

Polyurethane Loaded with Vegetable Activated Carbon for Heavy Metals Removal from Water

Wassim El Malti^{1*}, Mostafa Hamieh², Amer Noaman³, Rim Nasser El-Dine², Akram Hijazi², Wassef Al-Khatib²

¹ College of Engineering and Technology, American University of the Middle East, Kuwait

² Research Platform for Environmental Science (PRASE), Doctoral School of Science and Technology, Lebanese University, Beirut, Lebanon

³ Baghdad University, College of Science, Biotechnology Department, Baghdad, Iraq

* Corresponding author's e-mail: wassim.elmalti@aum.edu.kw

ABSTRACT

The heavy metals pollutants resulting from industrial wastewater are a major environmental problem due to their toxicity and non-biodegradability. Their removal became a trending environmental subject. The preparation of low-cost and eco-friendly adsorbents for industrial wastewater treatment has been widely investigated. Furthermore, the use of polymeric material for this purpose is highly increasing. In this study, banana stem agro-waste was valorized by preparing and characterizing its derived activated carbon used as a filler to improve the adsorption performance of polyurethane foams. The loaded polyurethane was synthesized in the shape of pellets, characterized by SEM, and tested in removing Pb_2^+ and Cu_2^+ from aqueous solutions. The effects of activated carbon filler concentration, number of filtering passes, and pH were examined. The loaded polyurethane demonstrated a good adsorption capacity that was enormously improved compared to the unloaded polymer. 77% Pb_2^+ and 40% Cu_2^+ removal were reached after one filtering pass only. The optimum pH was determined to be 4. After the 10th pass, and at any pH, almost 100% of the studied metals were eliminated. Rapid and straight-forward selectivity and seawater deionization tests were carried out and confirmed the capacity performance of the prepared pellets in removing different aqueous ions.

Keywords: activated carbon, adsorption, banana stem, heavy metals, polyurethane.

INTRODUCTION

Excessive release of organic and inorganic pollutants due to urbanization, industrialization, agriculture, and domestic waste, is a critical global environmental problem. The discharge of wastewater from industrial activities releases effluents rich in toxic and carcinogenic pollutants. Heavy metals are inorganic pollutants that have high solubility in aquatic environments. They are biologically non-gradable and accumulate in the living tissues through the food chain [Kinuthia et al., 2020].

Lead (Pb) is one of the most toxic environmental components. It is a poisonous element affecting nearly every organ in the body, especially the nervous system. In addition, it belongs to the

mutagenic and carcinogenic heavy metals class. Lead has several industrial, agriculture, and domestic applications. It is used in batteries, insecticides, solder and pipes, x-ray shields, and other industries. Lead is released in the atmosphere by burning fossil fuels and sulfides ores smelting. In the lakes, it is emitted by acid mine drainage [Moradi & Baniamerian, 2011].

On the other hand, Copper (Cu) is a common contaminant in the environment. It is an essential element for living organisms apart from its toxicity upon a considerable amount of exposure. Moreover, it can inhibit cell metabolism at high concentrations. Copper is mainly used to manufacture cables, wires, and electrical equipment, because of its excellent electrical conductivity.

In addition, it is used in certain activities such as mining, metal smelting, fungicides, paper industries, tanneries, petroleum refining, explosives, and other related sectors, which are considered the significant sources of contamination of copper in wastewater [Davarnejad & Panahi, 2016].

Traditional chemical methods such as precipitation and oxidation/reduction, and physical processes such as ion exchange and electro dialysis were used to treat various pollutants-contaminated wastewater. Nevertheless, most of these techniques have disadvantages, including incomplete removal of wastes, high consumption of reagents and energy, low selectivity, and generation of secondary wastes that are difficult to be eliminated [Akinhanmi et al., 2020].

Nowadays, adsorption is one of the most common and effective processes for treating domestic and industrial wastewater. It is cheap, minimizes the generation of sludge, and allows the adsorbent recovery. A large variety of solid substances were employed as adsorbents for heavy metal ions. Biomass has demonstrated good sorption capacity and affinity for all types of inorganic ions. Moreover, it is an available, eco-friendly, and renewable crude carbon material involved in synthesizing essential carbon products [Nadhirah et al., 2020], i.e., activated carbon (AC). Due to their surface properties, porosity, and high specific surface area, various types of biomass and its derived AC were tested and reported in the literature for several heavy metals removal from aqueous solutions: rice husk [Wong et al., 2003], wheat straw and corncob biochar [Amen et al., 2020], orange peel [Hasan et al., 2021] and its AC [Ali & Abdel-Satar, 2017], activated watermelon [Gupta & Gogate, 2016], olive solid waste [Chouchene et al., 2014], sugar beet pulp [Aksu & İ̇sođlu, 2005], tea [Wan et al., 2014], groundnut shell, yam and cassava peels AC [Thompson et al., 2020], date seed-derived biochar [Mahdi et al., 2018], sugarcane bagasse AC [Tao et al., 2015], and many other agro-waste.

Bananas are one of the most consumed fruits around the world, especially in tropical countries. For this reason, banana stem and peel became a major agro-waste. In literature, banana peel and its AC were frequently described as adsorbent [Anwar et al., 2010; Hossain et al., 2012]. However, to the best of our knowledge, very few studies were done on the banana stem for heavy metals removal from water [Praveena et al., 2020]. In this study, banana stem activated carbon was used

as a filler to modify polyurethane foams (PUR) adsorbent.

Polyurethane foams are known for treating wastewater and their adsorption capabilities to remove heavy metals due to their porosity distribution and high surface area. Additionally, they are thermally and chemically stable, highly accessible, and inexpensive. Polyurethane consists of monomers linked together through the urethane link (-NHOCO-) by reacting a polyol with a diisocyanate [Teodosiu et al., 2014].

The unloaded and loaded (physically or chemically) PUR for heavy metals removal from water were investigated and reported in many studies [Teodosiu et al., 2014; Zhang et al., 2017]. Interestingly, polyurethane foams loaded with adsorbents such as activated carbon, zeolite, bentonite, hydroxyapatite, castor oil led to encouraging metal ions removal efficiency [Iqhrammullah et al., 2020; Jang et al., 2008; Pinto et al., 2006].

This work aimed to valorize banana stem agro-waste and study the adsorption efficiency of a new activated carbon-loaded polyurethane adsorbent in removing heavy metals from water. For this purpose, banana stem AC was prepared, characterized, and employed as a filler in PUR. The latter was synthesized in the shape of pellets in a one-step method and examined in removing lead and copper ions from aqueous solutions by studying several experimental parameters: effect of AC filler concentration, the number of filtering passes, and impact of pH. Simple selectivity and seawater deionization tests were conducted as well. In addition, iodine and methylene blue numbers, zeta potential, Fourier transform infrared spectroscopy (FT-IR), x-ray diffraction (XRD), particles size analysis, and scanning electron microscopy (SEM) were employed to characterize either the AC filler or the loaded foams.

MATERIALS AND METHODS

Banana stem activated carbon preparation

The banana stem was collected from a region situated in the south of Lebanon, cut into small pieces, washed several times with ultra-pure water, and left to dry at room temperature for one week before drying in an oven at 60 °C for two days. The dried biomass was ground and sieved to 0.25 mm particles. The fine powder obtained was placed in lid-covered crucibles and carbonized in

a furnace (Wise-Therm, 4 °C/min) at 600 °C for 2 hours. The biochar was then collected, washed several times with ultra-pure water, and dried in an oven at 90 °C for 2 hours. The chemical activation was carried out by adding 400 mL of ultra-pure water and 30 mL of nitric acid (HNO₃, 99%) to a 50 g charcoal sample and stirring for 24 hours at room temperature. The mixture was then neutralized by adding sodium hydrogen carbonate solution (NaHCO₃). The prepared banana stem activated carbon (AC) was then filtered and dried in an oven at 100 °C for 24 hours.

Banana stem activated carbon properties determination

The yield of the AC particles was calculated according to Eq. (1).

$$\text{Yield (\%)} = \frac{M(\text{AC})}{M(\text{raw material})} \times 100 \quad (1)$$

The degree of oxidation or activation rate, usually called “burn-off” was calculated using Eq. (2).

$$\begin{aligned} \text{Burn-off (\%)} = \\ = \frac{M(\text{charcoal before activation}) - M(\text{AC})}{M(\text{charcoal before activation})} \times 100 \quad (2) \end{aligned}$$

The pH of AC was determined after adding 0.5 g of AC in 50 mL of ultra-pure water and stirring for 2 hours at room temperature. The ash content was evaluated using Eq. (3).

$$\text{Ash content (\%)} = \frac{M(\text{ash})}{M(\text{AC})} \times 100 \quad (3)$$

The water content was determined as shown in Eq. (4).

$$\begin{aligned} \text{Water content (\%)} = \\ = \frac{M(\text{AC before drying}) - M(\text{dried AC})}{M(\text{dried AC})} \times 100 \quad (4) \end{aligned}$$

The iodine number of the synthesized AC particles was examined as shown in Eq. (5). It is defined as mg of iodine adsorbed per 1 g of AC. The ASTM D4607-94 [2006] method was implemented. It consisted of treating 0.2 g of AC with 2 mL of HCl solution (5%). The mixture of 0.2 M iodine solution was added to the room temperature cooled mixture and stirred for 30 seconds. Soon afterward, the mixture was filtered, and a 20 mL filtrate sample was titrated

with 0.1 M sodium thiosulfate solution in the presence of starch as an indicator.

$$\text{Iodine number} = \frac{25.4 \times (20 - V_n)}{M(\text{AC})} \quad (5)$$

where: V_n is the volume of sodium thiosulfate at the equivalence point.

The methylene blue number was assessed using Eq. (6). It is described as the maximum mass of dye adsorbed per 1 g of AC adsorbent.

$$\text{Methylene blue number} = \frac{(C_o - C_e) \times V}{M(\text{AC})} \quad (6)$$

where: C_o and C_e are the initial and equilibrium methylene blue concentrations, and V represents the volume of the methylene blue solution.

It was conducted by dissolving 1.2 g of dye in 1 L of ultra-pure water. Then, in an Erlenmeyer flask, 0.1 g of AC sample is added to 25 mL dye solution and stirred at room temperature until the color disappeared. At that point, the equivalence point was determined by adding the methylene blue solution from a burette while the mixture was continuously stirring.

Polyurethane foams preparation

In a typical procedure, the polyurethane foams (PUR)/AC-loaded PUR were prepared by mixing polypropylene glycol triol (1750 g/mol, Sigma Aldrich), an appropriate mass of AC, ultra-pure water, 6 drops of dibutyltin dilaurate catalyst (DBTL, 95%, Merck), and Bis(4-isocyanatocyclohexyl)methane (90%, Merck). The mixture was stirred at room temperature for 3 min. The PUR (or AC-loaded PUR) was then collected and left to dry for 24 hours.

Adsorbate solutions preparation

Stock solutions of the metal ions were prepared by dissolving an appropriate amount of Pb(NO₃)₂ (Sigma Aldrich, ACS reagent) and Cu(NO₃)₂·3H₂O (Sigma Aldrich, puriss) in ultra-pure water. Different specific concentrations of adsorbate solutions were then prepared from the stock solutions.

Metal ions removal experiments

In a typical procedure, the adsorption experiments were done by placing a PUR/AC-loaded PUR pellet (0.45 µm diameter) in a plastic syringe. Then, the metals solutions were passed through it. Next, atomic adsorption spectroscopy (BRAIC spectrophotometer, flame, 217 nm wavelength) was conducted to assess the adsorption (%) of metal ions solutions before and after filtration as presented in Eq. (7).

$$\text{adsorption (\%)} = \frac{(C_o - C_f)}{C_o} \times 100 \quad (7)$$

where: C_o is the initial concentration of the metal ion, and C_f is the metal ion concentration after filtration.

Characterization

The AC powder and the PUR/AC-loaded PUR were characterized using the following techniques: Zeta potential (Zeta-Meter 4.0, 200 mg AC sample in 50 mL ultra-pure water), Fourier transform infrared spectroscopy (JASCO FTIR-6300, 400–4000 cm^{-1}), x-ray diffraction (Philips X'pert Pro MPD diffractometer, $\text{CuK}\alpha$, 0.154 nm, 2θ : 5–80°, Bragg–Brentano scanning mode), particles size (*Partica* LA-950 Laser Diffraction Particle Size Distribution Analyzer-HORIBA), and scanning electron microscopy (AIS 2100C, 20 kV).

RESULTS AND DISCUSSION

Properties of banana stem activated carbon

The vegetable AC prepared and used in this study as filler in PUR was analyzed, and the determined properties are summarized in Table 1. The relatively low yield obtained can be explained by losing highly volatile particles during the pyrolysis process.

The activation reaction is the process that involves an oxidizing agent leading to the formation of a porous product of lower mass. This mass loss indicates the degree of oxidation, or activation rate, usually called “burn-off”. A burn-off lower than 50% can favor the production of micro and mesopores that contribute to the AC’s adsorption capacity. Higher than 50%, macropores can be formed upon the micro and

mesopores deterioration [Fernandez Ibanez & Stoeckli, 2003; Wigmans, 1989].

The pH of AC was determined to be basic (8.12) due to the presence of calcium oxide (CaO) in the AC structure in addition to other bases such as Na_2O , MgO , and K_2O that could be considered as well [Baudu et al., 2001].

Charcoal can be viewed as a promising adsorbent if its ash content is not higher than 10%. The ash is an impurity that can reduce the adsorption ability of the activated carbon [Silgado Correa et al., 2014].

The water content (%) is the amount of water physically bounded to AC. In general, a good quality AC should not contain more than 15% moisture [Silgado Correa et al., 2014; Zulkania et al., 2018].

The iodine number is a simple and rapid test conducted in this study to estimate the approximate AC surface area related to their adsorption performance. The calculated iodine number is comparable to a surface area between 900 and 1100 m^2/g [Saka, 2012], reflecting the high adsorption capacity of these particles.

The methylene blue test was assessed to estimate the approximate surface area and the porosity developed in the additive. The resulting large methylene blue number correlates with the high surface area of the AC in addition to the presence of large micropores, mesopores, and less likely macropores in these particles [Warhurst et al., 1997], which can lead to excellent adsorption capacity.

Table 1. Properties of banana stem AC

AC properties	
Yield (%)	31.10
Burn-off (%)	34.96
pH	8.12
Ash content (%)	6.01
Humidity (%)	10.38
Iodine number (mg/g)	990.6
Methylene blue number (mg/g)	361.2

Characterization

AC filler characterization

Zeta potential

As shown in Figure 1, the synthesized vegetable AC exhibits negative zeta potentials, which can improve the ability of these particles to bind to metal ions. The curve below shows that the zeta potentials became more negative upon increasing the pH at room temperature. Since the zeta

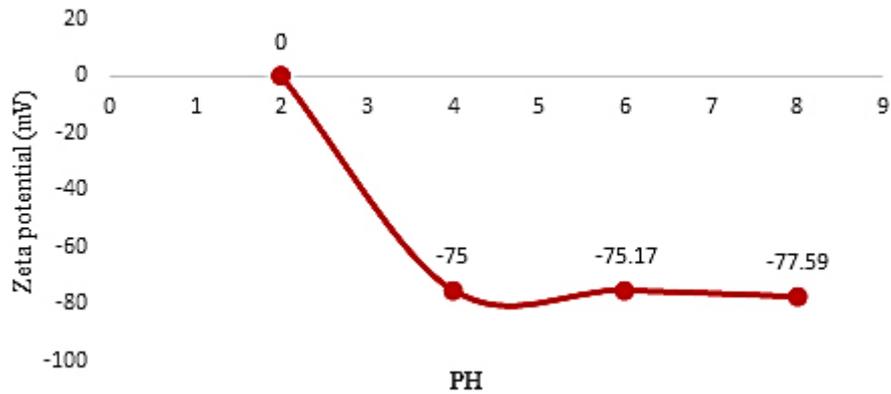


Figure 1. Zeta potentials of AC as a function of pH

potentials reach highly negative values starting from pH = 4, the colloidal AC particles can exhibit high stability [Pelissari et al., 2014; Tholstrup Sejersten et al., 2007] as their negative charge inhibits coalescence. The isoelectric point was found to be at pH = 2, where the AC particles can aggregate. The high acidity of the material can explain the negative zeta potential of the AC, and carboxylic functional groups seemed to remain on the surface although the pyrolysis at high temperature.

Fourier transform infrared spectroscopy (FTIR)

The banana stem was reported to include cellulose, hemicellulose, lignin, ash content, and pectin [Li et al., 2010]. Our synthesized vegetable AC powder derived from the banana stem was characterized by FTIR to investigate the main functional groups present on its surface after pyrolysis and activation. Figure 2 shows a broad band at approximately 3431 cm^{-1} corresponding to O-H stretching in carboxyl and hydroxyl groups. In addition, it shows two peaks at 2933 cm^{-1} and 2855 cm^{-1} that correspond to alkane C-H stretching. The peak at approximately 1740 cm^{-1} may be due to C=O

stretching by a carbonyl group. The peak at around 1630 cm^{-1} may be attributed to the C-O stretching vibration in carbonyl and carboxy groups and can be assigned to -C=C-C stretches of aromatic ring groups. The peak at around 1385 cm^{-1} may refer to hydroxyl (-OH) bending vibration and C=O stretching of carboxylate ions. The peak at 1090 cm^{-1} could be attributed to the O-H bending vibration [DeMessie et al., 2015; Li et al., 2016].

X-ray diffraction (XRD)

The X-ray diffraction patterns of our synthesized AC (Figure 3) reveal, in general, an amorphous structure despite the pyrolysis process. However, the two broad peaks at around 26° and 46° and the other sharper peaks appearing between 25 and 29 degrees denote the formation of a crystalline carbonaceous structure [Omri et al., 2013].

Particles size analysis

The original banana stem was ground and sieved to 0.25 mm particles. After pyrolysis and activation, the size of the smallest AC particle is $6\text{ }\mu\text{m}$, and the largest particle is approximately

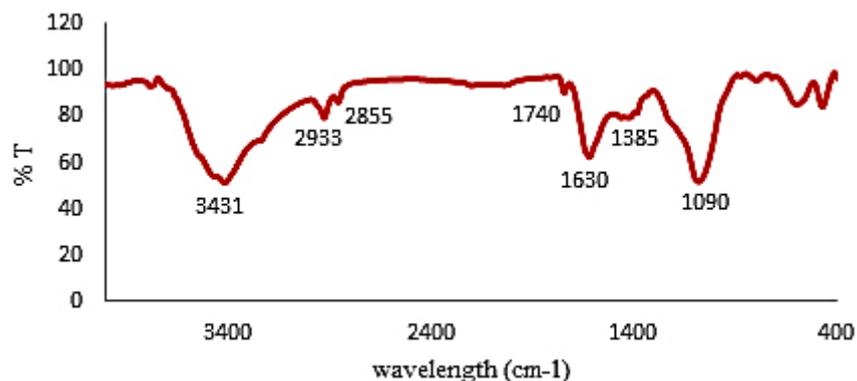


Figure 2. FTIR spectrum of AC powder

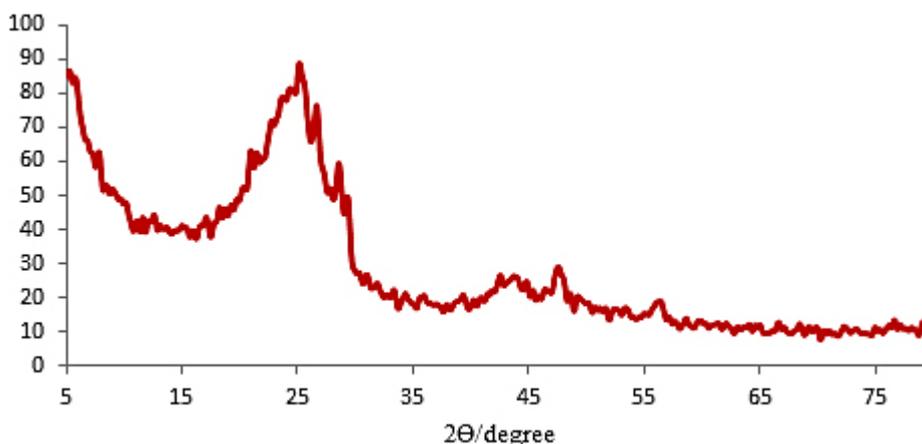


Figure 3. XRD profile of AC

180 μm (Figure 4). However, the size of the majority of the particles is around 17 μm . Therefore, our particles are categorized as powdered activated carbon having a distinctive average size of 15–25 μm [Ahamed et al., 2020]. Due to their tiny size leading to form dust, powdered AC was reported to be implemented as a filler in other process units rather than being used independently, favoring the adsorption process [Ahamed et al., 2020].

Adsorbent characterization

Scanning electron microscopy (SEM)

Figure 5 shows the SEM images that can give an insight about the aspect of the surfaces of the synthesized AC particles used as filler, unloaded PUR, and AC-loaded PUR that was

implemented as an adsorbent in this work. Irregular and uneven pores were observed on the surface of the AC before adding it to PUR (Figure 5A & A’), which can be the reason behind boosting the interactions between the adsorbent and the metal ions. The PUR have a porous structure (Figure 5B & B’), favoring the adsorption of metal ions as well. The pores identified in the AC-loaded PUR (Figure 5C & C’) became more evenly distributed in the matrix.

Effect of various experimental parameters on the metal ions removal process

In this work, several experimental parameters were studied to evaluate their impact on the copper (Cu) and lead (Pb) ions removal by polyurethane foams. The metal adsorption was determined using atomic absorption spectroscopy (AAS).

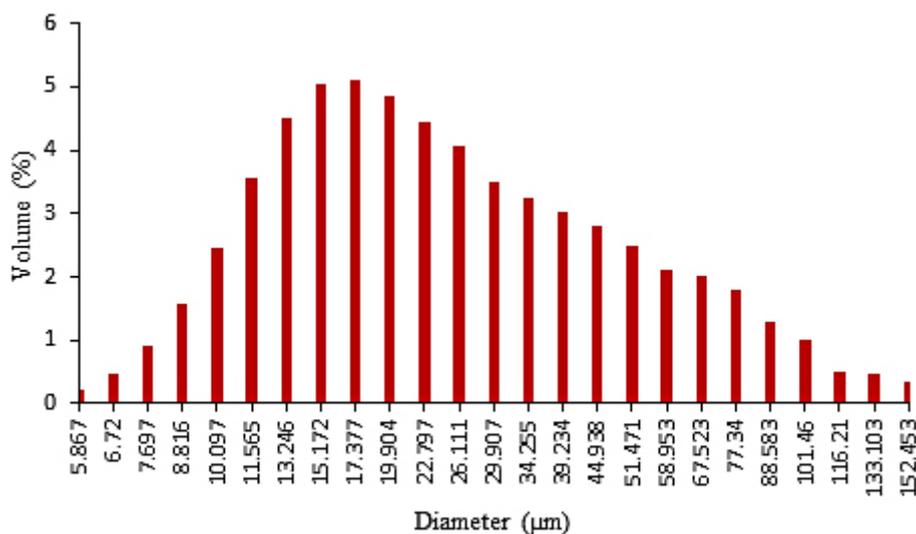


Figure 4. Particles size distribution of AC

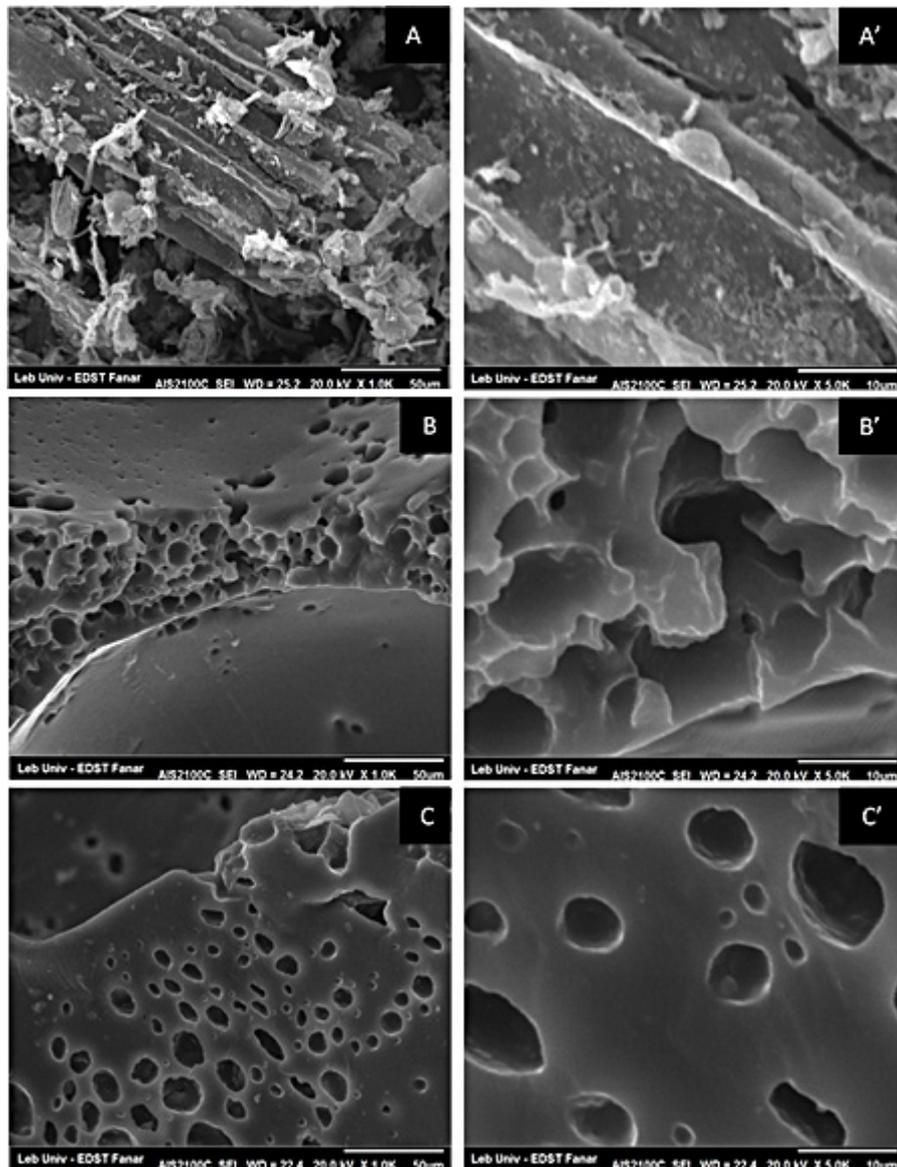


Figure 5. SEM images of AC (A), unloaded PUR (B), and AC-loaded PUR (C)

Effect of AC filler concentration

The evolution of the adsorption of copper and lead ions as a function of the concentration of the AC filler loaded in the synthesized PUR was followed (Figure 6). Due to the porous structure of PUR, and although the absence of AC filler, 16% and 14% adsorption was observed for Pb^{2+} and Cu^{2+} , respectively. Additionally, the adsorption was enormously improving by increasing the filler concentration to reach 77% for lead and 40% for copper at 8% AC concentration. This is due to the addition of specific sites in PUR, allowing for more metal ions capture. However, when more than 8% AC was loaded, the mixture became too dense and challenging to be stirred. This was reflected in a drastic dropping of the

adsorption for both metal ions. This may be due to the physical destruction and malformation of the filter's structure. Furthermore, the adsorption of the lead ions was always higher than that of copper ions (Figure 6).

Effect of number of filtering passes

Two AC-loaded PUR were synthesized using two different concentrations of additive (4 and 8%) and compared to unloaded PUR in removing lead (Figure 7A) and copper ions (Figure 7B). 1, 5, and 10 passes through the pellets were applied to investigate their effect on the adsorption. As expected, it was noticed that the adsorption of both metal ions increased by increasing the number of passes. After the 10th pass, 100% metal ions removal was

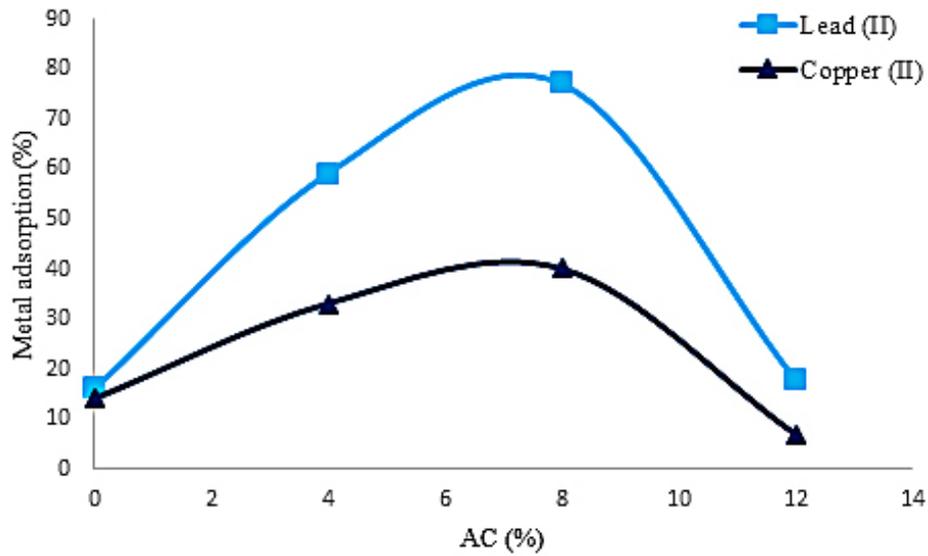


Figure 6. Effect of the AC concentration (%) loaded in PUR on the metal adsorption (%)

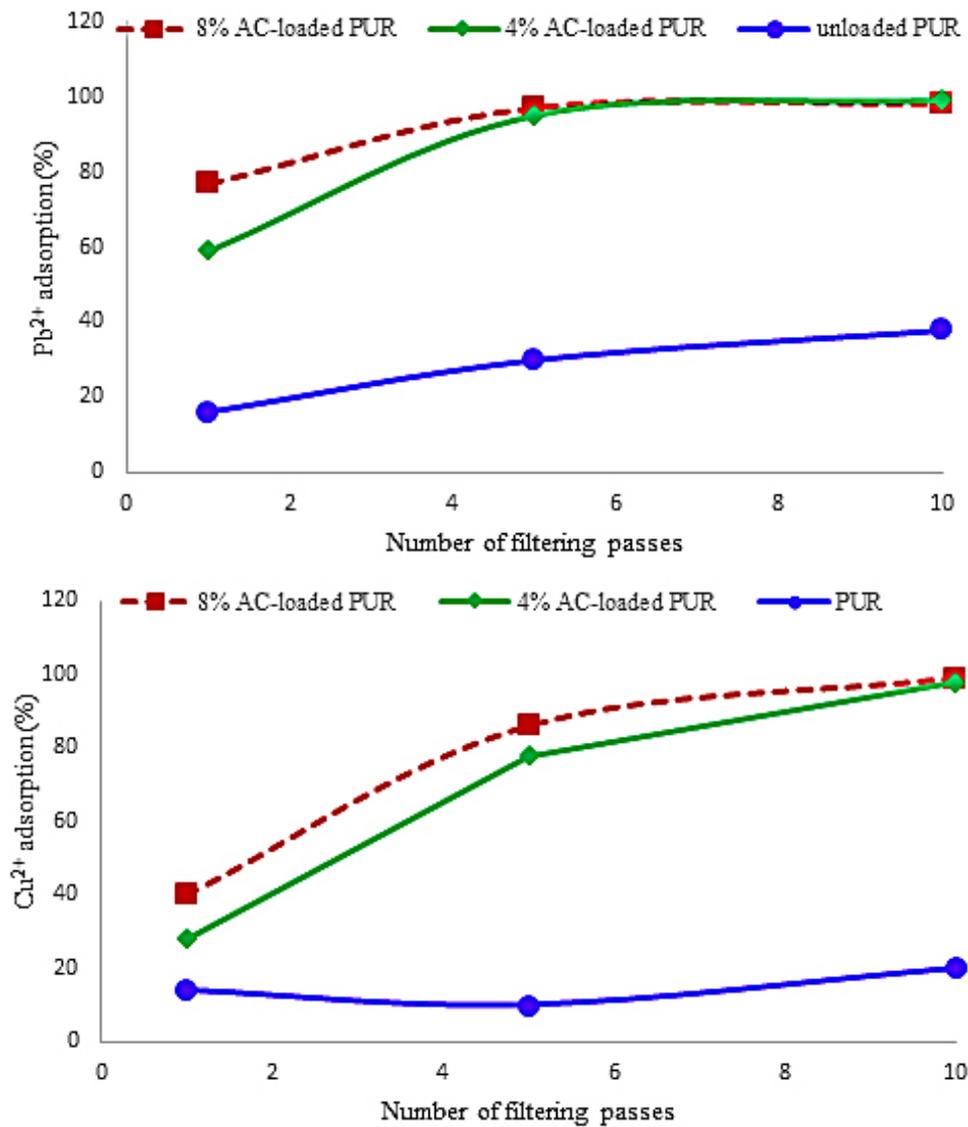


Figure 7. Effect of the number of filtering passes through the different synthesized PUR: a) on the lead ions adsorption (%); b) on the copper ions adsorption (%)

achieved for both AC-loaded PUR. For the unloaded PUR, low adsorptions were observed even after 10 passes. These results confirm the advantage of using the AC-loaded pellets for both metal ions removal.

Effect of pH

8% AC-loaded PUR were synthesized and studied by applying 1, 5, and 10 passes at different pH (2, 4, and 9). The results are represented in Figure 8A for lead and Figure 8B for copper ions. After the 10th pass, 100 % adsorption was achieved for both metal ions at any pH. For 1 and 5 filtering passes, the optimum pH was 4, where maximum adsorption was reached for the two studied metal ions. When 1 and 5 passes were applied at low pH (2), lower adsorption was observed. This can be

explained by the excessive protonation of the specific sites on the adsorbent surface, which depreciated the bonds formed with the metal ions. At moderate pH (4), the H⁺ ions were released, and the adsorption became more remarkable. Moreover, at higher pH (9), the precipitation of lead and copper ions as hydroxide salts may predominantly lead to the lower adsorption by the AC-loaded PUR.

Simple adsorption tests

Selectivity test

In wastewater, the metal ion is not found alone; it always exists with other ions. While ions can compete for binding sites, a test was carried out to investigate the selectivity of unloaded PUR

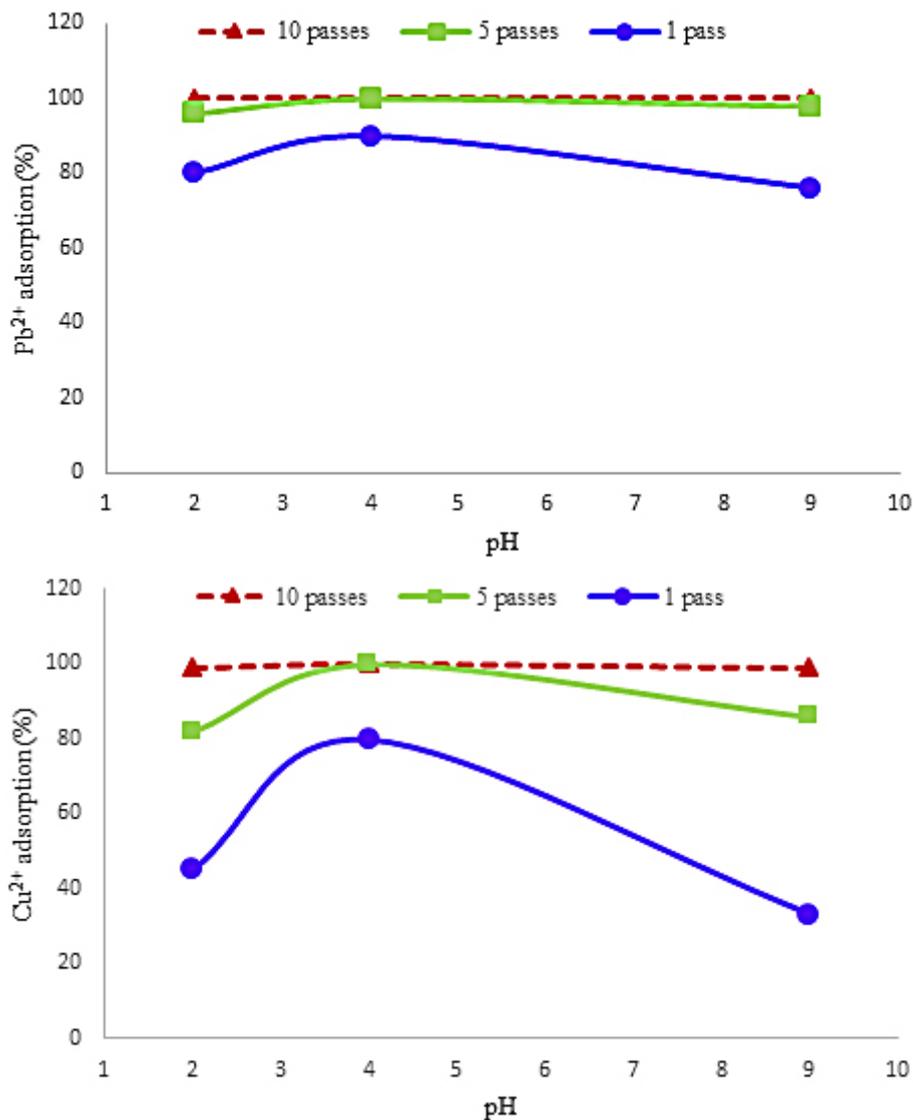


Figure 8. Effect of pH: a) on the lead ions adsorption (%) with various number of filtering passes; b) on the copper ions adsorption (%) with various number of filtering passes

and 8% AC-loaded PUR in removing lead and copper ions. For this purpose, an aqueous solution of similar concentrations of both ions (10 ppm) was prepared and filtered at room temperature, and the metal adsorption was determined using AAS. The results are summarized in Figure 9 below. It shows that lead ions were eliminated in higher amounts than copper, whether using unloaded or loaded PUR. This may be explained by the ionic radius of lead which is larger than copper. The higher metal adsorption held by the modified PUR demonstrates the advantage of increasing the surface-specific binding sites by adding 8% of AC.

Seawater deionization test

A seawater solution was used to conduct a simple deionization test through unloaded PUR, vegetable 8% AC-loaded PUR, and an industrial AC loaded in the synthesized PUR. 1 and 10 filtering passes were applied at room temperature. The results are shown in Table 2.

The results show the important ability and high efficiency of our vegetable AC-loaded PUR to eliminate several ions (Cu^{2+} , Fe^{2+} , Zn^{2+} , Mg^{2+} , Ca^{2+} , Mg^{2+} , NO_3^- and PO_4^{3-}) from seawater whether after 1 or 10 passes. After 1 pass filtration, the vegetable AC-loaded polyurethane decreased the concentration of the cations by 26% for calcium up to 70% for copper. At the same time, it lessened the concentration of the anions by 52% for nitrate and 23% for phosphate. After the 10th pass filtration, the vegetable AC-loaded polyurethane showed a drop of 44 to 94% for the cations and 49 to 60% for the anions in the seawater sample. The reduction of the different ions concentration in the sample was interestingly higher in the vegetable AC-loaded polyurethane compared to the pure polyurethane foams.

Nevertheless, our AC-loaded PUR showed relatively comparable results to polyurethane foams that industrial AC filled. The AC filling was done using the same procedure and the same AC concentration.

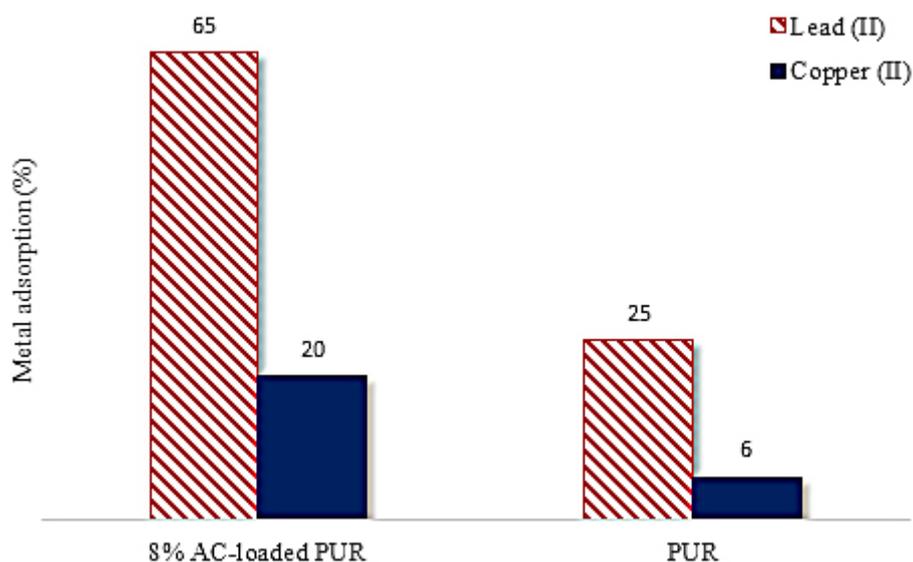


Figure 9. Metal adsorption (%) by unloaded PUR and AC-loaded PUR in the selectivity test

Table 2. Simple seawater deionization test comparison between unloaded PUR, vegetable AC-loaded PUR, and AC (industrial)-loaded PUR after 1 and 10 filtering passes

Ion		Cu^{2+}	Fe^{2+}	Zn^{2+}	Mg^{2+}	Ca^{2+}	NO_3^-	PO_4^{3-}
Initial concentration (ppm)		30	35	44	15	70	100	65
Residual concentration (ppm) after 1 filtering pass	Unloaded PUR	20	28	25	14	60	90	55
	8% vegetable AC-loaded PUR	9	15	20	10	52	48	50
	8% AC (industrial)-loaded PUR	10	9	24	12	55	64	45
Residual concentration (ppm) after 10 filtering passes	Unloaded PUR	10	15	23	8	50	80	40
	8% vegetable AC-loaded PUR	4	2	15	5	39	40	33
	8% AC (industrial)-loaded PUR	5	0.5	16	6	44	59	20

CONCLUSION

In this study, activated carbon was prepared from banana stem natural by-product by carbonization at 600 °C and activation with nitric acid. The yield was around 31% with encouraging activation burn-off (37.96%), ash (6.01%) and humidity (10.38%) content, and relatively high iodine (990.6 mg/g) and methylene blue (361.2 mg/g) numbers. The synthesized particles were characterized using several methods. Their zeta potential was negative at $\text{pH} > 2$, FTIR spectrum was comparable with other synthesized vegetable activated carbon from the literature. The XRD profile showed a generally amorphous to an almost crystalline structure. In addition, the average AC particles size was 17 μm , and their SEM images showed an irregular porous surface.

Low-cost and eco-friendly vegetable AC-loaded polyurethane foams were synthesized in one step and proved to be a promising adsorbent for removing lead and copper ions from aqueous solutions. The SEM images of the loaded PUR indicated an almost uniform porous structure. By studying the effect of AC-loaded concentration, the number of filtering passes, and pH, the results obtained by AAS showed better adsorption of Pb^{2+} compared to Cu^{2+} . Furthermore, 8% AC-loaded PUR yielded the maximum metal ions removal after one filtering pass, and the optimum pH was 4. Almost 100% adsorption was obtained after 10 filtering passes at any pH with 4 or 8% AC concentrations opening the door for a future application by assembling a series of modified polyurethane foams to ensure a remarkable wastewater one-pass purification. Finally, the loaded foams exhibited promising results in the purification of a seawater sample by removing several ions.

Acknowledgements

The authors wish to thank the Lebanese University - research program for its financial support.

REFERENCES

- Ahamed M.I., Lichtfouse E., Asiri A. 2020. Green Adsorbents to Remove Metals, Dyes and Boron from Polluted Water. Springer, Cham, 49(1).
- Akinhanmi T.F., Ofudje E.A., Adeogun A.I., Aina P., Joseph I.M. 2020. Orange peel as low-cost adsorbent in the elimination of Cd(II) ion: Kinetics, isotherm, thermodynamic and optimization evaluations. *Bioresources and Bioprocessing*, 7(1), 34.
- Aksu Z., İšoğlu İ.A. 2005. Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp. *Process Biochemistry*, 40(9), 3031–3044.
- Ali M.H.H., Abdel-Satar A.M. 2017. Removal of some heavy metals from aqueous solutions using natural wastes orange peel activated carbon. *IJRDO - Journal of Applied Science*, 3(3), 13–30.
- Amen R., Yaseen M., Mukhtar A., Klemeš J.J., Saqib S., Ullah S., Bokhari A. 2020. Lead and cadmium removal from wastewater using eco-friendly biochar adsorbent derived from rice husk, wheat straw, and corncob. *Cleaner Engineering and Technology*, 1, 100006.
- Anwar J., Shafique U., Waheed-uz-Zaman null, Salman M., Dar A., Anwar S. 2010. Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana. *Bioresource Technology*, 101(6), 1752–1755.
- Baudu M., Guibaud G., Raveau D., Lafrance P. 2001. Prediction of Adsorption from Aqueous Phase of Organic Molecules as a Function of Some Physicochemical Characteristics of Activated Carbons. *Water Quality Research Journal*, 36(4), 631–657.
- Chouchene A., Jeguirim M., Trouvé G. 2014. Biosorption performance, combustion behavior, and leaching characteristics of olive solid waste during the removal of copper and nickel from aqueous solutions. *Clean Technologies and Environmental Policy*, 16(5), 979–986.
- Davarnejad R. & Panahi P. 2016. Cu (II) removal from aqueous wastewaters by adsorption on the modified Henna with Fe₃O₄ nanoparticles using response surface methodology. *Separation and Purification Technology*, 158, 286–292.
- DeMessie B., Sahle-Demessie E., Sorial G.A. 2015. Cleaning Water Contaminated With Heavy Metal Ions Using Pyrolyzed Biochar Adsorbents. *Separation Science and Technology*, 50(16), 2448–2457.
- Fernandez Ibanez E., Stoeckli F. 2003. Etude de la carbonisation et de l'activation de précurseurs végétaux durs et mous.
- Gupta H. & Gogate P.R. 2016. Intensified removal of copper from waste water using activated watermelon based biosorbent in the presence of ultrasound. *Ultrasonics Sonochemistry*, 30, 113–122.
- Hasan M.B., Al-Tameemi I.M., Abbas M.N. 2021. Orange Peels as a Sustainable Material for Treating Water Polluted with Antimony. *Journal of Ecological Engineering*, 22(2), 25–35.
- Hossain M.A., Ngo H., Guo W., Nguyen T. 2012. Removal of Copper from Water by Adsorption onto Banana Peel as Bioadsorbent. *International Journal of GEOMATE*, 2(2), 227–234.

15. Iqhrammullah M., Marlina Hedwig R., Karnadi I., Kurniawan K.H., Olaiya N.G., Abdulmadjid S.N. 2020. Filler-Modified Castor Oil-Based Polyurethane Foam for the Removal of Aqueous Heavy Metals Detected Using Laser-Induced Breakdown Spectroscopy (LIBS) Technique. *Polymers*, 12(4), 903.
16. Jang S.H., Min B.G., Jeong Y.G., Lyoo W.S., Lee S.C. 2008. Removal of lead ions in aqueous solution by hydroxyapatite/polyurethane composite foams. *Journal of Hazardous Materials*, 152(3), 1285–1292.
17. Kinuthia G.K., Ngure V., Beti D., Lugalia R., Wangila A., Kamau L. 2020. Levels of heavy metals in wastewater and soil samples from open drainage channels in Nairobi, Kenya: Community health implication. *Scientific Reports*, 10(1), 8434.
18. Li K., Fu S., Zhan H., Zhan Y., Lucia L. 2010. Analysis Of The Chemical Composition And Morphological Structure Of Banana Pseudo-Stem. *Bio-Resources*, 5(2), 576–585.
19. Li Y., Liu J., Yuan Q., Tang H., Yu F., Lv X. 2016. A green adsorbent derived from banana peel for highly effective removal of heavy metal ions from water. *RSC Advances*, 6(51), 45041–45048.
20. Mahdi Z., Yu Q.J., El Hanandeh A. 2018. Removal of lead(II) from aqueous solution using date seed-derived biochar: Batch and column studies. *Applied Water Science*, 8, 181.
21. Moradi S. & Baniamerian M.J. 2011. Applications Of Chemically Modified Ordered Mesoporous Carbon As Solid Phase Extraction Sorbent For Preconcentration Of Trace Lead Ion In Water Samples. *Chemical Industry & Chemical Engineering Quarterly*, 17, 397–408.
22. Nadhirah Z.N.A., Manisah M.R., Karim N. Abd., Pa F.C. 2020. Overview of activated carbon derived from biomass for heavy metal removal. *AIP Conference Proceedings*, 2291(1), 020045.
23. Omri A., Benzina M., Ammar N. 2013. Preparation, modification and industrial application of activated carbon from almond shell. *Journal of Industrial and Engineering Chemistry*, 19(6), 2092–2099.
24. Pelissari F.M., Sobral P.J. do A., Menegalli F.C. 2014. Isolation and characterization of cellulose nanofibers from banana peels. *Cellulose*, 21(1), 417–432.
25. Pinto M.L., Pires J., Carvalho A.P., de Carvalho M.B., Bordado J.C. 2006. Synthesis and regeneration of polyurethane/adsorbent composites and their characterization by adsorption methods. *Microporous and Mesoporous Materials*, 89(1), 260–269.
26. Praveena S.M., Rashid U., Rashid S.A. 2020. Application of activated carbon from banana stem waste for removal of heavy metal ions in greywater using a Box-Behnken design approach. *Environmental Technology*, 41(25), 3363–3374.
27. Saka C. 2012. BET, TG–DTG, FT-IR, SEM, iodine number analysis and preparation of activated carbon from acorn shell by chemical activation with ZnCl₂. *Journal of Analytical and Applied Pyrolysis*, 95, 21–24.
28. Silgado Correa K., Marrugo G., Juliana P.-M. 2014. Adsorption of Chromium (VI) by Activated Carbon Produced from Oil Palm Endocarp. *Chemical Engineering Transactions*, 37, 721–726.
29. Tao H.-C., Zhang H.-R., Li J.-B., Ding W.-Y. 2015. Biomass based activated carbon obtained from sludge and sugarcane bagasse for removing lead ion from wastewater. *Bioresource Technology*, 192, 611–617.
30. Teodosiu C., Wenkert R., Tofan L., Paduraru C. 2014. Advances in preconcentration/removal of environmentally relevant heavy metal ions from water and wastewater by sorbents based on polyurethane foam. *Reviews in Chemical Engineering*, 30(4), 403–420.
31. Tholstrup Sejersen M., Salomonsen T., Ipsen R., Clark R., Rolin C., Balling Engelsen S. 2007. Zeta potential of pectin-stabilised casein aggregates in acidified milk drinks. *International Dairy Journal*, 17(4), 302–307.
32. Thompson C.O., Ndukwe A.O., Asadu C.O. 2020. Application of activated biomass waste as an adsorbent for the removal of lead (II) ion from wastewater. *Emerging Contaminants*, 6, 259–267.
33. Wan S., Ma Z., Xue Y., Ma M., Xu S., Qian L., Zhang Q. 2014. Sorption of Lead(II), Cadmium(II), and Copper(II) Ions from Aqueous Solutions Using Tea Waste. *Industrial & Engineering Chemistry Research*, 53(9), 3629–3635.
34. Warhurst A.M., McConnachie G.L., Pollard, S.J.T. 1997. Characterisation and applications of activated carbon produced from *Moringa oleifera* seed husks by single-step steam pyrolysis. *Water Research*, 31(4), 759–766.
35. Wigmans T. 1989. Industrial aspects of production and use of activated carbons. *Carbon*, 27(1), 13–22.
36. Wong K.K., Lee C.K., Low K.S., Haron M.J. 2003. Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions. *Chemosphere*, 50(1), 23–28.
37. Zhang Z., Zhu L., Jin J. 2017. Preparation of Polyurethane Foam Adsorbents and Their Application on Preconcentration/Removal of Metal Ions. *Cailiao Daobao/Materials Review*, 31, 34–39.
38. Zulkania A., Hanum G.F., Rezki A.S. 2018. The potential of activated carbon derived from bio-char waste of bio-oil pyrolysis as adsorbent. *MATEC Web of Conferences*, 154, 01029.