Immobilization and Adsorption Study Related to the Mechanisms of Lead (II) and Cadmium (II) Retention by Phosphate Rock in Multi-Metal System: Analysis via Differential Pulse Stripping Voltammetry Method

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Abstract: ***The feasibility of phosphate rock, PR as an adsorbing and immobilizing agent for Cd^{2+} and Pb^{2+} in multi-metal solution and the interface reaction of PR and the metals were investigated. The equilibrium concentration of Pb^{2+} in each solution adsorbed by PR surpassed the detection limit of the analytical method employed (DPASV) such that no peaks of Pb^{2+} were detectable. This indicates that Pb^{2+} was highly immobilized during metal retention since very low concentration of Pb^{2+} remained in the solution compared to Cd . In pH-free and pH–controlled systems adsorption on PR of Pb was up to 91.96% while for Cd, adsorption was only about 60-95% of the initial amount. Three adsorption isotherm models were studied; Freundlich, Langmuir, and Temkin. The equilibrium sorption data were evaluated and found that Langmuir model exhibits the highest correlation coefficient value. In the Langmuir model, the maximum monolayer coverage capacity q_m is 81.97 mg/g, Langmuir constant K_L is 0.0632, and the separation factor R_L is 0.148 which is $0<R_L<1$. This means that equilibrium sorption was favourable. In the Freundlich isotherm, the adsorption capacity K_F is 5.130 mg/g and the adsorption strength 1/n is 0.801 where n is equal to 1.248. Since n value lies from one to ten, it points out that sorption process is favourable. In the Temkin isotherm, the binding constant K_T is 0.443 L/g and the heat of adsorption is 28.552 J/mol indicating a physical adsorption process. Additionally, upon quantifying the P content of the solution after adsorption, it was observed that P content decreases as the equilibrium concentration of Cd^{2+} increases. This suggests that P was consumed during metal retention. Furthermore, the decrease of pH in solution after adsorption indicates that H^+ is released in the solution, displacing the metal ion. The stability of the metal was also examined through desorption experiment. It was observed that at lower pH (pH 3) of extracting solution, the amount of metal desorbed is greater compared to higher pH (pH 7 and 9).***

Keywords: adsorption. heavy metals, phosphate rock, adsorption isotherm **.**

1. Introduction

Naturally, metals such as lead and cadmium are present in the environment in different concentrations. Its balance in the environment changes due to human activities. It is accumulated from excessive application of fertilizers, pesticides, herbicides and animal manure in soil. Moreover, wastewater, milling processes, mine tailings and industrial wastes are also sources of heavy metals in the environment. It easily enters the food chain through various routes and exposure that gives dangerous consequences and threats to humans.

Lead is found as a mineral together with other elements, naturally occurring and with bluish-gray color. It has a very low melting point of 327°C. It combines mostly with sulfur and oxygen. About 10-30 $mgKg^{-1}$ are present in earth's crust.1 It is used for ceramic glazes, batteries, fishing sinkers, old pipes, solders and gasoline in order to minimize engine knocking.[2] It is also used as white paint pigments in forms of basic salts. In addition, lead is used in building industry for roofing and flashing, pipes, paints, ceramics and dishware, for electronics and ammunition.[3] Lead chloride and lead sulfates are used for lead storage batteries, which are responsible for reversible reaction when charging and discharging occurs.[4] In ancient time, it is used as a structural metal for weather proofing buildings, in water ducts and in cooking vessels. During the roman times, analysis of ice-core samples from Greenland indicates that atmospheric lead concentration reached a peak.

Exposure of heavy metals through the body is mainly due to direct ingestion, dermal contact and inhalation. Massive amount and concentration of lead are mostly found in leafy vegetables. Its toxicity increases its risk as the level of lead in soil increases above 300 ppm.[5] At high concentrations, it is a general metabolic poison. It greatly affects the neurological and reproductive systems. Blood–brain barriers are damaged and cause interferences with the normal development of brain in infants. It can be transferred from the mother in her breast milk and results lower IQ level in children. Elevated levels of Pb poisoning can result to death.

Cadmium is one of the three dangerous heavy metal poisons and a nonessential heavy metal.[4] Coal burning is the main source of cadmium in the environment. Cadmium is used for Ni/Cad batteries and coatings to vehicles that are responsible for good corrosion resistance. It is used as a pigment in paints, as well as in photovoltaic devices and TV screens. It is an impurity in fertilizers, detergents and refined petroleum products. Additionally, cadmium is present in acid rain causing to increase mobility of cadmium that results contamination of surface waters.[2] The greatest proportion of human exposure to cadmium comes from food supply such as sea food, organ meats, potatoes, rice and other grains.[3]

Cadmium is most toxic in ionic form and high level of exposure to human body would have great effects. Most common exposure comes from the consumption of food supply (seafood, organ meats, food crops) and drinking water, inhalation of cadmium containing particles from ambient air or cigarette smoke, or ingestion of contaminated soil and dust.[3,7] Cadmium compounds are known to be human carcinogens based on sufficient evidence of carcinogenicity from studies in humans.[11] It can cause severe pain in joints, bone diseases, kidney problems, renal damage (proteinuria) and affect several enzymes. High levels of Cd may eventually result in death.[8,9]

In order to reduce heavy metal's bioavailability and prevent the unavailable metals from becoming available, immobilization is necessary. Immobilization is a soil remediation technique over which toxic heavy metals bind to the soil reducing their mobility and bioavailability.[10] Remediation processes are classified into source control and containment remedies.[11] *In situ* and *ex situ* treatment is under source control. *In situ* treatment is done without removing the contaminated soil on the site. While *ex situ* treatment means that the soil is removed from the subsurface. For containment remedies, construction of vertical engineered barriers, caps and liners are used to avoid contaminant migration. Contaminants are immobilized and its concentration is reduced to an acceptable level by addition of amendments to the soil.[12] Using organic and inorganic amendments, heavy metals in contaminated samples can be converted into a more stable form by adsorption, precipitation and complexation. Phosphorus-bearing material such as phosphate rock is widely used as fixing agents to immobilize heavy metals in soil. Phosphate rock (PR) is a non-renewable resource. Deposits of PR are mined and utilized for P fertilizer production. Other PR is used for manufacturing animal feeds, detergents and chemicals. It is widely used as a source of phosphorus for amendments in immobilization. It has different efficiency for every heavy metals being treated. Efficiency of heavy metal immobilization is affected by incubation time and mixing process. It is more effective when PR is mixed with the soil and phosphoric acid is added at the same time.[13] Phosphoric acid is used as a combination of PR to facilitate precipitation of heavy metal-phosphate compounds. The particle size of the PR also influences the immobilization capacity. Particle size less than 63 μm is more efficient than larger size.14 Moreover, PR is said to be efficient in Pb immobilization upon formation of stable Pb-phosphate minerals, pyromorphite [$Pb_5(PO_4)_3$(F, Cl,OH)].[15, 16] It is the most insoluble form of Pb mineral in soil.[17, 18]

The presence of other metals and the composition in a solution affect the sorption of heavy metal on solid surface.6 Components in the solid surface such as calcium, phosphorus, magnesium and potassium may give effect on heavy metal retention. Concentration of calcium increases with metal disappearance during metal retention, which means that Ca is release into the solution. In contrast, phosphorus decreases with increasing metal reduction.[6] This suggests that P is consumed during metal retention. There is a significant decrease on the pH up to 1.5 unit change of the solution during metal uptake. It was found that complexation of Cu and Zn occurred on the surface when mixed with PR. It partially displaces H+ ions and cause pH to decrease.[6] But in case of Pb, formation of fluoropyromorphite predominates and hence this will not cause a large pH change.19 Hence, the decrease of pH in the solution is due to other mechanisms aside from PR dissolution and fluoropyromorphite precipitation.

Immobilization of these metals is more challenging since heavy metals co-existing in the soil interact with one another. A single treatment of P-bearing material may not be enough to immobilize different metals present in soil. It may mobilize again due to microbial activity, rainfall, and landfill and plant growth under field conditions.[20] Long-term stability of initially amended metals is particularly of concern since metals only changes its form but still remains in the soil.[21]

There are several mechanisms for heavy metal retention due to immobilization using PR. One is formation of Ca(10-x)Pbx$(PO_4)_6(OH)_2$, a stable Pb-phosphate produced due to ion exchange mechanism. In an aqueous solution, Pb substitutes the Ca ion on the hydroxyapatite lattice.$_6$ Other investigation for immobilization using PR shows formation of fluoropyromorphite ($Pb_{10}(PO_4)_6F_2$).[22] Another mechanism of Pb immobilization is dissolution of PR and subsequent precipitation of a pyromorphite-like mineral ($Pb_{10}(PO_4)_6X_2$), X= OH, Cl, F). It is said to be a primary mechanism, though Pb is also precipitated as hydrocerussite.[4] The simplified reaction equations for Pb immobilization are:[23]

$$Ca_{10}(PO_4)_6F_2 + 12H^+ \leftrightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^- \quad (1)$$
$$10Pb^{2+} + 6H_2PO_4^- + 2F^- \leftrightarrow Pb_{10}(PO_4)_6F_2 + 12H^+ \quad (2)$$

The effectiveness of heavy metal adsorption on the adsorbent can be evaluated through adsorption isotherm models. Sorption capacity is determined to measure the efficiency of the adsorbent to adsorb metals. It also helps to describe the distribution of the adsorbate among liquid and solid phases. Assumptions are considered which are related to the heterogeneity or homogeneity of solid surface, type of adsorbent and the possible interaction between the adsorbate.[24]

Langmuir isotherm model assumes that the adsorption takes place on a homogeneous surface by monolayer adsorption without any interaction between adsorbed ions.24 This can be represented by the equation:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

and its linear form is

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \quad (4)$$

This model helps to determine the adsorption capacity with respect to the assumption stated previously.

Freundlich Equation can be represented by

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where its linear form is

$$ln q_e = ln K_F + \frac{1}{n} ln C_e \quad (6)$$

In this model, it is assumed that adsorption takes place on a heterogeneous surface. It estimated the adsorption intensity of the adsorbate on the adsorbent.[24]Higher adsorption intensity shows the ability of the adsorbent to remove metal ions from solution.

The equation for Temkin isotherm model is represented as:

$$q_e = \frac{RT}{b}\ln(K_T C_e) \qquad (7)$$

and its linear form is:

$$q_e = B_T lnK_T + B_T lnC_e \qquad (8)$$

The assumption considered in this model is that there is a linear decrease of the heat of adsorption due to the interaction of the adsorbent and the adsorbate. The process of adsorption includes the bonding energies, up to the maximum binding energy. Adsorption potential of the adsorbent for the adsorbates is determined in this model.[24]

Determination of inorganic elements in samples can be accomplished using anodic stripping voltammetry (ASV). Information about the inorganic analyte can be obtained using this technique in which the relation of voltage and current is observed during an electrochemical reaction.[25]The relationship between the current and potential of the analyte is presented by a voltammogram. These signals are correlated to the amount of metal ion present in sample solution. And so, quantitative analysis can be accomplished using this technique.

Generally voltammetric analysis consists of electrodes namely working (indicator) electrode, a reference electrode, and counter or auxiliary electrode. It involves reduction and oxidation reactions of the desired species at the surface of a working electrode, with appropriate applied potential this results to a mass transport of new material to the electrode surface and generate current.[26]

The applied potential controls the concentrations of the redox species at the electrode surface and the rate of the reaction, as described by the Nernst equation[27]

$$E = E^0 - \frac{RT}{nF} ln \frac{c_R^0}{c_O^0} \qquad (9)$$

Where R is the molar gas constant (8.3144 Jmol^{-1}K^{-1}), Tis the absolute temperature in Kelvin, n is the number of electrons transferred, F Faraday constant (96,485 C/equiv),E^0 is the standard reduction potential for the redox couple, c$_R^0$ and c$_o^0$ are concentrations of the redox species at the electrode surface.[27]The current resulting from redox reactions at the working and auxiliary electrodes is called a faradaic current and mass transport is the movement of material toward or away from the electrode surface.[27]

Two factor affect the rate of the electrochemical reaction: the rate at which the reactants and products are transported to and from the surface of the electrode, and the rate at which electrons pass between the electrode and the reactants and products in solution.[26] Diffusion, migration, and convection are the modes of mass transport that influence the rate of the reaction. Diffusion is the region from a high concentration to a region of low concentration which occurs whenever the concentration of the desired ion at the surface of the electrode is different from that in bulk solution. When the potential applied to the working electrode is sufficient to reduce or oxidize the analyte at the electrode surface, diffusion layer is formed. This layer increases with time as the concentration of reactants near the electrode surface decreases.[26, 27] Convection occurs when reactants goes toward the electrode and to remove products from the electrode usually by means of stirring the solution. The final mode of mass transport is migration, which occurs when charged particles in solution are attracted or repelled from an electrode that has a positive or negative surface charge.[27] Other currents such as exist in an electrochemical cell which are unrelated to any redox reaction.[28]

DPV method composes of potentiostat, computer, and the electrochemical cell. Potentionstat is where the flow of current is monitored through electrodes. Glassy carbon electrode (GCE) was used as the working electrode which transports electrons to and from the desired ion.[26] Silver – silver chloride electrode was used which acts as half-cell or reference electrode. It is made by taking a wire of solid silver and coding it in AgCl and placed in a tube containing KCl and AgCl solutions.[26] The counter electrode used was SHE or standard hydrogen electrode that makes sure that the current does not pass through the reference cell. The potential is scanned with a series of pulses.[26] This potential pulse is fixed, of small amplitude (10 to 100 mV), and is superimposed on a slowly changing base potential. Sensitivity of current measurement is attributed by two points for each pulse, the first point the application of the pulse and the second the end pulse. These points are selected to decrease the non-faradaic (charging) current.[28]The difference between current measurements at these points for each pulse is determined and plotted against the base potential. The resulting measurement is displayed on a plot called voltammogram.[26]

It is quite complicated to conduct determination of analytes in complex sample matrix because of the adsorption and deposition of the different components in the sample onto the electrode surface. This leads to the loss of electrode activity and non-reproducible results.[29]To prevent this, different electrolytes can be used to extend the efficiency of electrochemical reactions.[30-32] However, this requires too much handling of data related to the properties and behaviour of inorganic elements in multi-element system. Also, interferences between the individual components of the multi-element system occur as well as overlapping of peaks.[29] Due to the factors that affect the capacity of the technique, this is seldom used. Fortunately, sample handling and experimental execution is enhanced using glassy carbon electrode instead of hanging mercury drop electrode. This allows electrochemical signal to be characterized more effectively.[29] This technique can be performed with differential pulse anodic stripping voltammetry (DPASV) which allows elimination of interferences for determination of inorganic elements in multi-metal system.[29]

2. Procedure

2.1 Preparation of Samples

PR sample purchased at Tough-D Agri Enterprises, Davao City was air-dried and passed through a 0.100-mm sieve. A solution containing 1000ppm of each analyte (Pb^{2+} and Cd^{2+}) in multi-metal system was prepared from their nitrate salts. Stock Solution of 0.250 M $NaNO_3$ was prepared in order to control the ionic strength of the solution at 0.05 M. This serves as the background electrolyte solution. The experiment was run in triplicate.

2.2 pH-Controlled Sorption System

A series of 50 mL of 0.05 M $NaNO_3$ containing different concentrations (0, 25, 50, 100, 200 ppm) of an equimolar mixture of Pb^{2+} and Cd^{2+} was placed in a separate 250-mL Erlenmeyer flask containing 0.100x g of PR. The pH of the solution was controlled at 5.5 ± 0.2 with diluted HCl and NaOH. The resulting suspensions were shaken using a mechanical shaker for 24 hours at 25 ± 0.2 °C to reach equilibrium. The supernatants were separated by centrifugation for 25 minutes, followed by filtration. The filtrate was saved for pH, P, Pb^{2+} and Cd^{2+} analysis while residues were reserved for the desorption experiment. The zero ppm in both ions serves as the blank reagent during the entire analysis. The amount of adsorbed metal was calculated as the difference between the initially added amount and that remaining in solutions after equilibration.

2.3 pH-Free Sorption System

This system helps in the evaluation of the amount of hydrogen ions that may be produced as metal uptake increases.

A set of 50 mL of 0.05 M $NaNO_3$ containing different concentrations (0, 25, 50, 100, 200 ppm) of Pb^{2+} and Cd^{2+} was placed in an Erlenmeyer flask containing 0.100x g of PR. The resulting suspensions were shaken for 24 hours using a mechanical shaker, centrifuged for 25 minutes and filtered. The residues in the test tubes were reserved for the desorption experiment. After 24 hours equilibration, the pH of the solutions was recorded.

2.4 Desorption of Multi-metal System

Desorption experiments were conducted to evaluate the stability of heavy metals adsorbed by PR. Three extracting solutions of varying pH (3, 7 and 9) were prepared to evaluate the stability of PR after interaction with metal ions in aqueous solution. The pH 3 extracting solution was prepared from dilute acetic acid while pH 7 and pH 9 extracting solutions were prepared from dilute HNO_3 and NaOH.

In this process, residues from 25 ppm and 200 ppm metal ion initial concentrations were chosen, and washed twice with distilled water. The washed residues were then treated with 50 mL of the prepared extracting solution. The resulting slurries were shaken for 24 hours, centrifuged for 25 minutes and filtered. The collected supernatants were used for the analysis of pH, P, Pb^{2+} and Cd^{2+}.

2.5 Analysis Method

The components of PR were determined by preliminary analysis using X-ray Fluorescence Spectrometer. The equilibrium concentrations of Pb^{2+} and Cd^{2+} in ppm were determined using the voltammetric method of Differential Pulse Anodic Stripping Voltammetry in Autolab PGSTAT302N. Total phosphate concentration was determined using Lasany Brand Double Beam UV-VISIBLE Recording Spectrophotometer via ammonium molybdate-aminonaphtholsulfonic acid method. The pH of the solutions was measured using Fischer Accumet digital pH meter.

2.5.1 Determination of Pb^{2+} and Cd^{2+} Using Differential Pulse Anodic Stripping Voltammetry

AUTOLAB PGSTAT302N was the instrument used for differential pulse anodic stripping voltammetry. In this study, the glassy carbon electrode (GCE) was used as working electrode (WE) and Ag/AgCl electrode as the reference electrode (RE). An Ultra High Pure nitrogen gas at pressure of 14.5 psi was used for purging the dissolved oxygen that may be present in the sample solution. The instrument parameters used during the analysis of Pb^{2+} and Cd^{2+} are listed in Table 1.

Table 1: Parameters Used during the Analysis

Purge	10 s
Conditioning otential	1.000 V
Conditioning time	15 s
Deposition Potential	-1.200 V
Deposition time	60 s
Equilibration time	15 s
Optimize current Range	5
Initial Potential	-1.200 V
End Potential	0.000 V
Step Potential	0.00500 V
Modulation Amplitude	0.02500 V
Modulation time	0.01000 s
Interval time	0.05000 s

2.5.2. Analysis of Pb^{2+} and Cd^{2+} in Sample Solutions

A calibration curve for the determination of Pb^{2+} and Cd^{2+}, using standard addition method, was constructed. A fixed volume of acetic acid-acetate buffer (pH 4.00) was pipetted into the vessel, purged with N_2 gas and scanned. Varying amount of standard solution (10ppm) was added (0.1 mL increment) into the vessel until a straight calibration curve was obtained. Determination of Pb^{2+} and Cd^{2+}in the sample was accomplished using the same method and same instrument parameter settings.

2.5.3 Total Phosphate Determination via UV-Vis Spectrophotometer(Ammonium molybdate/ Aminonaphtholsulfonic Acid method)

Before constructing a calibration curve (from different concentrations of standard solution) and conducting analysis of sample, preliminary investigation of the phosphate-aminonaphtholsulfonic acid complex was conducted.

Phosphate ion of 1.0 ppm complexed with aminonaphtholsulfonic acid reagent was scanned from 300-1000 nm. From the produced spectrum, the wavelength of maximum absorption, λ_{max} was determined. Because the complexation reaction of the phosphate ion with aminonaphtholsulfonic acid reagent is time dependent, kinetic study for the reaction was conducted. A time scan was performed for a period of 30 minutes and from the produced time scanned data, the wider time range that showed constant absorbance reading was noted. Results of the preliminary investigation of the complex showed that λ_{max} was detected at 737 nm and time range for safe absorbance measurement was at 10-12 minutes after the complexing agent was added. Construction of the calibration curve and analysis of sample for phosphorus (in a form of phosphate ion) was done using the obtained conditions from preliminary experiments. Hence absorbance measurement for the construction of calibration curve and analysis of sample were done at 737 nm and at 10-12 minutes after the aminonaphtholsulfonic acid was added.

Table 2: Standard Preparation for the Construction Of The Calibratkion Curve

Volume of stock solution, mL	Volume of Reagent, Ml		Volume of Water, mL
	Ammonium Molybdate	Aminonaph-tholsulfonic Acid	
0.00	0.5	0.5	9.00
0.50	0.5	0.5	8.5
1.00	0.5	0.5	8.0
1.50	0.5	0.5	7.5
2.00	0.5	0.5	7.00
2.50	0.5	0.5	6.5
5.00	0.5	0.5	4.00

Table 3: Sample Preparation for UV-VIS Analysis

Volume of sample solution, mL	Volume of reagent, mL		Volume of water, mL
	Ammonium Molybdate	Aminonaphthol sulfonic acid	
1.00	0.5	0.5	8.00

3. Result and Discussion

3.1. Amounts of Pb^{2+} and Cd^{2+} after Adsorption with PR (via Differential Pulse Anodic Stripping Voltammetry)

Immobilization ofPb^{2+} and Cd^{2+}in a solution using PR sample was successfully performed using the set of parameters listed in Table 1. Preliminary experimental results (optimization) showed that the best voltammogram in DPASV was observed when acetic acid-acetate buffer of pH 4.00 was used. For standard mixture (Pb^{2+} and Cd^{2+}), most resolved peaks were observed when 20 mL of the buffer solution have been added. Figure 1, shows the voltammogram of lead and cadmium mixture. From the figure, the current peaks due to Pb and Cd were detected at potential range of -0.54V to -0.50V and -0.76V to 0.71V, respectively.

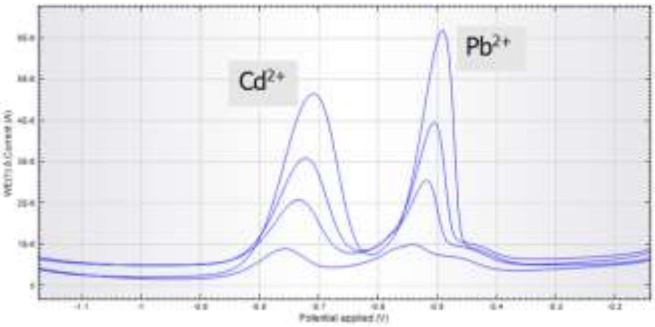

Figure 1: The voltammograms of standard Pb^{2+} and Cd^{2+} in varying concentrations during construction of the calibration curves.

Sensitivity of the linear range was observed from 0.03 ppm to 0.3 ppm. These most resolved peaks resulted only after 20mL of acetic-acetate buffer have been added.

3.2. Calibration Curve of Standard Mixture of Lead(II) and Cadmium(II)

The corresponding calibration curves of standard metal ions were depicted in Figure 2. The points plotted produced an equation of the lines $y=2x10^{-5}x -3x10^{-7}$ and $y=2x10^{-5}x - 2x10^{-7}$ for lead and cadmium, respectively. These equations were used in the determination of the equilibrium concentration of each metal ion in the mixture.

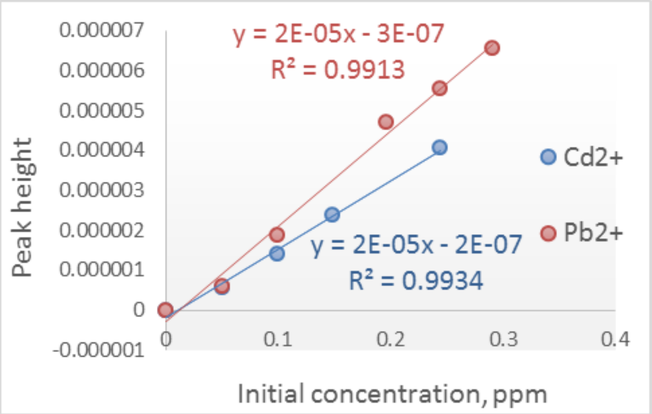

Figure 2: The constructed calibration curves for Pb^{2+} and Cd^{2+}

3.3. Data and Calculated Measurement of Adsorption process

The resulting peak heights of Cd^{2+} displayed in the voltammogram as measured by Autolab instrument after adsorption process were tabulated in Table 4. Given these peak heights and substituting this to the equation of the line of Cd^{2+}, equilibrium concentrations were calculated. The final concentration of the sorption sample was subtracted from the initial concentration of the sample and the amount of Cd^{2+} adsorbed was obtained.

Table 4: Data and Calculation Obtained from the Adsorbed Cd^{2+}After Ph-Free Adsorption Process

Initial Con Centration	Metal adsorbed (ppm)	Initial con-centration	Metal adsorbed (ppm)
25 ppm		50 ppm	
1	20.33	1	43.21
2	19.47	2	44.05
3	20.50	3	43.57
Average	20.10±0.55	Average	43.61±0.42
100 ppm		200 ppm	
1	43.21	1	188.77
2	44.05	2	191.58
3	43.57	3	190.68
Average	43.61±0.42	Average	190.34±1.43

Data and results from pH-controlled adsorption process are presented in Table 5. Same calculations were done in determining the equilibrium concentration of this system.

Table 5: Data and Results Obtained of the Adsorbed Cd^{2+} after pH-Controlled Adsorption Process

Initial Concentration	Metal Adsorbed (ppm)	Initial Concentration	Metal adsorbed (ppm)
25 ppm		50 ppm	
1	20.52	1	39.41
2	----	2	40.67
3	9.50	3	40.95
average	**15.01±7.79**	Average	**40.34±0.82**
100 ppm		200 ppm	
1	91.08	1	139.50
2	96.92	2	176.99
3	88.75	3	191.78
average	**92.25±4.21**	Average	**169.42±26.95**

Table 6 is the average concentration (ppm) of the adsorbed lead ion after adsorption process of both pH-free and pH-controlled system. It shows no peak height due to Pb^{2+} as observed in the voltammogram. This means that in all equilibrium concentrations only peak due to Cd^{2+} was produced from the sample mixture.

Table 6: Average Data of the Adsorbed Pb^{2+} after Adsorption Process

Initial concentration, ppm	25	50	100	200
Peak height	0	0	0	0
Equilibrium concentration	0.01	0.01	0.01	0.01
Amount adsorbed, %	22.99	22.99	22.99	22.99

The data summarized in Table 7 are the percentages of the adsorbed metal ion (for three trials) in the mixture of the pH-free system. Results showed an increasing trend of the concentration of Cd^{2+} adsorbed by PR as the initial concentration of Cd^{2+} is increased. The amount of Cd^{2+} adsorbed by PR also increases as the initial concentration of standard mixture increases.

For the analysis of Pb^{2+} in the mixture, since no peaks were detected assumptions were made that Pb^{2+} in all equilibrium concentrations were almost totally adsorbed. This is explained by the very small concentration that remained in the sample which limits the chance for Pb^{2+} to be detected.

Table 7: Percentage Sorption of Metal Ions by PR in pH-Free Multimetal System

pH-Free		
Initial concentration Ppm	Sorbed Pb^{2+}, %	Sorbed Cd^{2+},%
25	91.96	80.40 ± 0.55
50	91.96	87.22 ± 0.42
100	91.96	87.51 ± 3.92
200	91.96	95.17 ±1.43

The percentage of adsorbed metal ion in pH–controlled were also obtained as shown in Table 8. Similar trend was observed: adsorbed Cd2+ increases with increasing initial concentration. Unfortunately its standard deviation system was quite high compared to pH-free. Hence, metal sorption is effective and reliable to be observed in pH –free system.

Table 8: Percentage Sorption of Metal By PR in pH-Controlled Multi-Metal System.

pH-Controlled		
Initial concentration ppm	Sorbed Pb^{2+}, %	Sorbed Cd^{2+}, %
25	91.96	60.04 ± 7.79
50	91.96	80.69 ± 0.82
100	91.96	92.25 ± 4.21
200	91.96	84.71 ± 26.95

Figure 3 is the voltammogram after sorption of the solution having 200 ppm initial concentration of each metal ion (Pb^{2+} and Cd^{2+}) in multi-metal system. The absence of Pb^{2+} in the voltammogram after sorption indicates that its presence in the solution is very small and beyond the detection limit of the employed method. However, peak due to Cd^{2+} was still detectable, implying that the extent of immobilization through adsorption is lower compared to Pb^{2+}.

Figure 3 (a): Voltammogram for 200 ppm multi-metal solution (Pb^{2+} and Cd^{2+})after adsorption, pH controlled.

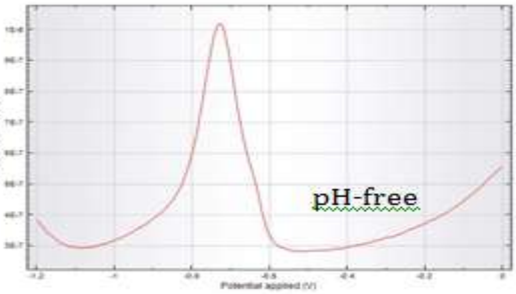

Figure 3 (b): Voltammogram for 200 ppm multi-metal solution (Pb^{2+} and Cd^{2+})after adsorption, pH free.

Comparing the sorption of Pb^{2+} and Cd^{2+}, Pb^{2+} has the highest amount sorbed by PR. This was confirmed by the voltammogram shown in Figure 3. Pb^{2+} is no longer detectable after sorption, hence its presence at equilibrium is very small, and is below the detection limit of the analytical method used (DPASV). It can also be concluded that immobilization of Pb^{2+} by PR was not highly affected by the presence of the other metal ion (Cd^{2+}). However, since the concentration of Cd^{2+} decreases at equilibrium, it suggests that Cd^{2+} also undergoes sorption but the extent of sorption is weaker compared to Pb^{2+}.

The average percentages of the sorbed amount of metal ions in two systems were plotted against initial concentrations. The relationships are illustrated in Figure 3 and Figure 4. These resulting graphs confirmed the effectiveness of PR in immobilizing heavy metals.

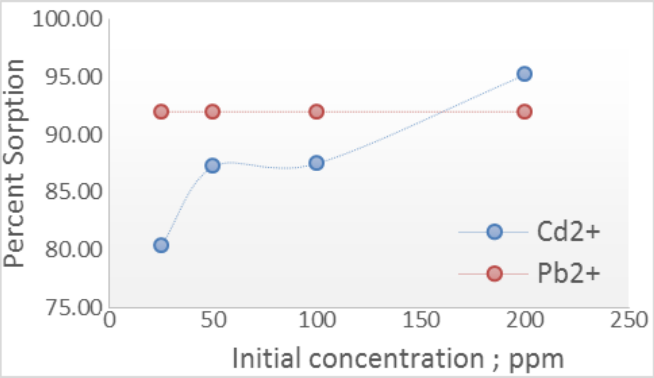

Figure 4: Percent sorption versus initial concentration in pH-free multi-metal system

The graph shown in Figure 5 is similar to that shown in Figure 4 except that in Figure 5, a significant decrease in the amount of adsorbed Cd^{2+} was observed at 200 ppm.

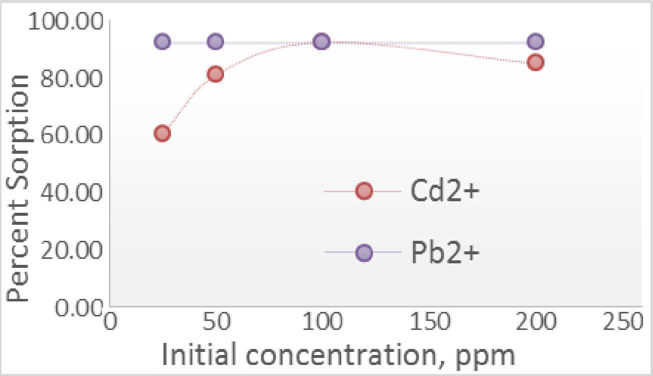

Figure 5: Percent sorption versus initial concentration in pH-control multi-metal system.

3.4. Adsorption Isotherms

It was universally accepted that adsorption process has been important for immobilization of pollutants, especially heavy metals.[33, 34] Equilibrium sorption data were evaluated using adsorption isotherms which represent mathematical models that approximates the efficiency of metal sorption on the adsorbing species.[24] Different assumptions are considered in each isotherm model.

3.5. Langmuir Adsorption Isotherm

This model defines the formation of a monolayer adsorbate on the adsorbent surface quantitatively.[35] It shows the equilibrium distribution of heavy metal ions in solid and liquid phase which is valid for monolayer adsorption on surface containing finite number of identical sites that is assumed to be homogeneous.[35, 36] The equation below shows the linear representation of Langmuir model.

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m K_L C_e} \qquad (10)$$

Where:
C_e = the equilibrium concentration of adsorbate (mg/L^{-1})
q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).
q_m = maximum monolayer coverage capacity (mg/g)
K_L = Langmuir isotherm constant (L/mg).
In this study, Langmuir model for pH-controlled system (pH 5.5 ± 0.2) is represented in Figure 6.

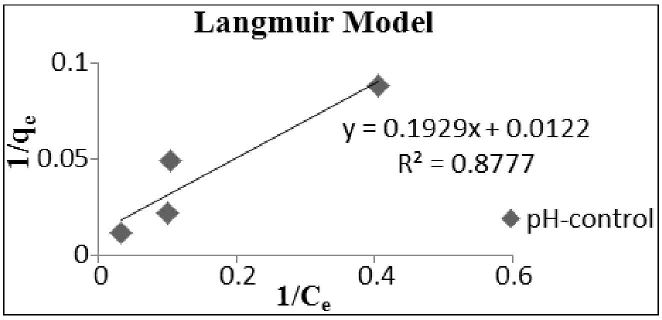

Figure 6: Langmuir equilibrium isotherm model for the sorption of Cd^{2+} on PR.

The equilibrium parameter, R_L that represents the essential features of Langmuir isotherm is referred as the separation factor.[37]

$$R_L = \frac{1}{1+(1+K_L C_0)} \qquad (11)$$

Where:
C_0 = initial concentration
K_L = the constant related to the energy of adsorption (Langmuir Constant).

The equilibrium parameter R_L specifies the nature of adsorption to be either:
Unfavourable if $R_L>1$
Linear if $R_L=1$
Favourable if $0<R_L<1$
Irreversible if $R_L=0$.
The parameters q_m and K_L were calculated from the slope and the intercept of the linear equation. The values of the parameters are shown in Table 9.

Table 9: Langmuir Adsorption Isotherm Parameters

q_m(mg/g)	K_L (L/mg)	R_L	R^2
81.97	0.0632	0.148	0.8777

In this research, the maximum monolayer coverage capacity of Langmuir model is 81.97 mg/g, Langmuir constant K_L is 0.0632, and the separation factor R_L is 0.148 which is within the range of $0<R_L<1$. This means that equilibrium sorption is favourable.

3.6. Freundlich Adsorption Isotherm

The adsorption in this model was assumed to take place on a heterogeneous surface. The equation proposed by Freundlich in linear form is

$$lnq_e = lnK_F + \frac{1}{n} lnC_e \qquad (12)$$

Where:
K_F = Freundlich isotherm constant (mg/g)
n = adsorption intensity;
1/n = function of the strength of adsorption process
C_e = the equilibrium concentration of adsorbate (mg/L)
q_e = the amount of metal adsorbed per gram of the adsorbent at equilibrium (mg/g).

The Freundlich Isotherm model for pH-controlled system (pH 5.5 ± 0.2) is shown in Figure 7.

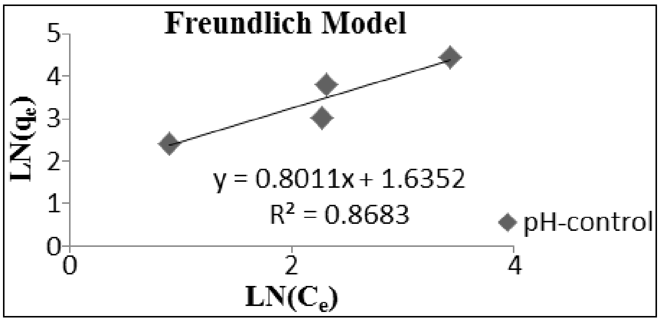

Figure 7: Freundlich equilibrium isotherm model for the sorption of Cd^{2+} on PR.

The following are some of the conditions considered:
If n=1, the partition between the two phases are independent of the concentration;
if 1/n<1, it indicates a normal adsorption;
if 1/n>1, it indicates cooperative adsorption[38];
if 1<n<10, sorption is favourable.[39]
The parameters for Freundlich Isotherm are shown in Table 10.

Table 10: Freundlich Adsorption Isotherm

1/n	N	KF(mg/g)	R2
0.801	1.248	5.130	0.8683

The parameter K_F represents the approximate indicator of the adsorption capacity, while 1/n indicates the function of adsorption strength during adsorption process.[40] The sorption data were correlated to the linearly transformed equation where 1/n indicates the heterogeneity parameter. Smaller 1/n value specifies greater heterogeneity. If n value lies from one to ten, the sorption process is favourable.[39] Freundlich parameters shown in Table 9 indicates that n is 1.24 which means that sorption of Cd^{2+} onto PR is favourable

Temkin Isotherm

In this isotherm, the adsorbate-adsorbent interaction is considered. Due to this interaction, the heat of adsorption decreases linearly with coverage, rather than logarithmically.[41, 42] The adsorption was characterized by a uniform distribution of bonding energies (up to some maximum binding energy).[43] The linear equation for this model is

$$q_e = B_T lnK_T + B_T lnC_e \qquad (13)$$

Where
B_T = Temkin constant related to the heat of adsorption (J/mol)
K_T = equilibrium binding constant (L/mg).
Temkin Isotherm model for pH-controlled system (pH 5.5 ± 0.2) is shown in Figure 8.

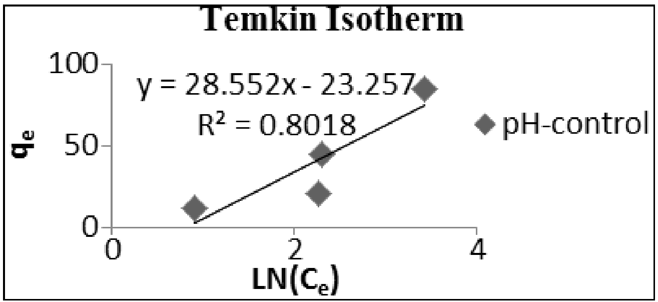

Figure 8: Temkin isotherm model for the sorption of Cd^{2+} on PR

The parameters for Temkin isotherm is shown in Table 11.

Table 11: Temkin Adsorption Isotherm

K_T (L/g)	B_T (J/mol)	R^2
0.443	28.552	0.8018

It was observed that of the three adsorption isotherms studied, Langmuir adsorption isotherm has the highest regression value (R^2= 0.8777) which means that it is the best fit for Cd^{2+} adsorption on PR.

3.7. Phosphorus Content of Multi-metal Solution Adsorbed by Phosphate rock

Phosphorus is one of the components of PR, hence, it also appears in solution equilibrated with PR. During metal retention in multi-metal system, it is apparent that there is a significant decrease in the amount of P as the equilibrium concentration of Cd^{2+} increases. This relationship is shown in Figure 9.

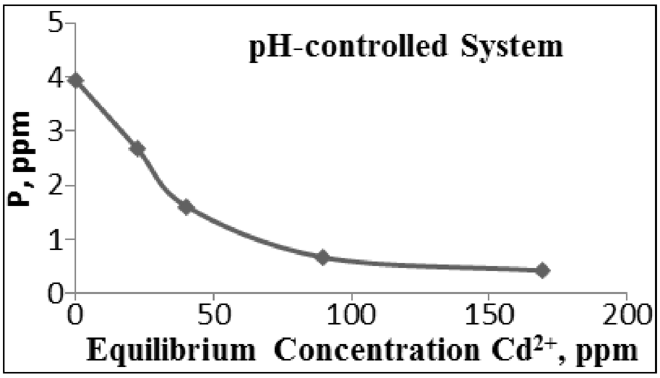

Figure 9: P content in pH-controlled system

The decrease of P content as metal disappearance proceeds is consistent with the hypothesis that P is consumed during metal retention. Particularly to Pb^{2+} immobilization, it was expected that fluoropyromorphite formation occurs during metal retention. Previous study proposed a mechanism for the formation of fluoropyromorphite from hydroxyapatite[6] due to the presence of Pb^{2+} in solution with phosphate rock. The reaction mechanism is shown below.

$$Ca_{10}(PO_4)_6F_2 + 12H^+ \leftrightarrow 10Ca^{2+} + 6H_2PO_4^- + 2F^- \quad (14)$$

$$10Pb^{2+} + 6H_2PO_4^- + 2F^- \leftrightarrow Pb_{10}(PO_4)_6F_2 + 12H^+ \quad (15)$$

$$Ca_{10}(PO_4)_6F_2 + 10Pb^{2+} \leftrightarrow Pb_{10}(PO_4)_6F_2 \quad (16)$$

In this study Pb^{2+} in the adsorbed solution was not detectable through the technique being used (DPASV). This provides evidence that very small equilibrium concentration of Pb^{2+} is present in the solution adsorbed by PR. It was highly immobilized through adsorption causing P content to decrease. Additionally, since Cd^{2+} also contributed to the decreased of P during metal sorption, it is also possible that Cd-Phosphate precipitation or co-precipitation of Cd^{2+} with PR took place.

3.8. The Possible Effect of P on the Environment upon Immobilization Using PR

Eutrophication promotes growth of algae due to large amount of phosphates present in water. This phenomenon affects the marine life under water surface. In connection to this study, when PR is used as an immobilizing agent, it is important to evaluate if P content could induce eutrophication. The results supported that P content decrease as the disappeared amount of metal ions in solution increases. This simply means that P is used up during metal retention, thereby lowering its concentration in solution. Therefore, immobilization using PR does not promote eutrophication and thus phosphate rock is safe to use as an immobilizing agent.

3.9. The Effect Heavy Metal Retention to the pH of the Solution

In pH-controlled system, pH was initially fixed at 5.5±0.2. The final pH of multi-metal solution containing Pb^{2+} and Cd^{2+} was measured at different equilibrium concentrations. Figure 10 shows the difference between the initial and final pH of the sample solution.

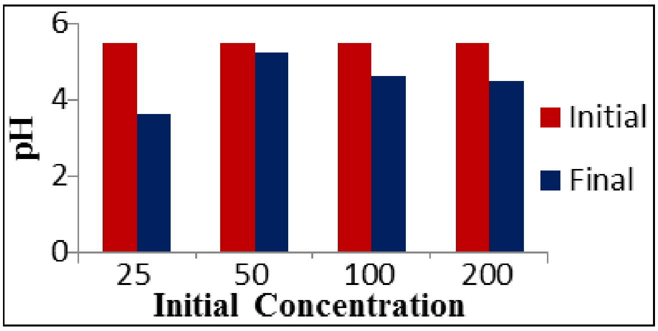

Figure 10: Representation for the decrease of pH before and after equilibration

As shown in the figure, it was observed that after metal sorption, the pH of the solution decreases. This significant decrease means that immobilization of Cd^{2+} and Pb^{2+} in multi-metal solution took place after equilibration with phosphate rock. In previous studies, it was confirmed that POH is the dominant functional group in PR at pH<6.87.[44] A possible reaction between the metal ion M and POH was then formulated from the decreases of pH which means that H^+ is released into the solution.[6]

$$POH + M^{n+} \rightarrow POM^{+} + H^{+} \quad (17)$$

In this study, the presence of Pb^{2+} and Cd^{2+} in solution induced pH reduction from 5.5 to 3.60-5.22.

System of free acidity was designed in order to predict what happened to the H^+ present in the sample before and after metal uptake. The graph of pH versus the metal disappearance of Cd^{2+} in ppm from multi-metal solution in Figure 11, shows that the amount of Cd^{2+} adsorbed by PR lowers the solution's pH.

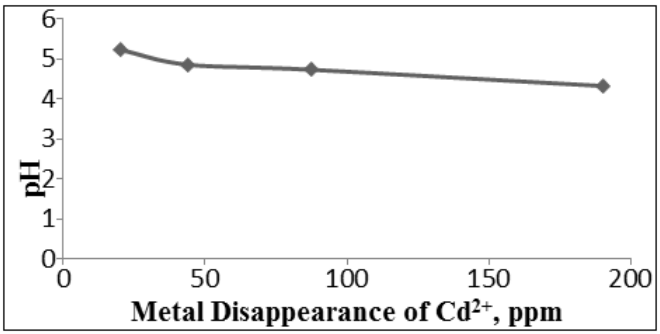

Figure 11: pH of the solution as Cd^{2+} disappearance proceeds

3.10. The Effect of pH to the Amount of Metal Desorbed in Multi-metal Solution by PR

The amount of heavy metal desorbed in **PR** is sensitive to the pH of the extracting solution (pH=3, 7, 9). Previous study proved that desorption of other heavy metals is largest at lower pH. In this study, the same results were obtained. Desorbed amount of Cd^{2+} was monitored against pH of the extracting solution. Desorbed Cd^{2+} is higher at lower pH. Figure 12 shows the desorbed amount of Cd^{2+} with pH of the extracting solution. Highest desorption is observed at the lowest pH.

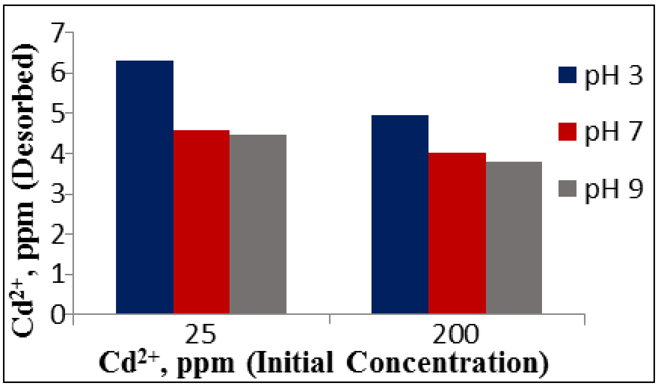

Figure 12: Amount of Cd^{2+} at different pH of extracting solutions

At 25 ppm, desorbed Cd^{2+} is 6.29 ppm, while with higher pH extracting solution, (pH=7, 9), desorbed amount of Cd^{2+} are 4.56 ppm and 4.48 ppm, respectively, which is lower than the amount desorbed by pH 3 extracting solution. If the desorption of metal is considered in the adsorption process, only 68.7 % of Cd^{2+} is adsorbed at pH 3, while 77.3 % and 77.7 % is adsorbed at pH 7 and 9, respectively. The same trend of Cd^{2+} desorption was observed at 200 ppm. Again, if the desorption of metal is considered in the adsorption process, only 97.4 % is adsorbed at pH 3, while at pH 7 and

9, the amount of Cd^{2+} adsorbed is 97.9 % and 98.0 %, respectively. From the reference journal related to this study, Cd^{2+} possibly reacted with phosphate rock by weak complexation. This simply means that pH reduction solubilizes Cd^{2+} more efficiently.

4. Conclusion

For the analysis of multi-metal solution containing Pb^{2+} and Cd^{2+} adsorbed with PR, only Cd^{2+} concentrations were detectable via DPASV. This implies that the extent of Pb^{2+} immobilization is higher compared to Cd^{2+}. For Cd^{2+} sorption process, up to 80.40%, 87.22%, 87.51%, and 95.17% of the concentrations were adsorbed by PR from 25 ppm, 50 ppm, 100 ppm, and 200 ppm respectively for the pH-free system and about 60.04%, 80.69%, 92.25%, and 84.17% for the pH-controlled system. Then, the sorption data for Cd^{2+} were fitted into the Freundlich, Langmuir and Temkin adsorption isotherms. Out of the three models, Langmuir adsorption model exhibit highest correlation coefficient value which means it is the best fit.

It was also confirmed that P decreases as metal disappearance proceeds. This means that P is consumed during immobilization and adsorption of metals, thereby promoting formation of fluoropyromorphite due to the presence of Pb^{2+}. Other mechanism can also occur due to the presence of Cd^{2+}, possibly precipitation and co-precipitation with PR. The reduction of pH after metal adsorption proves that immobilization took place through complexation and displacement of the H^+ ion. Desorption experiment using extracting solutions of varying pH indicates that at lower pH, amount of metal desorbed is greater compared to higher pH. Cd^{2+} exhibits the trend described for pH reduction, thus it is weakly bound by complexation and induced greater solubility as pH is lowered.

This study can be repeated using Atomic Absorption Spectroscopy AAS, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy SEM-EDX and other voltammetric method. It is also recommended to study other adsorption isotherm models and other toxic heavy metals. Additionally, other adsorbing agents aside from phosphorus-bearing minerals can be used to study heavy metal retention.

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