

Aqueous Lead Removal under Optimized Conditions Using Phosphoric Acid Activated Coconut Coir Activated Carbon

Vithushana Thangarajah¹ , W. M. Yalini Hansika Wijesundara², A. H. M. Lihini Nilma Kumari³, M. G. Gayan Sasanka Nirodha Thilakarathna^{4*}

¹Department of Aquaculture and Fisheries, Faculty of Livestock Fisheries & Nutrition, Wayamba University of Sri Lanka, Makadura, Gonawila (NWP), Sri Lanka

²Department of Chemistry, University of Texas at Dallas, Richardson, TX, USA

³Environmental Science Degree Programme, Faculty of Science, University of Peradeniya, Peradeniya, Sri Lanka

⁴Postgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka

Email: *gayansnthilakarathna@gmail.com

How to cite this paper: Thangarajah, V., Wijesundara, W.M.Y.H., Kumari, A.H.M.L.N. and Thilakarathna, M.G.G.S.N. (2020) Aqueous Lead Removal under Optimized Conditions Using Phosphoric Acid Activated Coconut Coir Activated Carbon. *American Journal of Analytical Chemistry*, 11, 389-405.

<https://doi.org/10.4236/ajac.2020.1112031>

Received: November 12, 2020

Accepted: December 28, 2020

Published: December 31, 2020

Copyright © 2020 by author(s) and Scientific Research Publishing Inc.

This work is licensed under the Creative Commons Attribution International License (CC BY 4.0).

<http://creativecommons.org/licenses/by/4.0/>



Open Access

Abstract

The global burden of heavy metal environmental pollution remains one of the most challenging issues to be addressed urgently. Lead (Pb) has been well recognized as a toxic environmental pollutant. The main objective of this study was to examine the adsorption efficiency of phosphoric activated coconut coir activated carbon for lead (II) removal from an aqueous solution. Synthesized activated carbon was characterized before and after the adsorption of Pb(II) by powder X-Ray diffraction, Fourier transforms infrared spectroscopy and scanning electron microscopy coupled with energy dispersive X-Ray. Furthermore, the removal efficiency of Pb(II) of synthesized activated carbon was tested with different concentrations of Pb(II) solutions, pH levels, adsorbent dosages, and contact time. Atomic absorption spectroscopy was used to analyze the Pb(II) concentrations in water samples. The maximum Pb(II) removal percentage of 100% was obtained with 50 mL of 5 mg/L Pb(II) ion solution and 0.20 g of the synthesized activated carbon. Adsorption data were well fitted with the Freundlich adsorption isotherm model, and adsorption kinetics were fitted with the pseudo-second-order kinetic model with R^2 of 0.99. These results conclude that the synthesized activated carbon can be used as a potential sorbent for the removal of lead from wastewaters.

Keywords

Activated Carbon, Adsorption, Lead Removal, Coconut Coir

1. Introduction

Industrialization and the increase in population have boosted the growth of different industries which lead to the discharge of pollutants into the water bodies. As a result, more and more heavy metals are being continually discharged into the environment. Therefore there is a necessity to take more concern of these heavy metals as they have significant effects on human health [1]. The most concerning toxic metals are Cd, Zn, Pb, and Ni. They enter the water bodies through wastewater from metal plating industries, mining, pigments, dezincification, and other industrial wastes.

Currently, lead pollution is becoming a global burden due to its spreading over the earth and groundwater. Lead is a heavy, soft, malleable, bluish-gray metal present as the form of lead(II) ions in an aqueous medium [2]. Also, lead is one of the most toxic heavy metals existing in wastewater, which comes from both natural sources and industrial effluents [3]. Exposure to high levels of lead in the environment may cause long-term health risks to humans and ecosystems by acute and chronic effects. According to the World Health Organization (WHO), the maximum permissible limit (MPL) of lead in drinking water is 0.05 mg/L and in wastewater is 0.05 mg/L as given by Environmental Protection Agency (EPA) [4].

Hence, there is an urgent need for efficient and cost-effective treatment of industrial wastewater to protect human, aquatic life, and land from lead toxicity. Removal of lead from wastewater can be accomplished through a range of chemical and physical processes. The traditional methods used for wastewater treatment are precipitation, adsorption, and coagulation. Although these processes are costly to hold, they are not efficient.

Over the last few decades, adsorption is used as one of the most feasible methods and has gained much attraction in industrial-scale purification, separation, and recovery process [5]. Recent research approaches are focused on the use of novel adsorbents for the removal of heavy metal ions from an aqueous solution that is low in cost and efficient compared to conventional adsorbents [6].

Adsorption is a widely used method for the efficient removal of lead ions [2] due to its high intensified metal binding capacity to prevent lead pollution and it can protect public health by improving the quality of the treated effluent [7]. However, the use of activated carbon as an adsorbent has been diminished due to its less adsorption capacity [8].

Activated carbon (AC) has been extensively utilized as an adsorbent [9] for environmental applications such as the removal of organic and inorganic pollutants from air and water streams over the past few decades. Most common applications of activated carbon include air and water purification, water filtration, groundwater remediation, adsorption of poisons, and drug overdoses [10]. Activated carbon is a carbonaceous material with a characteristic high surface area with microporosity consists of 87% to 97% carbon with other trace elements [10]. Most of the low-cost materials with high carbon content and low inorganic

elements can be used as a raw material for the mass production of activated carbon [5]. The demand for activated carbon will benefit from the continuing intensification of the global environmental movement with industrialization.

There are several methods available for the production of activated carbon. However, for specific industrial applications, through chemical activation, a solid adsorbent with wide pore size distribution can be preferably obtained. In recent years, agricultural wastes are notably utilized as the raw material for the preparation of activated carbon and, also previous studies have reported the removal of heavy metal ions with many agricultural byproducts [11]. This bio-char application is one of the most attractive alternatives for environmental remediation because of the abundance of cheap biomass that can be used for biochar production. Furthermore, the cost of biochar is six times lower than the cost of activated carbon because of the lower energy requirement of biochar production. It can be used without further chemical or physical activation [12].

Coconut coir is one of the low-cost agricultural wastes with a higher abundance in Sri Lanka that can act as an ideal carbon precursor [13]. Coconut coir is a soft biomass residue that is separated during the processing of coconut (B Ash) and it is rich in lignin (16% - 45%), hemicellulose (24% - 47%), and pectin (2%) content [14]. The physical and chemical properties of activated carbon depend mainly on the activation methods used [11]. Commonly there are two different types of processes for the preparation of activated carbon. They are physical activation and chemical activation, and they increase the adsorption capacity by combining with other adsorbents, modification with acids, grafting with various functional groups, and combining mineral and metal adsorbents with some polymers [2].

Chemical activation is considered the best activation method over physical activation due to its ability to develop a better porous structure. Furthermore, the chemicals added for activation can be easily recovered for reuse. The activation of carbon by phosphoric acid is largely used in industrial-scale applications to impregnate lignocellulose materials, such as coir and wood [15]. Phosphoric acid increases the yield by making important changes in the pyrolytic decomposition of the lignocellulosic materials and promotes depolymerization, dehydration, and redistribution of constituents [8]. Nowadays, phosphoric acid has become more popular due to the improvements introduced in the process of acid recovery.

As mentioned earlier, there is understandably a great effort to find low-cost material to produce activated carbon. In this work, we have described our efforts to remove lead ions from contaminated aqueous solution by using the activated carbon produced from coconut coir along with chemical activation by phosphoric acid. The ultimate goal of this work is to develop and utilize a microporous activated carbon from coconut coir for the efficient removal of lead ions from the aqueous phase. This study provides an ideal platform to convert coconut coir, which is highly abundant in Sri Lanka, into activated carbon by phos-

phoric acid that can be commercialized for the removal of lead (II) ion contaminants from the aqueous phase.

2. Method

2.1. Materials

All the chemicals were of analytical grade. Pd(NO₃)₂ (98% assay) and H₃PO₄ (85% assay) were purchased from Sigma-Aldrich, and were used without further purification. Water used was distilled.

2.2. Preparation of Activated Carbon (ACC)

Coconut coir was washed using hot distilled water and oven dried at 110°C for 12 hours. Then, cleaned coconut coir was sieved through a 1 mm mesh. About 25.0 g of sieved coir was treated with 500 ml of 50% (V/V) phosphoric acid and boiled for few hours. Next, it was oven dried at 100°C for 48 hours followed by pyrolysis at 450°C for 1 hour to obtain phosphoric activated ACC. The sample was allowed to become room temperature and washed thoroughly with distilled water followed by low concentrated KOH washing to remove any traces of remaining phosphoric acid until the pH of water reaches pH of 6.0 - 7.0 range. Then, ACC was dried for 4 h at 90°C.

2.3. Characterization of ACC

Morphological analysis of the synthesized ACC was done using Hitachi SU6600 Scanning Electron Microscope (SEM) depositing gold on prepared ACC to an optimum 5 nm thick layer. The crystallographic analysis of the ACC was performed using Siemens D5000 powder X-ray Diffractometer (XRD). Fourier transform infrared (FTIR) spectroscopy for identifying chemical composition of the ACC was done using Shimadzu IR Prestige-21 spectrometer using the KBr pellet method. The sample was mixed with dry KBr solid in 1:40 mass ratio for pellet preparation.

2.4. Methylene Blue (MB) Adsorption Test

First, (0.500 ± 0.001 g) of synthesized ACC was added to a 250 ml beaker. Next, about 50 ml of methylene blue solution (1000 ppm) was added into it followed by stirring with a mechanical stirrer for 1 hour at a speed of 500 rpm. Then the mixture was filtered through a filter paper in a funnel. Then the absorption of the sample was measured at wavelength of 664.5 nm using a UV-VIS spectrophotometer.

2.5. Iodine Adsorption

First, three samples of synthesized ACC of masses (1.000 ± 0.100 g), (1.500 ± 0.100 g) and (2.000 ± 0.100 g) were placed in three reagent bottles equipped with stoppers. Then 10.00 ml of 5% (wt./v) hydrochloric acid solution was added into each reagent bottle containing activated coir. After that, bottles were stoppered

and swirled the solution gently until the activated coir get completely wetted. Then the stoppers were loosened, and the reagent bottles were placed on a hot plate in the fume cupboard. The contents were brought to boil for 30 s to remove any Sulphur which may interfere during the reactions. Thereafter the bottles containing ACC were removed from the hot plate and cooled to room temperature. After that, 50.00 ml of iodine solution (0.100 N) was added to the reagent bottle. The bottle was vigorously shaken for 1 min. Then the content was quickly filtered, and the filtrate was collected. Moreover, the pipette was rinsed using the first 10 ml of the filtrate. The remaining filtrate was collected on a clean reagent bottle. Then 50.00 ml of the filtrate was pipetted out into a clean reagent bottle and the titrated with standard sodium thiosulphate solution (0.100 M) until the pale yellow colour appeared. Then a few drops of starch were added, and the titration was continued until the blue solution turned colourless. The volume of the Sodium thiosulphate was recorded and the iodine number was calculated.

2.6. Batch Adsorption Study

To prepare lead(II) (Pb^{2+}) ion solution, lead nitrate (98%) solid was dissolved in 1.0 L of deionized water in a volumetric flask to prepare a 1000 mg/L of stock Pb^{2+} solution. This stock solution was used to prepare the 10-ppm Pb^{2+} solution and other concentrations ranges used in isotherm studies and initial concentration optimization. Optimization studies were done using a 50.0 mL volume of synthetic Pb^{2+} solution at room temperature ($25^\circ\text{C} \pm 2^\circ\text{C}$) with a 150-rpm shaking speed for optimizing the parameters affecting for lead adsorption such as contact time, initial Pb^{2+} concentration, pH of the solution and the ACC dosages. **Table 1** shows the conditions used in parameter optimization studies.

All treatments were done as triplicates and at the end of each optimization, solutions were allowed 60 min for settling and filtered using filter papers. Finally, the remaining Pb^{2+} concentration of each solution was measured using Thermo Fisher Scientific iCE 3500 AAS Atomic Absorption Spectrometer.

2.7. Kinetic and Adsorption Isotherm Studies

Kinetic studies were carried out as follows. First, 10 mg/L of Pb^{2+} solution was prepared using 1000 mg/L stock solution. Then, 1 L of 10 mg/L solution was added into a 2 L beaker and 4.00 g of ACC was added into the solution. The mixture was stirred using the magnetic stirrer at 150 rpm. After the addition of ACC, 10 ml of Pb^{2+} solution was withdrawn at desired time intervals. It was filtered using filter papers. Then, the remaining concentration of Pb^{2+} was determined using Atomic Absorption Spectrometer (AAS). Equilibrium adsorption studies were carried out at the optimized conditions of agitation time, ACC dosage and pH of the initial lead ion concentration of the solution. Langmuir and Freundlich adsorption isotherm equations have been tested in this adsorption study and the goodness-of-fit between experimental data and the model predicted was expressed by the correlation coefficient.

Table 1. Conditions used in parameter optimization studies.

Optimizing parameters		Constant parameters
Contact time (CT)	(5 - 60) min	pH—8
		PD—0.10 g
		IC—10 mg/L
Particle dosage (PD)	(0.10 - 1.00) g	pH—8
		CT—10 min
		IC—10 mg/L
pH	2 - 10	PD—0.20 g
		CT—10 min
		IC—10 mg/L
Initial concentration (IC)	(5 - 600) mg/L	pH—8
		PD—0.20 g
		CT—10 min

2.8. Desorption Studies

A 1000 mg/L Pd²⁺ ion solution was treated with 2.000 (± 0.001) g of synthesized ACC for 10 minutes and it was filtered using filter paper. Then the treated ACC was washed gently using deionized water to remove excess lead ions which were not adsorbed onto the ACC surface. Then it was dried at 100 C for 24 hours. After that, a concentration series of HCl was prepared as 0.025, 0.050, 0.100 and 0.200 M and 0.100 (± 0.001) g of treated ACC was added into each solution. Then the solutions were agitated for 30 minutes and filtered solutions were tested for lead(II) ions using the Atomic Adsorption Spectroscopy (AAS).

2.9. Comparison Study

Commercial activated charcoal, raw coconut coir and KOH activated ACC were treated with lead solutions at the optimized conditions. Then the percentage removal of lead ions was compared with the percentage removal of lead obtained from phosphoric activated ACC.

2.10. Bed Column Filtration

About 0.0100 (± 0.001) g of ACC was placed on a funnel with sintered glass disc and 25 mL of 96.54 mg/L lead solution was added into it. The filtrate was collected, and it was passed again through a new set up with 0.100 (± 0.001) g ACC on the funnel with sintered glass disc. The process was repeated three times and the concentration of the filtrate was measured using the Atomic Adsorption spectrometer (AAS).

3. Results and Discussion

In this study, the Pb²⁺ adsorption efficiency of activated carbon was studied.

Coconut coir was selected as the low-cost precursor for ACC production and the chemical activation process was followed using the phosphoric acid in order to increase the adsorption efficacy of activated carbon.

3.1. Characterization of ACC

Figures 1(a)-(c), respectively, express the XRD patterns of raw coconut coir and phosphoric acid activated coconut coir (PA-ACC) based activated carbon and lead adsorbed PA-ACC.

Coconut coir is mainly composed of lignin (46.4%), cellulose (21.6%) and hemicellulose (17.3%) [16]. According to the XRD pattern of **Figure 1(a)**, it clearly shows the contribution of highly amorphous lignin for the crystalline structure while indicating the cellulose crystalline plane at broad peak around $22^\circ - 23^\circ$ [17]. After the activation process (**Figure 1(b)**), it clearly shows the absence of sharp peak defining the predominant amorphous structure which can be considered as a beneficial property of ACC in adsorption mechanism. The adsorption process of the activated carbon in liquid phase is based on the molecular size and chemical structure of the adsorbate as well as the porous properties and the surface characteristics of the adsorbent or kind of the solvent. The ability of activated carbon to adsorb desired adsorbates depends on the surface area, porosity and the available functional groups. The random amorphous structure of activated carbon is highly porous and the pore sizes are highly variable. It may vary from cracks which are visible, to crevices and molecular slits. This nature of activated carbon is really useful as an adsorbent. As a result of having stable structure with high adsorption capacity and rich surface reactivity activated carbon is highly used in range of applications. Strong broad peaks at around 25° and 45° might be due to the graphitic crystalline nature of activated carbon with well-developed porous structure.

Figure 2(a) and **Figure 2(b)** illustrate that there is a clear difference between the FT-IR spectrum before and after the activation process.

The FT-IR technique is a vital tool to identify the characteristic functional groups which are crucial in the adsorption mechanism. FT-IR spectrum of raw coconut (**Figure 2(a)**) coir has several functional groups with a broad peak around 3450 cm^{-1} for hydroxyl group (O-H stretching) which might be due to the available lignin and moisture in coir. The peak at 2941 cm^{-1} can be attributed to the asymmetric stretching of methylene (C-H stretching) while the weak band around $1500 - 1262\text{ cm}^{-1}$ for plane bending of OH group and C-N stretching of aromatic amine. A strong narrow peak at 1630 cm^{-1} is corresponding to the alkenyl C=C stretching. The peak at 1067 cm^{-1} might be due to the availability of the methyne skeletal and C-C vibrations. The last peak at 540 cm^{-1} is assumed to be a C-Cl stretching. After the activation process (**Figure 2(b)**), the peak at 3450 cm^{-1} can be attributed to the available hydroxyl groups (-OH group stretching) as same as in the raw coconut coir but it is apparent that the transmittance has been increased. This may be due to the removal of lignin in the activation

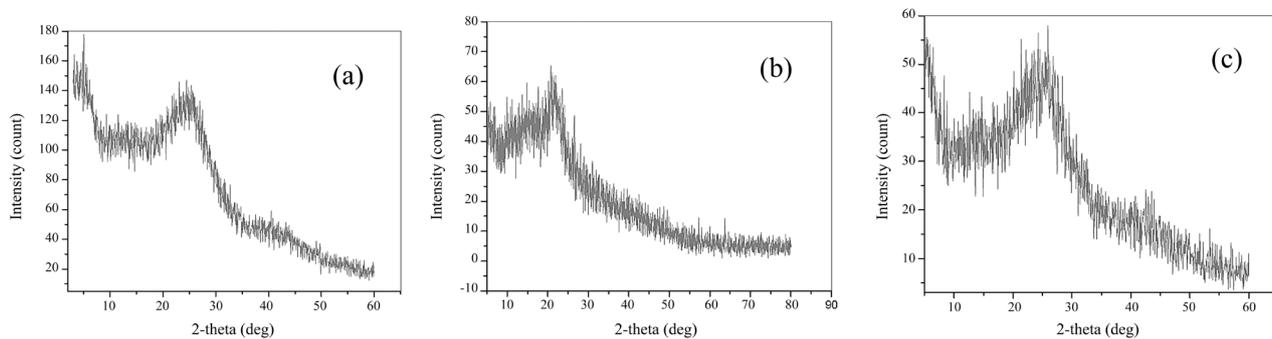


Figure 1. XRD diffractogram of (a) raw coconut coir, (b) phosphoric activated ACC (PA-ACC) and (c) lead adsorbed PA-ACC.

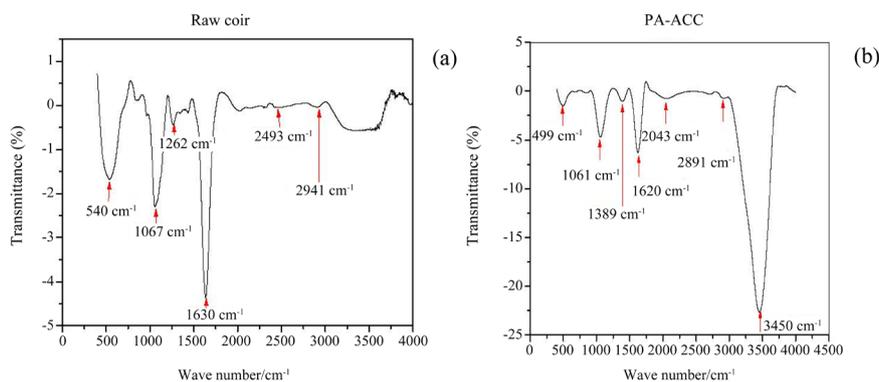


Figure 2. FT-IR analysis of (a) raw coconut coir and (b) (PA-ACC) activated coconut coir based carbon.

process and the dryness of the ACC. Peak intensity at 2891 cm^{-1} which was corresponded to C-H group stretching has been reduced in the ACC. The peak (1630 cm^{-1}) corresponding to alkenyl C=C stretching also reduced the intensity which was predominant in raw coir. Peaks at 1389 cm^{-1} and 1061 cm^{-1} can be attributed to the carboxylate group and primary or secondary alcohol C-O stretching respectively. The peak at wavenumber 499 cm^{-1} represents the C-Cl bond stretching [18]. When compare the FT-IR spectrum of raw coir with the phosphoric acid activated ACC, there are more peaks observed in ACC than in raw coir which was formed during the activation process. Therefore, the adsorption capacity of ACC is higher than the raw coir.

The surface morphology of the raw coir and phosphoric acid-treated were analyzed using scanning electron microscopy (SEM). SEM images present the wide varieties of pores present in the compounds with various structures. The surface of the raw coconut coir (**Figure 3(a)**) appears clean and smooth while the treated ACC (**Figure 3(b)**) shows the availability of mesoporous of diameter less than 50 nm and the many sites of macropores with a diameter of above the 50 nm . Furthermore, there are many defects and imperfections available on the phosphoric acid-treated ACC surface. Therefore, it can be assumed that the synthesized ACC has a great surface area compared to the raw coir increasing the adsorption capacity.

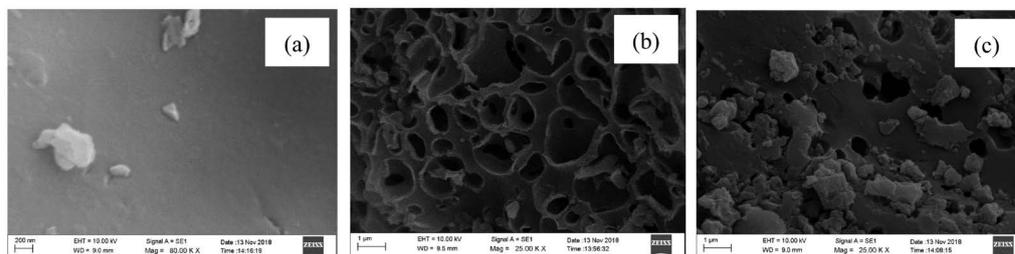


Figure 3. SEM images of (a) raw coconut coir and (b) ACC.

For the elemental characterization of the surface EDX was done for the prepared N-TR-ACC. **Table 2** illustrates the C and O elemental nature and presence of P as impurities which was the residue of PA in the sample of N-TR-ACC.

3.2. Methylene Blue (MB) Adsorption and Iodine Adsorption

Methylene blue and iodine value tests were performed to estimate the surface area and porosity of the prepared ACC compared to the commercially available ACC. Usually, Iodine numbers may be used as an approximation to identify micro porosity while MB is used to get an idea about mesoporosity. Related data for this study (MB value and iodine value) are shown in **Table 3**. According to the data, phosphoric acid activated ACC has a higher adsorption capacity than commercially available ACC.

3.3. Batch Adsorption Study

To optimize the conditions used in lead(II) removal, it was studied as a function of contact time, pH of the medium, ACC dosage and initial lead(II) ion concentration used. Results are depicted as graphs in **Figure 4** from (a) to (d), respectively. **Figure 5(a)** shows that the lead(II) removal percentage has been dramatically increased from 1 min to 10 min and reached a constant value of $\sim 82\%$. The reason for this phenomenon is the high active site concentration of the ACC at the beginning of the adsorption process and saturation after 10 minutes of shaking time. Under the conditions used 82% of lead(II) ions from 50.0 mL of 10 mg/L solution has been adsorbed by 0.100 g of phosphoric activate ACC at pH 8. Therefore, 10 min shaking time was considered to be the optimum contact time. **Figure 5(b)** clearly shows that the lead(II) removal capacity depends on the pH of the synthetic lead(II) solution. The removal percentage of lead(II) in low pH values is comparatively lower than in higher pH values. Although it shows a gradual increasing of the removal percentage from pH 4 to 8, again it shows a sharp increasing beyond the pH 8. This can be explained with the surface charge of the ACC. At low pH values, the solution contains more H⁺ ions and they are dominant on the surface of the synthesized ACC developing a positive charge on the surface. This creates a repulsion between the surface of the ACC and the positively charged lead(II) ions [19] [20]. Therefore, with the increasing of pH, this repulsion can be minimized facilitating the adsorption of lead(II) ions on to the ACC surface. According to the results, it shows almost 100% removal percentage

of lead(II) around pH 10. But in practical, however, high pH values around 10 - 11 pH is not suitable since another chemical must be added to the water to increase the pH. Therefore, the 8 pH was selected as the optimum condition which shows almost 82% lead(II) removal percentage.

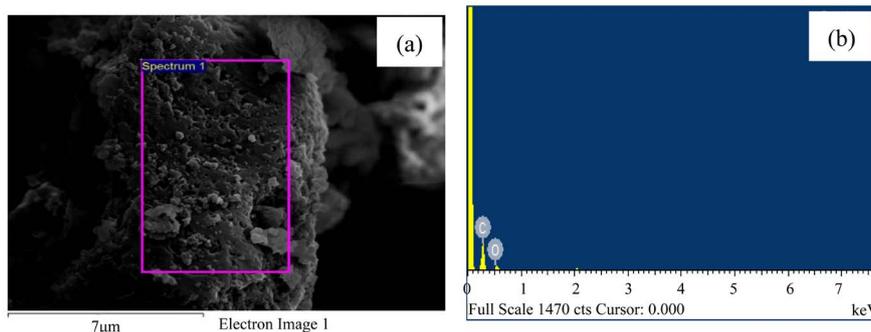


Figure 4. (a) Focused area on the surface and (b) EDX spectrum of the ACC surface and (b) EDX spectrum of the ACC.

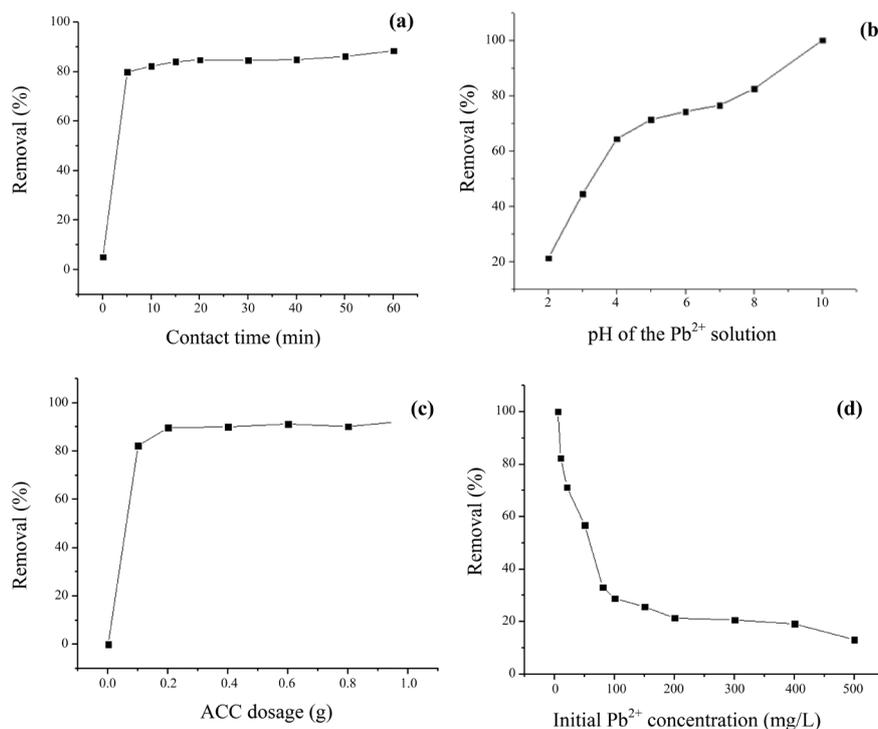


Figure 5. Lead(II) removal percentages at different (a) contact times (min) (b) pH levels and (c) ACC dosages (g) and (d) initial lead(II) concentrations (ppm).

Table 2. Weight% & atomic% of elements present in samples.

Element	Weight %	Atomic %
C K	66.92	73.31
O K	31.79	26.14
P K	1.29	0.55
Totals	100.00	

Table 3. Methylene Blue number and Iodine value of commercially available ACC and Phosphoric impregnated ACC.

ACC sample	MB number/mg·g ⁻¹	Iodine number/mg·g ⁻¹
Commercial	132.15	599.86
Phosphoric acid treated	279.20	694.08

Figure 5(c), depicts that the increasing the adsorbent dosage from 0.1 g to 1.0 g, the lead(II) removal percentage increases from 82% to 92% at the optimized 10 min contact time and pH 8. 0.2 g was selected as the optimum dosage of ACC as it shows a constant removal percentage around 92% beyond that level. This might be due to the saturation of active sites in ACC with the lead(II) ions available in the solution. The effect of initial lead(II) concentration on lead(II) removal is shown in the final graph in **Figure 5(d)**. The maximum lead(II) removal percentage of 100% was observed at the 5 mg·L⁻¹ lead(II) solution and the lead(II) removal percentage decreases as the initial concentration are increased. This might be due to the fact that, at higher lead(II) concentrations, the binding capacity of the ACC reaches saturation, resulting in a decrease of overall lead(II) removal percentage by the ACC. Therefore the 5 mg/L was selected as the optimum concentration of lead(II) under all other optimized conditions.

3.4. Kinetic Studies

Heterogeneous kinetics of adsorption of solution species on solid surfaces usually follows pseudo-first order proposed by Lagergren or pseudo-second order kinetics and the linearized form of pseudo-first order is given in Equation (1) as you can see in **Figure 6** [20] [21].

$$\log(q_e - q_t) = \log q_e - \frac{K_{1p}}{2.303} t \quad (1)$$

The linearized form of the pseudo-second-order expression is given in Equation (2).

$$\frac{t}{q_t} = \frac{1}{K_{2p} q_e^2} + \frac{1}{q_e} t \quad (2)$$

Here, q_t and q_e are considered as the amount of solute adsorbed per mass of sorbent (mg·g⁻¹) at any time (t) and equilibrium (e), respectively and K_{1p} is the rate constant of the pseudo first-order adsorption (1/min) and K_{2p} is the rate constant of the (g·g⁻¹·min⁻¹) pseudo second-order adsorption.

According to the kinetic results show in **Figure 5**, the data obtained from lead(II) uptake with respect to the time, well fitted with the pseudo-second-order kinetic model which shows a 0.99 of R^2 value. This indicates that the rate of occupation of adsorption sites is proportional to the square number of unoccupied sites, because the pseudo second order model is based on a second order mechanism. It proves the adsorption process of lead ions onto the synthesized

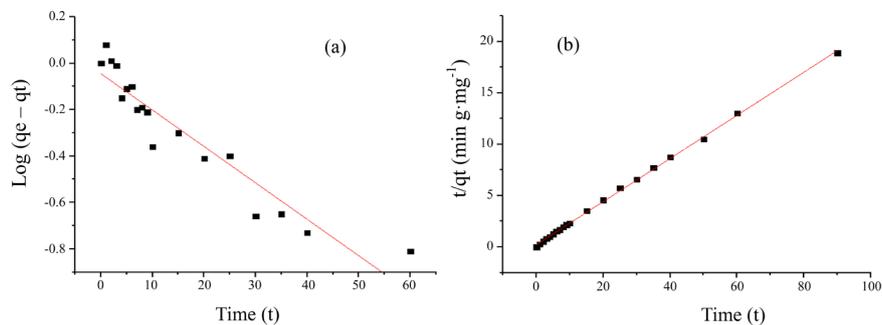


Figure 6. Adsorption kinetic study of Pb^{2+} adsorption on phosphoric activated ACC (a) pseudo first order kinetic model (b) pseudo second order kinetic model.

ACC happens through the formation of covalent bonds or the mechanism is more relevant towards the chemisorption than the physisorption described by pseudo-first-order kinetic model (Table 4). However, it doesn't confirm that the only way of adsorption is happening through the chemisorption as the pseudo second order says only that the probability of being a chemisorption is high. Therefore, the isotherm studies may give a clear idea about the process.

3.5. Isotherm Studies

Linear forms of the isotherms models are also widely adopted to determine the isotherm parameters or the most fitted model for the adsorption system due to the mathematical simplicity. The Langmuir isotherm model assumes that the adsorption is occurring as a homogeneous monolayer adsorption onto a surface containing a limited number of adsorption sites of uniform strategies, adsorbed molecules do not interact with no transmigration of adsorbate in the plane adsorbent surface [22].

The linear form of the Langmuir isotherm model can be expressed as Equation (3):

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

where, q_e , q_m , C_e and K_L are corresponding adsorption capacity (mg/g), maximum adsorption capacity (mg/g), equilibrium concentration (mg/L) and adsorption equilibrium constant called the Langmuir constant (L/mg) [23].

The Freundlich isotherm model describes that the adsorption is a multilayer heterogeneous adsorption and its linear form can be expressed as Equation (4):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where, K_F , n , C_e and q_e are Freundlich constant (mg/g), a constant, equilibrium concentration (mg/L) and corresponding adsorption capacity (mg/g), respectively.

According to the graph given in Figure 7, the data were well fitted with the Freundlich isotherm model which proves that the adsorption of lead ions on

phosphoric activated ACC is a heterogeneous multilayer adsorption. Additionally, the “ n ” value of the Freundlich isotherm shows that the process is a physisorption as it is a value above 1 (Table 5). Because, it is considered $n = 1$ as a linear adsorption, $n < 1$ as a chemical process and $n > 1$ as a physical process [24]. The physisorption process was assumed to be happened due to the formation of van der waals bonds. According to the kinetics study, it shows the adsorption process much weighted towards the chemisorption. But still the adsorption mechanism follows the Freundlich isotherm model with 2.21 n value which proves that the adsorption is done by physisorption. However, it can be assumed that the phosphoric activated ACC adsorb lead ions through van der waal bonds and covalent bonds with remaining phosphate ions or the first adsorption layer might be occurred through covalent bonds and then other layers may occur through van der waal bonds.

Table 4. The kinetic adsorption parameters obtained using pseudo-second-order at room temperature for the Pb^{2+} adsorption on PA-ACC.

Kinetic model	$R^{2,a,b}$	Rate constant	Value of Rate constant ^b	Unit of Rate constant
Pseudo first order	0.8970	K_{1p}	0.0361	1/min
Pseudo second order	0.9991	K_{2p}	0.1956	$\text{g}\cdot\text{g}^{-1}\cdot\text{min}^{-1}$

^a— R^2 , regression coefficient. ^b—The K_1 , K_2 values and the nonlinear regression correlations for pseudo-first-order, and pseudo-second-order were measured by nonlinear regression analysis using Origin Pro 8.0.

Table 5. Adsorption parameters of the Langmuir and Freundlich isotherms at room temperature for the adsorption of $\text{Pb}(\text{II})$ on PA-ACC.

Langmuir constant			Freundlich constant		
q_{\max}^b	$K(\text{L}/\text{mg})^b$	$R^{2,a,b}$	$K_f(\text{mg}/\text{g})^b$	n^b	$R^{2,a,b}$
41.05	0.0107	0.9626	3.4397	2.6690	0.9995

^a— R^2 , regression coefficient. ^b—The K , K_s , q_{\max} , n , values and the nonlinear regression correlations for Langmuir isotherm model and Freundlich isotherm model were measured by nonlinear regression analysis using Origin Pro 8.0.

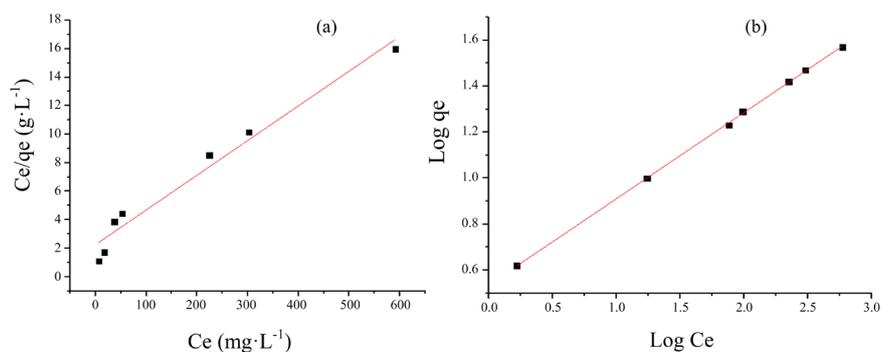


Figure 7. Adsorption isotherms study of Pb^{2+} adsorption on phosphoric activated ACC (a) Langmuir isotherm model (b) Freundlich isotherm model.

3.6. Desorption Studies

Desorption study was carried out to investigate desorption of Pb^{2+} from the ACC. This study also gives an insight into the possibility of regeneration of the ACC. If used ACC can be regenerated and reused, the same adsorbent can be used several times in many cycles in the removal process and also lead can be extracted from the concentrated solution. A lead(II) solution of 1000 mg/L was used in the initial treatment of ACC to saturate the adsorption sites. Obtained desorption percentages are tabulated in **Table 6**.

Maximum percentage desorption of 71.72% was observed at the HCl concentration of $0.025 \text{ mol}\cdot\text{dm}^{-3}$ and with the increasing concentrations, desorption was decreased. Therefore, it can be assumed that the HCl can efficiently desorb the Pb^{2+} ions from the ACC surface. This observation also leads to believe that the washing with distilled water might have removed some amount of lead ions which was loosely bound to the ACC surface reducing the desorption percentage. Since the calculations assumed that the all the adsorbed Pb^{2+} was retained in the ACC and if distilled water can wash them away while removing unadsorbed Pb^{2+} from the surface, the adsorbed amount of lead in the ACC is less than the calculated value. Otherwise, a higher percentage of desorption could be observed. Also, the observation implies that the adsorbed Pb can be removed from the ACC without energy-intensive methods and the use of a large amount of water which is an advantage. However, it can be assumed that, after desorption, phosphoric activated ACC can be again used in the removal process.

3.7. Comparison Study

The comparison study was done to examine the removal efficiency of lead from the aqueous solutions by commercially available activated charcoal and compare it with the phosphoric activated ACC. Also, the raw coir and the KOH activated carbon was used in this study. **Table 7** tabulates the percentage removal of Pd(II) with the respective compound.

According to the data obtained, the Phosphoric activated ACC has a higher percentage removal of Pb^{2+} than the commercially available activated charcoal at the optimized conditions. It is significant that the KOH activated ACC and Raw coir also show a comparatively higher removal percentage of Pb^{2+} than the commercially available ACC.

3.8. Bed Column Filtration

This experiment was carried out to determine the efficiency of removal without agitation. In this experiment, a 25 ml of lead solution was passed through 5 funnels with sintered glass disc which contained 0.100 (+ 0.001) g of synthesized ACC. The solution was passed through ACC by gravitational pull and the solution was not agitated. **Table 8** consists of the data used to calculate the Pb^{2+} removal percentage of this method.

Table 6. Percentage desorption with different HCl concentrations.

HCl concentration of the solution (mol·dm ⁻³)	Percentage desorption (%)
0.025	71.72
0.050	66.74
0.075	59.28
0.100	58.11
0.200	58.36

Table 7. Pb(II) removal percentage with different adsorbents.

Compound	Percentage removal (%)
Commercial AC	42.53
Raw coir	81.83
Phosphoric activated ACC	92.17
KOH activated ACC	91.97

Table 8. Bed column filtration data.

Initial Concentration (±0.0001 mg·L ⁻¹)	Final Concentration (±0.0001 mg·L ⁻¹)	Removal percentage (%)
96.5417	3.0517	96.84

96.84% removal was observed without agitation. This confirms that the phosphoric activated ACC can be used to remove heavy metals without using mechanical agitators with high removal efficiency. This is an important observation giving a potential solution for industrial waste water treatment to remove heavy metals.

4. Conclusion

In this study, Pb(II) removal behavior was studied using chemically activated coconut coir activated carbon. Activated carbon was synthesized using phosphoric acid as the activation agent and characterized using XRD, FT-IR, SEM, and EDAX. The maximum Pb(II) removal behavior of 100% removal was observed under 10 min of contact time, 0.20 g of activated carbon dosage, under pH 8, and 5 mg/L of initial lead(II) concentration. The data were well fitted with the pseudo-second-order kinetic model and the Freundlich isotherm model which described the adsorption mechanism as heterogeneous multilayer adsorption. According to the study, it can be concluded that the synthesized phosphoric activated coconut coir activated carbon is a potential candidate application for removing Pb(II) ions in wastewater to prevent environmental contamination and associated health risk.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

References

- [1] Mousavi, H.Z., Hosseynifar, A., Jahed, V. and Dehghani, S.A.M. (2010) Removal of Lead from Aqueous Solution Using Waste Tire Rubber Ash as an Adsorbent. *Brazilian Journal of Chemical Engineering*, **27**, 79-87. <https://doi.org/10.1590/S0104-66322010000100007>
- [2] Ehsan, S., Goodarzi, M., Khademian, E. and Sanaeepur, H. (2019) Removal of Lead Ions from Aqueous Solutions by Adsorption Operation: A Review. *Journal of Applied Research of Chemical-Polymer Engineering*, **3**, 3-28.
- [3] El-Naggar, I.M., Ahmed, S.A., Shehata, N., Sheneshen, E.S., Fathy, M. and Shehata, A. (2019) A Novel Approach for the Removal of Lead(II) Ion from Wastewater Using Kaolinite/Smectite Natural Composite Adsorbent. *Applied Water Science*, **9**, Article No. 7. <https://doi.org/10.1007/s13201-018-0845-0>
- [4] Mohsen, A., Hemati, S. and Amiri, M. (2015) Removal of Lead Ions from Industrial Wastewater: A Review of Removal Methods. *International Journal of Epidemiologic Research*, **2**, 105-109.
- [5] Ramakrishna, G. (2012) Preparation and Characterization of Microporous Activated Carbon from Biomass and Its Application in the Removal of Chromium (VI) from Aqueous. Ph.D. Thesis, National Institute of Technology, Rourkela.
- [6] Murat, E., Ucar, S., Karagöz, S. and Tay, T. (2013) Removal of Lead(II) Ions from Aqueous Solutions onto Activated Carbon Derived from Waste Biomass. *The Scientific World Journal*, **2013**, Article ID: 146092. <https://doi.org/10.1155/2013/146092>
- [7] Yayuan, H., Wu, P., Xiao, W., Li, G., Yi, J., He Y., Chen C., Ding, P. and Duan, Y. (2019) Efficient Removal of Pb(II) from Aqueous Solution by a Novel Ion Imprinted Magnetic Biosorbent: Adsorption Kinetics and Mechanisms. *PLoS ONE*, **14**, e0213377.
- [8] Rangari, P.J. and Chavan, P. (2017) A Review on Preparation of Activated Carbon from Coconut Shell. *International Journal of Innovative Research in Science, Engineering and Technology*, **6**, 5829-5849.
- [9] Alam, M., Hossain, A., Hossain, D., Johir, M.A.H., *et al.* (2007) The Potentiality of Rice Husk-Derived Activated Carbon: From Synthesis to Application. *Processes*, **8**, 203.
- [10] Sanni, E. S., Emetere, M.E., Odigure, J.O., Efevbokhan, V.E., Agboola, O. and Sadiqu, E.R. (2017) Determination of Optimum Conditions for the Production of Activated Carbon Derived from Separate Varieties of Coconut Shells. *International Journal of Chemical Engineering*, **2017**, Article ID: 2801359. <https://doi.org/10.1155/2017/2801359>
- [11] El-Wakil, A.M., Abou El-Maaty, W.M. and Awad, F.S. (2014) Removal of Lead from Aqueous Solution on Activated Carbon and Modified Activated Carbon Prepared from Dried Water Hyacinth Plant. *Journal of Analytical & Bioanalytical Techniques*, **5**, Article No. 187. <https://doi.org/10.4172/2155-9872.1000187>
- [12] Mahdi, Z., Yu, Q.J. and Hanandeh, A.E. (2018) Removal of Lead(II) from Aqueous Solution Using Date Seed-Derived Biochar: Batch and Column Studies. *Applied Water Science*, **8**, Article No. 181. <https://doi.org/10.1007/s13201-018-0829-0>
- [13] Rahman, M.M., Adil, M., Yusof, A.M., Kamaruzzaman, Y.B. and Ansary, R.H. (2014) Removal of Heavy Metal Ions with Acid Activated Carbons Derived from Oil Palm and Coconut Shells. *Materials*, **7**, 3634-3650. <https://doi.org/10.3390/ma7053634>

- [14] Chaudhuri, M. and Saminal, S.N.B. (2011). Coconut Coir Activated Carbon: An Adsorbent for Removal of Lead from Aqueous Solution. *WIT Transactions on Ecology and the Environment*, **148**, 95-104. <https://doi.org/10.2495/RAV110101>
- [15] Laine, J., Calafat, A. and Labady, M. (1989) Preparation and Characteristics of Activated Carbons from Coconut Shell Impregnated with Phosphoric Acid. *Carbon*, **27**, 191-195. [https://doi.org/10.1016/0008-6223\(89\)90123-1](https://doi.org/10.1016/0008-6223(89)90123-1)
- [16] Ding, T.Y., Siew, L.H. and Lisa, O. (2012) Comparison of Pretreatment Strategies for Conversion of Coconut Husk Fiber to Fermentable Sugars. *BioResources*, **7**, 1540-1547. <https://doi.org/10.15376/biores.7.2.1540-1547>
- [17] Supriadi, C., Kartini, E., Honggowiranto, W. and Basuki, K.T. (2017) Synthesis and Characterization of Carbon Material Obtained from Coconut Coir Dust by Hydrothermal and Pyrolytic Processes. *International Journal of Technology*, **8**, Article No. 8. <https://doi.org/10.14716/ijtech.v8i8.731>
- [18] Zhang, Z. and Jilie, K. (2011) Novel Magnetic Fe₃O₄@C Nanoparticles as Adsorbents for Removal of Organic Dyes from Aqueous Solution. *Journal of Hazardous Materials*, **193**, 325-329. <https://doi.org/10.1016/j.jhazmat.2011.07.033>
- [19] Santhy, K. and Selvapathy, P. (2004) Removal of Heavy Metals from Wastewater by Adsorption on Coir Pith Activated Carbon. *Separation Science and Technology*, **39**, 3331-3351. <https://doi.org/10.1081/SS-200036561>
- [20] Singha, B. and Das, K. (2013) Adsorptive Removal of Cu(II) from Aqueous Solution and Industrial Effluent Using Natural/Agricultural Wastes. *Colloids and Surfaces B: Biointerfaces*, **107**, 97-106. <https://doi.org/10.1016/j.colsurfb.2013.01.060>
- [21] Azizian, S. (2004) Kinetic Models of Sorption: A Theoretical Analysis. *Journal of Colloid and Interface Science*, **276**, 47-52. <https://doi.org/10.1016/j.jcis.2004.03.048>
- [22] Tan, K.L. and Hameed, B.H. (2017) Insight into the Adsorption Kinetics Models for the Removal of Contaminants from Aqueous Solutions. *Journal of the Taiwan Institute of Chemical Engineers*, **74**, 25-48. <https://doi.org/10.1016/j.jtice.2017.01.024>
- [23] He, J., Zhang, K., Wu, S., Cai, X., Chen, K., Li, Y., Sun, B., Jia, Y., Meng, F., Jin, Z., Kong, L. and Liu, J. (2016) Performance of Novel Hydroxyapatite Nanowires in Treatment of Fluoride Contaminated Water. *Journal of Hazardous Materials*, **303**, 119-130. <https://doi.org/10.1016/j.jhazmat.2015.10.028>
- [24] Desta, M.B. (2013) Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (*Eragrostis tef*) Agricultural Waste. *Journal of Thermodynamics*, **2013**, Article ID: 375830. <https://doi.org/10.1155/2013/375830>