ppm. Dynamic cadmium adsorption capacity is 17 mg/g from aqueous solution when the feed solution is 220 ppm with pumpkin peel biowaste sorbent. The biowaste materials can be regenerated with acid washing.

Keywords

Cadmium Ion, Biowaste Sorbent, Ion-Selective Electrode, ICP-OES

1. Introduction

Over the last few years, pollution of water has been a high concern from both

natural and anthropogenic sources. Another apprehensive fact of pollution is the high presence of contaminants in the environment, especially those with toxic and hazardous properties [1] [2]. Some of the major contaminants that affect the safety of drinking water are the presence of heavy metals at a concentration higher than the permissible standard [1]. The metals that pose the most risk to humans include cadmium, lead, arsenic, mercury, zinc, copper, chromium, and nickel. Overexposure to these metals may lead to severe cases of illness and often death. Cadmium toxicity poses detrimental effects on the human body upon overexposure to these metals. The most significant natural sources of cadmium pollution in water are the weathering of rocks leading to cadmium release into soils and waterways, and airborne soil particles from forest fires and volcanic activity. There are also anthropogenic sources of cadmium emission resulting from non-ferrous metal production, stationary fossil fuel combustion, and iron and steel production [3].

Cadmium affects the human body at a cellular level. At high concentrations, cadmium is carcinogenic and can interact with DNA repair mechanisms and may even lead to the generation of reactive oxygen species [2]. Even at lower concentrations, cadmium interacts with the mitochondria and inhibits many cellular respiration processes [4]. At a non-cellular level, cadmium toxicity negatively affects the renal, reproductive, and cardiovascular systems.

With a high amount of contaminants, remediation of the environment has an enormous cost, and reducing pollution is critical. The big challenge currently is to find the most eco-friendly path that leads to the decontamination of the environment. One potential solution to remove these contaminants from drinking water is the use of low cost biosorbents [5]-[15]. The biosorbents surfaces are known to have COOH, C=O, C=C, CONH, NH and OCH functional groups that could physically adsorb, ion-exchange or chemically complex with metal ions, thus retaining them especially when these groups are above the iso-electric point. The most prominent chemical feature of biosorbents that makes it effective for adsorbing metal ions is the presence of several kinds of polysaccharides including pectic acid, alginic acid, and chitosan. Polyphenol compounds and other proteins present in biosorbents may also aid in the adsorption process of metal ions. Although some sorbents may not exhibit significant adsorption activity naturally, it has been shown that treatment of sorbents, such as using sodium hydroxide, may significantly increase the adsorption process. [16] While there is a lot of work done with various biowaste sorbents, there is less work done with the pumpkin and potato peels for cadmium adsorption. The major advantages of using pumpkin and potato peels are their low costs and high availability in the environment.

Currently, the metal ion concentration determination methods used in the adsorption of metal ion studies are mostly based on the atomic spectroscopy, atomic absorption (AAS), inductively coupled plasma atomic emission (ICP-AES/OES) [14] [15] [17] [18] [19]. Compared to spectroscopic methods, electrochemical methods [20] [21] require inexpensive and smaller equipment.

Ion-selective electrodes (ISE) offer further advantages such as they measure free ion activity, and in-situ continuous monitoring without sample pre-treatment [22] [23] [24]. This is especially convenient for kinetic studies with multi-phase systems, without separation to monitor the free ion concentration/activity during the adsorption. This work showed that a commercial solid state ion-selective electrode for Cd(II) works satisfactorily in following the free concentration change during the adsorption process. Pumpkin and potato peels were selected as sorbents due to the high availability, the base treated sorbent showed high adsorption to cadmium at higher pH values. Fixed bed column adsorption of cadmium was also performed to evaluate the dynamic adsorption of cadmium for water treatment and sorbent reuse when regenerated with nitric acid.

2. Experimental

2.1. Materials

Biosorbents:

Potato and pumpkin were ordinary ones obtained from New York stores. Their peels were collected, rinsed with tap water, then with distilled water several times and air dried for three days at ambient conditions. The dried peels were hand-milled in a mortar with pestle and sieved through an 18-mesh sieve. To find the best adsorption conditions, biosorbents were treated with acid or base. Their treatment was done by adding 7.5 g of adsorbents to 200 mL of 0.4 M HNO₃ or NaOH. The mixture was left for 24 hours, and then filtered and the solid biosorbents were collected. The material was left to air dry in the laboratory for 3 to 5 days before use.

Chemical reagents:

All chemicals used in the experiment were of analytical grade. Solutions were prepared with ultrapure deionized water. The argon gas purity for the ICP-OES spectrometer was 99.99%.

2.2. Preparation of Metal Ions Solutions

Cadmium ion solutions were prepared from solid cadmium chloride 1.5 hydrate (purity 97%, Millipore Sigma), with distilled water. The lower concentrations were made with serial dilution to obtain metal ion concentrations for 8.8, 44, 88, 220, 440 and 880 ppm.

Buffer solutions: acetic acid buffer was made with 0.1 M acetic acid and sodium acetate and adjusted to pH 5.6 monitored with a pH electrode. Tri-HNO₃ buffer was made with 0.1 M Tris(hydroxymethyl)aminomethane and adjusted to pH 7.2. Metal ion buffered solutions were made with one-to-one volume dilution of the stock solution with the buffered solution.

2.3. Characterization of the Adsorbent

Bulk densities were measured by weighing the loose dry sorbents in graduate cylinder containing 5 cm³ of the sorbents. Morphological analysis was carried out

by scanning electron microscopy (JSM-6010LA, JEOL. USA).

Fourier transform infrared (FTIR) analysis in solid phase before and after metal ion adsorption was performed using a Spectrum two FTIR (Perkin Elmer) spectrometer with a diamond-attenuated total reflectance (ATR) accessory. Typically, 4 scans at 1 cm^{-1} resolutions were recorded within the $4000 - 650\text{ cm}^{-1}$ region.

2.4. Batch Experiments

Adsorption experiments were performed on base treated biowaste substrate. The adsorption study was performed in isothermal conditions at $20^\circ\text{C} \pm 2^\circ\text{C}$ for 24 h using batch equilibration procedure by treating 0.100 or 0.200 g of the substrate with equal volume of increasing Cd(II) concentration (8.8 to 880 ppm) in buffered or non-buffered solutions under stirring for the first 2 hours. After 24 hours, the pH and equilibrium concentration was measured with the cadmium combination electrode (Cd(II)-ISE) (Orion, ionplus sure-flow solid state, 9648BNWP) for Cd(II) ion adsorption with a Thermo Scientific Orion STAR A112 pH-meter. For unbuffered adsorption experiments, 5.0 mL of unfiltered solution was mixed with 5 mL of 0.1 M acetic acid buffer (pH 5.6) for a fixed pH and ionic strength ISE measurement. The remaining supernatant solutions of some selected sets were filtered with regular filter paper, and then with a 0.45 mm HPLC filter paper. 5.00 mL of the filtered solution was mixed with 5.00 mL of 4% nitric acid for the atomic emission measurements. Cd(II) ion concentration was measured with an ICP optical emission spectrometer (Perkin Elmer, Optima 2100DV ICP-OES) at 228.802 nm.

Adsorption efficiency ($A\%$) was calculated with Equation (1) with the initial concentration introduced into the solution C_0 and equilibrium concentration (C_{eq}). The adsorption isotherms were obtained by plotting the amount of Cd adsorbed (Q_e , Equation (2)) against the C_{eq} in the solution with the linear form (Equation (4)) of the Freundlich Equation (3) [25].

$$\%A = \frac{C_0 - C_{eq}}{C_0} \% \quad (1)$$

$$Q_e = \frac{(C_0 - C_e)V}{w} \quad (2)$$

$$Q_e = K_f \times C_{eq}^{1/n} \quad (3)$$

$$\log Q_e = \log K_f + \frac{1}{n} \log C_{eq} \quad (4)$$

where (Q_e) is the mass ratio between the amount of adsorbed species and the amount of adsorbent (w), V is the volume of the aqueous solution, K_f and $1/n$ are constants which represent the adsorption capacity and the adsorption intensity respectively. By plotting $\log Q_e$ vs $\log C_{eq}$, the linear correlation coefficient, R can be quantified. Significant linearity was tested according to the significance statistical test for R coefficient [26]. The K_f constant (adsorption capacity) is

given by the intercept and n value is given by the slope.

2.5. Adsorption Kinetics

Kinetics study was performed in batch mode with 0.100 g of substrate and 20 ml of various initial metal ion concentrations under constant stirring for up to two hours. The pH and the Cd(II)-ISE potential was continuously recorded. The final concentration after 24 hours was measured again with metal ion selective electrode and ICP-OES. The kinetics of adsorption was fitted with the pseudo-second order model using the following equation:

$$Q_t = \frac{(C_0 - C_t)V}{w} \quad (5)$$

$$\frac{t}{Q_t} = \frac{1}{K_2 Q_e^2} + \frac{t}{Q_e} \quad (6)$$

where C_t is the concentration of the Cd(II) ion measured with the Cd(II)-ISE and, Q_t is the mass ratio at time t . K_2 is the second-order adsorption rate constant in $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$ computed from the linear plot of t/Q_t versus t . Q_e can be calculate with the slope, $Q_e = 1/\text{slope}$. The rate constant is calculated as: $K_2 = 1/(\text{intercept} \times Q_e^2)$ with unit of $\text{g}\cdot\text{mg}^{-1}\cdot\text{min}^{-1}$.

2.6. Dynamic Adsorption and Desorption/Recovery of the Bio-Sorbents

Waste treatment-dynamic adsorption of cadmium from aqueous solution was carried out as follows. Six grams of ground pumpkin peel was placed in a flash chromatography column tube, soaked in 170 mL of 0.4 M NaOH overnight, drained, washed with 200 mL of ultra-pure water and subsequently drained. A solution of 220 ppm cadmium was added continuously with a draining speed of 2 mL/min. The draining solution was collected in 50 (in the beginning) or 20 mL (after 400 mL) beaker batch and monitored with a cadmium ion-selective electrode and pH electrode, the process is stopped when the Cd(II)-ISE showed significant potential increase.

The biosorbent was then regenerated with 800 mL of 0.4 M HNO_3 , slowly drained, and washed with 800 mL of ultra-pure water, to obtain neutral pH of the draining solution. The process of cadmium adsorption was repeated using a 200 ppm Cd solution in dilute Tris- HNO_3 buffer of pH 7.2 for a pH control. Cadmium adsorption-regeneration was repeated 3 times to evaluate the regeneration efficacy.

3. Results and Discussion

3.1. Calibration Curves

Table 1 shows the calibration curve equations for cadmium quantification at 228.802 nm in 2% nitric acid with ICP-OES. For the Ion-selective electrode, the calibration was carried at pH 5.6 in acetic acid buffer. As **Table 1** shows, the slopes of the electrode is slightly below the manufacture certified value of 27 ± 2 mV/dec

at 22 °C after a two week use. However, there is a wide response range for the electrode to be used to measure a wide range of ion concentration when adsorption of these ions occurs by biosorbents.

Table 1. Calibration statistics for the ICP and ion-selective electrodes.

Method	Equation	R^2	Range (ppm)
Cd-ICP at 228.702 nm	$I = [0.1976[\text{Cd}] + 0.897] \times 10^6$	0.996	1 - 50
Cd(II)-ISE	$E = 22.6\log[\text{Cd}] - 211.1 \text{ (mV)}$	0.999	1 - 500

3.2. Sorbent Treatment and Characterization

Many raw materials used for the metal ion adsorption were treated with acid or base [12] [13] [14] for better performance. The biowaste sorbents used here were treated with acid or base. Base treatment removed a good amount of the colored compound from the biosorbents. Preliminary test showed that when unbuffered, the based treated sorbent has higher adsorption (>80%), and acid treated sorbent showed the lowest adsorption (~30%) with 440 ppm Cd. Further, the cadmium ion-selected electrode works better with the base treated sorbents at pH above 3. The untreated biosorbents affected the Cd(II)-ISE potential dramatically. Thus, base treated sorbents were studied further with or without buffer.

The SEM images of the base treated biosorbents are shown in **Figure 1**. Both ground biosorbents are porous with densities of 0.41 and 0.71 g/cm³.

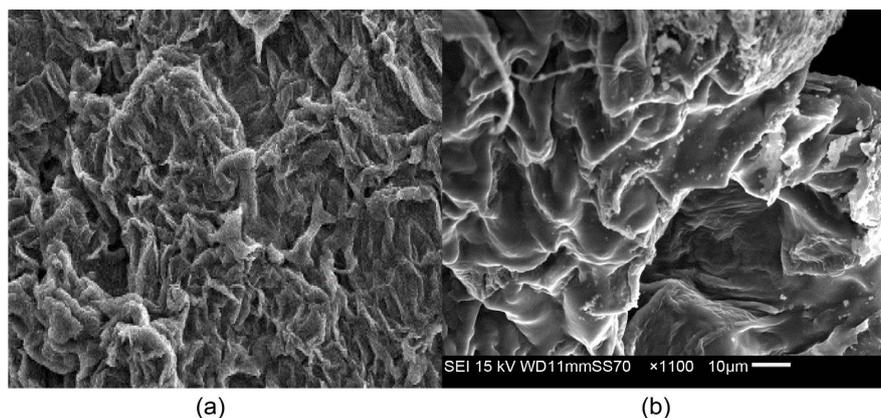


Figure 1. Scanning electron microscopy of (a) pumpkin peel and (b) potato peel porous biosorbents.

The FTIR spectra of pumpkin and potato peel sorbents before and after cadmium ion adsorption show similar IR spectra with peaks for O-H, N-H groups at 3600 - 3100 cm⁻¹ range, C-H at 2921 and 2851 cm⁻¹, C=N, C=C at 1611 cm⁻¹, C-H, O-Hat 1413 cm⁻¹, C-C, C-N at 1013 cm⁻¹. In the presence of Cd(II), peaks at 1733, 1611, 1413 and 1013 cm⁻¹ are significantly changed as shown in **Figure 2** of the pumpkin peel biosorbent. This may indicate that C=O, C-O, C-N are some binding sites to the cadmium ion.

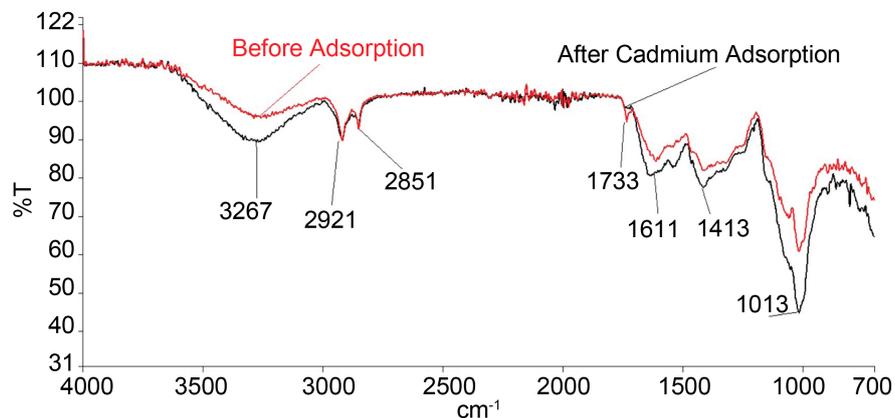


Figure 2. IR spectra of base treated pumpkin peel before and after Cd(II) adsorption.

3.3. Time Response Monitored with Cd(II)-ISE

The electrode was inserted in a 20 mL solution with or without buffer containing a certain cadmium concentration, then 0.100 gram of sorbents was added into the solution, the electrode potential was continuously monitored for 30 - 60 minutes. **Figure 3(a)** shows the electrode potential plotted against the time after the base treated pumpkin peel sorbent was added in a non-buffered solution. There is a gradual decrease of cell potential as time progressed after the addition of the sorbent. To show that the adsorption is second order, the concentration of the cadmium ions was calculated with the calibration curve shown in **Table 1**, the quantity of adsorption (Q_t) at time t was calculated with the Equation (6), the t/Q_t was then plotted and is shown in **Figure 3(b)**. As shown in **Figure 3(b)**, the second order kinetic model plot has a high linearity with a R^2 of 0.999. Thus, the adsorption kinetics is assumed to be second order, which relates that the adsorption of cadmium by pumpkin peel has a great degree of chemisorption.

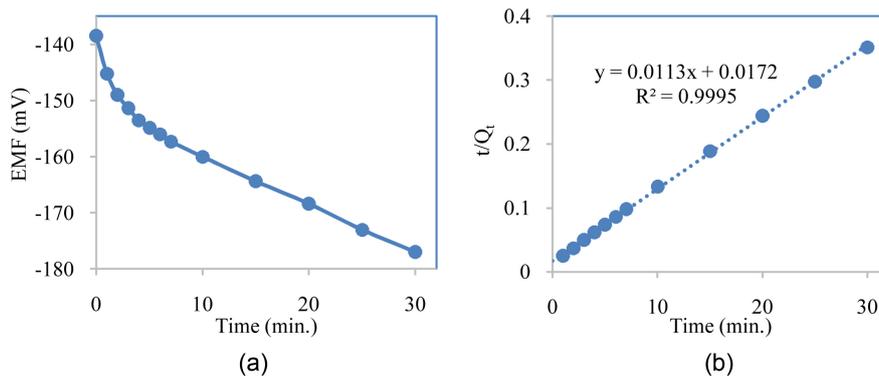


Figure 3. (a) Time response of the Cd(II)-ISE with 20 mL of 440 ppm initial cadmium in water when 0.10 g of base treated pumpkin peel was added. (b) Linear plot of the second order model.

Adsorption of cadmium by potato peel sorbents showed similar pattern with base treated sorbents. The kinetic adsorption at lower pH buffered solution using base treated sorbents all showed good fitting to the second order model. As

an example, **Figure 4(a)** shows the electrode potential change in buffered solution with two initial Cd(II) concentration after potato base sorbent was added. Shown in **Figure 4(b)**, excellent linearity is obtained for both initial Cd(II) concentrations. As Equation (6) shows, the lower initial concentration corresponds to a lower adsorption quantity Q_e , higher slope (**Figure 4(b)**). And then the higher slope in lower pH medium corresponds to lower adsorption Q_e quantity. The second order fitting data with an initial Cd(II) ion concentration of 440 ppm for the potato and pumpkin peels sorbents at three different solution medium are summarized in **Table 2**. These data show that the Q_e values derived from equilibrium measured concentration (Q_e^m) are close to calculated value (Q_e^{cal}) from the second order kinetic plots. For the sets equilibrium concentration were run with ICP-OES, the Q^m values are also very close to the ISE measured values. These data confirm that the Cd(II)-ISE measurement is accurate following the adsorption process even at the unbuffered solution. The reaction kinetic is second order confirmed also by all the linear regression R^2 nearly unity. With high Cd(II) initial concentrations used, Q_e values are among the highest with the biosorbent materials reported [13] [14] [16] [17].

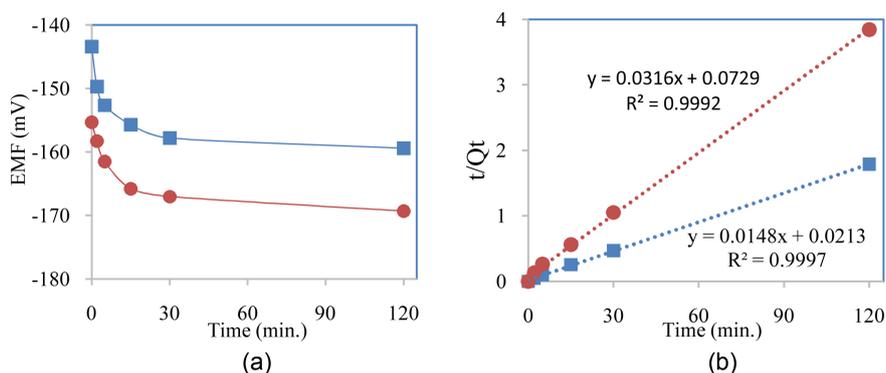


Figure 4. (a) Time response of the Cd(II)-ISE with 20 mL of (•) 440 ppm, (●) 220 ppm initial cadmium in acetate buffer pH 5.6 when 0.10 g of base treated potato peel was added. (b) Linear plot of the second order model.

Table 2. Freundlich isotherm fitting and kinetics constants (440 ppm) for Cd(II) at various sorbents measured with Cd(II)-ISE.

Sorbent	K_f	n	Q_e^m *	Q_e^{cal} #	K_2	R^2
Pumpkin base-pH > 8	56	6	87	88	0.031	1
Pumpkin-base-pH 7.2	27	5	68	68	0.0084	0.993
Pumpkin base pH 5.6	2.0	1.5	49	51	0.0056	0.997
Potatobase-pH > 8	79	12	88	88	1.29	1
Potato base-pH 7.2	39	5	87	87	0.037	1
Potato base-pH 5.6	27	1.5	67	67	0.010	0.999

*: Q_e^m -ISE are the values obtained with the equilibrium concentration of 440 ppm initial concentration measured with ISE. #: Q_e^{cal} is the value derived from the second order kinetic plot of the same initial concentration.

3.4. Adsorption Isotherms

The base treated pumpkin and potato peels are basic, when no buffer is used, the pH of the sorbent-cadmium solutions at equilibrium changed significantly due to adsorption of cadmium. The higher the initial concentration was used, the lower the pH became at equilibrium. There was no precipitation observed with all the concentration used. Due to the higher adsorption, much higher initial concentrations were used to obtain detectable equilibrium concentrations with both ICP-OES and ISE. **Figure 5** shows the pH values measured after 24 hours equilibrating with different initial cadmium solutions contacting with the two sorbents. This graph clearly shows the decrease in pH values from basic to near neutral as initial cadmium concentration increased from 44 to 880 ppm. The equilibrium concentration of the cadmium measured with the ISE again with the solution was mixed with acetic acid buffer of pH 5.6 and ICP-OES all show there was a great reduction in cadmium concentration. The pH decrease is increasing with the higher initial cadmium concentration added. The decrease of pH may be a result in the cation-exchange with sodium or proton at various anion sites: e.g. COO^- , O^- [14].

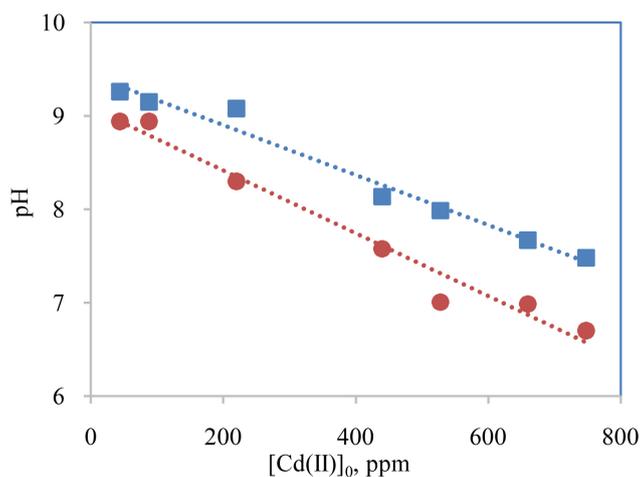


Figure 5. Variation of pH along the adsorption reaction of Cd(II) at various initial Cd(II) concentrations with base treated substrates (▪) potato peel, (●) pumpkin peel.

The equilibrium cadmium concentration measured with ICP-OES showed undetectable values for the lower initial concentrations. Isotherms are then calculated only including the last four points that are shown in **Figure 6(a)**, the linear fitting has a better correlation with the Freundlich model (**Figure 6(b)**) with the both base treated biosorbent. The concentration of Cd(II) at equilibrium measured with the ISE at pH 5.6 also showed that low initial concentration were out of the calibration range, thus only the higher four concentrations were calculated and used to calculate the Q_e and obtain the isotherm and the curve fitting data are shown in **Table 2**. The Langmuir model was used to fit the data; however, poor linearity was obtained for all the sets.

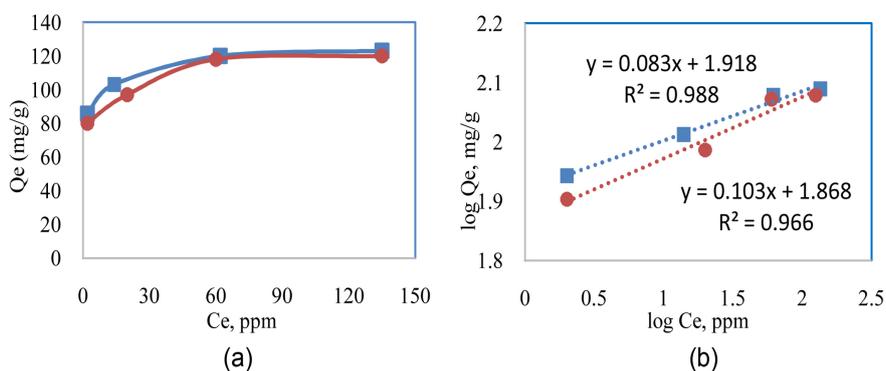


Figure 6. (a) Adsorption isotherm and (b) Freundlich fitting equations for Cd(II) adsorption on base treated (•) potato and (●) pumpkin peel biosorbents.

Equilibrium studies were carried out for Cd(II) adsorption at lower pH (7.2 and 5.6) conditions with the Cd(II)-ISE and pH electrode on two sorbents to observe the pH effects. In the buffered medium, the pH of the solution changed to less than -0.2 pH unit with all the initial Cd(II) concentrations. The isotherms all showed L-shape and fit well on the Freundlich model. **Table 2** also presents the isotherm studies for cadmium adsorption in various solution media. Along with the kinetic values at the same initial concentration, these data show that the adsorption is higher at higher pH as indicated with the higher amount of cadmium adsorbed (Q_e), adsorption capacity (K_f), and adsorption rate constant (K_2). The effect of pH clearly indicates that the cation-proton exchange is a key factor in the cadmium adsorption as suggested by previous research [14].

3.5. Column Adsorption of Cadmium

6.0 g of ground pumpkin was introduced into a flash chromatography column with a porous frit at the bottom. 200 mL of 0.4 M NaOH was applied to the column and kept for 24 hours before it was drained and washed with 50 mL of water. Then 220 ppm Cd(II) in dilute acetic acid buffer was introduced into the column. At a draining speed of 2 mL/min, the electrode potential remained at blank value until 460 mL of draining solution was collected. This corresponds to 101.2 mg of cadmium that was adsorbed on the 6 g sorbent, which gives a 16.9 mg/g capacity.

Then the column was regenerated by introducing 800 mL 0.4 M nitric acid, with a draining speed of 1 mL/min, followed by washing with water until the pH was showing neutral with pH paper. 200 ppm of Cd(II) solution in dilute Tris- HNO_3 solution was introduced. Draining at a speed of 1 - 2 mL/min, the regenerated sorbent gives 15.0 and 15.4 mg/g capacity at the second and third time. **Figure 7** shows the potential of the cadmium electrode (a) and the pH (b) measured in the draining solution when Cd(II) solution was continuously applied to the sorbent. This shows that acid regeneration is sufficient without base treatment. The adsorption is reversible due largely to the cation-proton ion exchange [14].

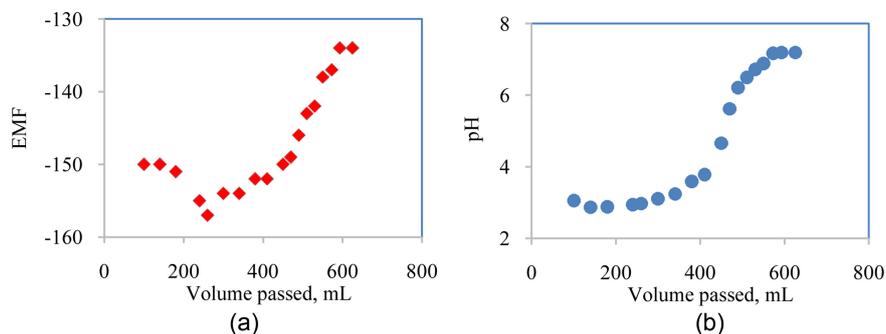


Figure 7. Column Cd²⁺ adsorption with 200 ppm Cd²⁺ in dilute pH 7.2 Tris-HCl buffer as feeding solution. (a) Cd(II)-ISE potential (b) pH vs. the solution volume collected.

4. Conclusion

The present study has clearly shown that simple cadmium ion-selective electrodes can be used for *in-situ* continuously monitoring of the adsorption process onto solid substrates. Biowastes, pumpkin and potato peels can efficiently adsorb toxic cadmium ions from aqueous solutions. The base-treated sorbents give higher adsorption at high pH which could be accounted for favorable chemisorption when the surface is negatively charged. The sorbent can be regenerated with acid washing. The ISE measurements gave comparable equilibrium concentrations obtained from ICP-OES measurements. Ion-selective electrodes do not need sample pretreatment, especially in buffered medium, and it is a much faster method to follow the kinetic process.

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Conflicts of Interest

There is no conflict of interest in the submission of this manuscript.

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