

Lead (Pb²⁺) removal in water using different forms of spent arabica coffee grounds at varying contact time

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Abstract. The availability of clean water for drinking and domestic use is a basic human right, but it is oftentimes denied to some users due to lack of facilities that could clean water. The use of cheap and abundant biomaterials can help solve this problem. Spent coffee grounds is a biomaterial that can remove heavy metals, such as lead (Pb²⁺) in water. In this study, the Ultraviolet Visible Spectrophotometry analysis resulted in the computation of the Total Removal Efficiency (R%) on lead (Pb²⁺) in water using raw, crushed, carbonized, and chemically treated spent coffee grounds of the Arabica variety. The crushed and carbonized samples had the highest Total Removal Efficiency (R%) at a shorter coffee-lead contact time. This is due to the exposure of more surfaces as seen in the Scanning Electron Microscopy micrographs, where more open pores and deeper cages or crevices are exposed for metal adsorption. The Atomic % of elemental Carbon was also high for the crushed sample. FTIR analysis revealed that the presence of charged amines (C=NH⁺) in the carbonized and chemically treated samples resulted to lead (Pb²⁺) adsorption in a short time. Abundant and cheap waste biomaterials, such as spent Arabica coffee grounds can exceed the Total Removal Efficiency (R%) on lead (Pb²⁺) of commercially available activated carbon.

Keyword. Biomaterials, Spent coffee grounds, Heavy metals, Adsorption

1 Introduction

The need for clean and potable water is also recognized by the United Nations General Assembly in 2010; water should be free of contaminants, readily available, and cheap [1]. Water is a very important commodity for everyone, but it is not oftentimes safe, accessible and cheap. Thus, there is a need to look for viable ways to increase water quality. One of the measures that can be done is the use of water filters but water filters are expensive for the low-average income earners because the cost is approximately ranging from Php 2,500.00 – Php 37,000.00 in the Philippines. Hence, there is a need to fabricate a low-cost filter from locally sourced materials so that everyone can be able to gain an access to safe and quality water. The province of Benguet in the Philippines is well known for producing tons of vegetables being supplied to the different parts of the country. Copper and gold mining is also done in some areas of the province. While this is economically sound, it is observed that these activities are causing water pollution. The vegetable terraces are often infested with pesticides and other chemical agents that leach into the soil and thereby go into the water system, such as springs and rivers. Chemical leaching from mines occurs and is directly affecting the water system. The springs and rivers are the water source that people in Benguet, Philippines use for drinking and other domestic needs. It is a basic human right to have an access to clean water but oftentimes people are not aware of this due to a lack of information. Water filters are also quite expensive and

some users do not have the means to buy one. Locally available materials that could be used as low-cost water filter includes coffee grounds, which are oftentimes considered as biodegradable waste materials. In the study of Moelyaningrum *et al.*, Robusta coffee ground residues were able to adsorb lead in water [2].

In Baguio City, Philippines alone coffee is a favorite commodity that is served in homes, coffee shops, and restaurants as a beverage. Ground coffee beans are brewed, the aromatic drink is enjoyed by coffee drinkers and the spent grounds are thrown away as waste material. This widely abundant and cheap waste biomass can be studied for its capacity to remove pollutants from water such as Pb²⁺ (lead). Figure 1 shows a picture of a locally available raw Arabica coffee ground that can be used to adsorb lead (Pb²⁺) in water.



Figure 1. A raw coffee ground

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Lead (Pb) is a p-block element in the periodic table found in group 14, period 6. It is a heavy metal used in industries for the production of batteries, ammunitions, solders, alloys, and sheathings. It is also found in the Polyvinyl chloride (PVC) pipes of water distribution system, which may possibly leach into tap water. Pb is also a by-product of copper, gold, or silver mining industries thus the possibility of leakage into our bodies of water. Human exposure to Pb includes neurological and behavioural effects, mortality due to cardiovascular disease, impaired renal function, hypertension, impaired fertility, adverse pregnancy outcomes, delayed sexual maturation, and impaired dental health [3]. The study of the use of cheap and low-cost material from abundant waste biomass could help in improving the water quality in each and everyone's tap.

Studies on the use of waste coffee grounds in removing pollutants from water have been performed by several researchers. Iron (Fe) ion removal in water was investigated by Mohamed and Lee. About 92.9 % of Fe ions were adsorbed by 0.10 g of spent coffee grounds at pH 4 in 60 minutes [4]. Untreated or raw coffee grounds alone can be able to remove lead in water as evidenced by the study by Medici *et al.* Using the Langmuir equation, the group found that the raw coffee grounds had a maximum adsorption of 2.46 mg/g [5]. A similar study on the efficiency of untreated coffee grounds by Azouaou *et al.*, but this time using a fixed-bed column found that the metal uptake capacity of the coffee grounds was 78.95 mg/g [6]. In the study of Seniunaite, *et al.*, they found out that coffee grounds were able to adsorb copper and lead in water and the cleaning efficiency is increased if the particle size is decreased to <200 μm [7]. Activated carbon produced from coffee grounds was effective in removing methyl orange in water via the adsorption process, which was investigated by Rattanapan *et al.* The adsorption process using the activated coffee grounds was found to be feasible and spontaneous [8]. The pH does also affect the adsorption potential of coffee grounds as a low-cost material used in the removal of heavy metals in water. Kyzas *et al.* found that at pH5, coffee ground as an adsorbent had its maximum performance in the adsorption of Copper from water at 76% [9]. In another study using coffee grounds and coffee husks from the Arabica variety, which are both effective in the removal of lead (Pb^{2+}) in water, pH was also seen to greatly affect the heavy metal biosorption process. At increasing pH, the repulsive forces between H^+ and metal ions decrease thus the sorption process is facilitated but at a very high pH, precipitation was observed as stated by Pariona-Palomino *et al.* in their discussion [10]. Malachite green, a synthetic dye was also effectively adsorbed by spent coffee grounds as studied by Mat *et al.* The contact time and percentage removal of dye both increased until equilibrium. It was also revealed that % the removal of dye increased from 77.35% to 94.47% as the dosage adsorbent increased [11]. Tanada *et al.* in 2005 investigated the possibility of removing lead ions in drinking water, findings implied that proteins and fats found in coffee grounds were able to cause greater adsorption of lead ions in water [12]. With the previous

works done by other researchers, it was the aim of this study to investigate the use of spent Arabica coffee grounds in removing heavy metals, such as lead (Pb^{2+}) in water. The use of cheap and abundant resources, such as spent coffee grounds to remove heavy metals, such as lead (Pb^{2+}) could benefit people who cannot afford to buy expensive water filters. Thus, the parameters in the preparation of a spent coffee ground sample to remove lead (Pb^{2+}) in water, if proven to be efficient can contribute to the fabrication of an adsorbent for better water quality.

2 Experimental

2.1 Materials and Methodology

2.1.1 Preparation of coffee ground samples

Arabica variety of coffee grounds is available in the local markets of Baguio City, Philippines. Arabica spent coffee grounds used in this study were collected from the waste from a coffee maker. Four forms of Arabica coffee grounds were produced for testing and these are (1) raw, (2) crushed, (3) carbonized, and (4) chemically treated samples. The raw coffee grounds used in the study were boiled for 10 minutes with stirring on a hot plate. This is to remove impurities and water soluble substances. The coffee grounds were vacuum filtered and then oven-dried for 12 hours at 100°C. To produce the crushed sample, the previously boiled raw coffee grounds were crushed using a food processor at maximum speed for 5 minutes and sieved using ASTM (American Society for Testing and Materials) test sieve to produce a uniform sample of 850 μm size. The carbonized sample was also produced from the previously boiled raw coffee grounds. The sample was subjected to a furnace at 600°C for 4 hours. It was crushed using a food processor at maximum speed for 5 minutes and sieved using ASTM test sieve to produce a uniform sample of 212 μm size. The treated sample was taken from the carbonized sample and was soaked in 0.1 M HCl for 48 hours. The coffee grounds were vacuum filtered and oven-dried for 24 hours at 105°C. Figure 2 shows the flowchart of the preparation of coffee ground samples.

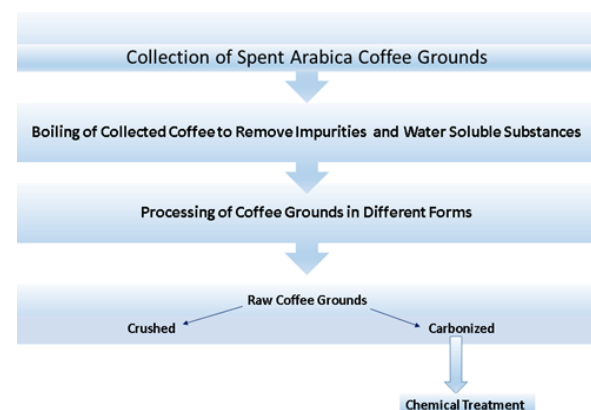


Figure 2. Flowchart for the preparation of coffee ground samples.

The four forms of Arabica coffee ground samples were placed in a sealed polyethylene container and stored in a desiccator. Figure 3 shows an actual set-up in the preparation of the sample where vacuum filtration and sieving were employed in the study.



Vacuum Filtration



Sieving

Figure 3. An actual laboratory set-up for processing of the coffee grounds.

2.1.2 Determination of Total Removal Efficiency (R%) of coffee grounds at varying contact time

For Ultraviolet Visible Spectrophotometry (UV-Vis) analysis, 4.83×10^{-3} M Lead (II) Standard Solution (from PbNO_3) was prepared by dissolving 160.00 mg of PbNO_3 in enough water, pouring the solution into the volumetric flask and filling the flask up to the 100 mL mark. This concentration was chosen in consideration to the response of the UV-Vis spectrophotometer to the Pb solution. Higher concentrations might not give a reliable calibration curve. The cationic micelle cetyltrimethyl ammonium bromide (CTAB) solution of 0.3 M was prepared by dissolving 10.93 g in enough water, pouring the solution in the volumetric flask and filling it up to the 100 mL mark.

The photometric reagent 1,5-Diphenylthiocarbazone (dithizone) solution with a concentration of 1.95×10^{-4} M was prepared by dissolving 5.00 mg dithizone in enough ethanol, pouring the solution in the volumetric flask and filling it up to the 100 mL mark. The dithizone-

lead solution was acidified using 4×10^{-3} M HCl. It was prepared by pouring enough water into a 100 mL volumetric flask, pipetting out 0.0333 mL concentration. HCl from the stock then into the flask, and filling the flask with water up to the 100 mL mark. The procedure was similar to the work reported by Khan *et al.* [13] with some modifications.

For the UV-Vis analysis of the sample, triplicates of each gram of coffee ground samples were placed on a 100 ml beaker, 50 ml of 0.000483 M $\text{Pb}(\text{NO}_3)_2$ solution was added. The samples were stirred for 1 hour, 2 hours, 3 hours contact time. The coffee-Pb sample solutions after 1 hour, 2 hours and 3 hours contact time were filtered into a cotton plugged funnel. A 25 ml of the filtrate was collected and transferred into a 100 ml volumetric flask containing 1.50 ml 0.000195M Dithizone solution, 4 ml 0.3M CTAB solution and 1 ml of 0.0004M HCl solution then diluted to mark with distilled water and shaken to mix the solution. The coffee-Pb was slightly acidic at pH 6.00. For comparison purposes, a similar procedure was also performed with a commercial activated carbon. The Pb^{2+} concentration in parts per million (ppm) was recorded before and after the batch adsorption experiment. The initial concentration was 197 ppm.

All of the reagents used in this experiment were purchased from Chemline Scientific Corporation in the Philippines and are of analytical reagent grade of known purity.

2.2 Characterization

The Shimadzu UV mini – 1240 UV-Visible (UV-Vis) spectrophotometer was used to determine the Total Removal Efficiency (R%) of coffee samples at various exposure times. The analytical wavelength for lead determination was found at 525 nm. The calibration curve has a linearity of 99.57 %.

Fourier Transform Infrared with Attenuated Total Reflectance (FTIR-ATR) Agilent Cary 630 FTIR spectrophotometer was used to determine the functional groups present in the coffee ground samples. The samples were scanned at a wavelength range of 650 to 4000 cm^{-1} at a resolution of 4 cm^{-1} and with sample and background scans of 32.

Scanning Electron Microscope with Energy Dispersive X-ray Analysis (SEM-EDS) JEOL JSM IT500HR/LA was used to determine the surface morphology and the atomic % of elements found in the different forms of coffee grounds. The samples were Platinum coated and processed using a landing voltage of 15.0 kV at 1,000 X magnification under high vacuum mode.

3 Results and discussion

3.1 Use of UV-Vis Spectrophotometry to obtain the concentration of Lead (Pb^{2+}) before and after treatment

Figure 4 is the summary of results from the UV-Vis analysis of Lead (Pb²⁺) water samples considering the contact time and types of coffee samples employed in the study. The Total Removal Efficiency (R%) was computed from the amount of lead in water samples before and after contact. This formula was used :

$$R\% = (C_o - C_e) / C_o \times 100 \quad (1)$$

Where: R% is the total removal efficiency
 Co is the initial Lead (Pb²⁺) concentration
 Ce is the Lead (Pb²⁺) concentration at Equilibrium

The total removal efficiency (R%) was computed from an initial lead (Pb²⁺) concentration of 197 ppm and an equilibrium concentration of 88 ppm and 89 ppm for both crushed and carbonized coffee ground samples at 1-hour exposure time. These were the parameters with the best adsorption capacity.

Considering the exposure time of commercial activated carbon and coffee ground samples with lead (Pb²⁺), it can be seen in Figure 4 that the raw coffee ground has the optimum removal efficiency at 3 hours of contact time, which also means that it is a better adsorbent than the commercial activated carbon. As the coffee grounds become smaller, the surface area exposed to lead (Pb²⁺) becomes bigger thus crushing to produce a uniform size of 850 μm resulting in a better lead (Pb²⁺) removal efficiency. It can be seen that the optimum removal efficiency occurred at 1 hour contact time, which means that it has better adsorption capacity in a short period of time when compared to the raw coffee ground. This is also observed with the carbonized sample at 212 μm where 1 hour contact time resulted in a similar result to that of the crushed sample. For the chemically treated sample, the optimum removal efficiency was seen at 2 hours of contact time. For 1

hour and 3 hours contact time, the chemically treated sample was not that efficient in removing lead from the solution. This might be due to the soaking of the coffee grounds with 0.1 M HCl. The H⁺ might have competed with the Pb²⁺ on the coffee ground surface. Gupta *et al.* mentioned in their review that desorption occurs at a low pH where the H⁺ ions replace the metal ions on the surface of the adsorbent [14].

The results also imply that the most practical parameter is 1 hour contact time for both crushed and carbonized coffee ground samples. The shorter the time, the more energy and resources are conserved in removing Pb²⁺ in water. In general, the chemically activated coffee ground has a poor adsorption capacity. The HCl activating agent might not be suitable so there is a need to explore other modes of activation for the Arabica coffee ground variety. At 1 hour contact time, the crushed and carbonized coffee gave the best result in terms of Total Removal Efficiency (R%) at around 55%, which is also seen to be higher than that of the commercial activated carbon with Total Removal Efficiency (R%) of 28%.

The raw coffee ground has also a high Total Removal Efficiency (R%) at 58%. This means that when using raw coffee ground, the contact time between lead (Pb²⁺) and water sample should be longer, but the 3 hours of contact time might not be practical in some other applications. It is recommended to explore crushing and carbonization as the Pb²⁺ removal efficiency was observed to be maximum at these parameters. When compared to commercially available activated carbon, the coffee ground samples have the potential to remove Pb²⁺ in water. In general, it can be gleaned from Figure 4 that the spent coffee ground is a promising low-cost and widely available material that can be able to remove pollutants such as lead (Pb²⁺) in water.

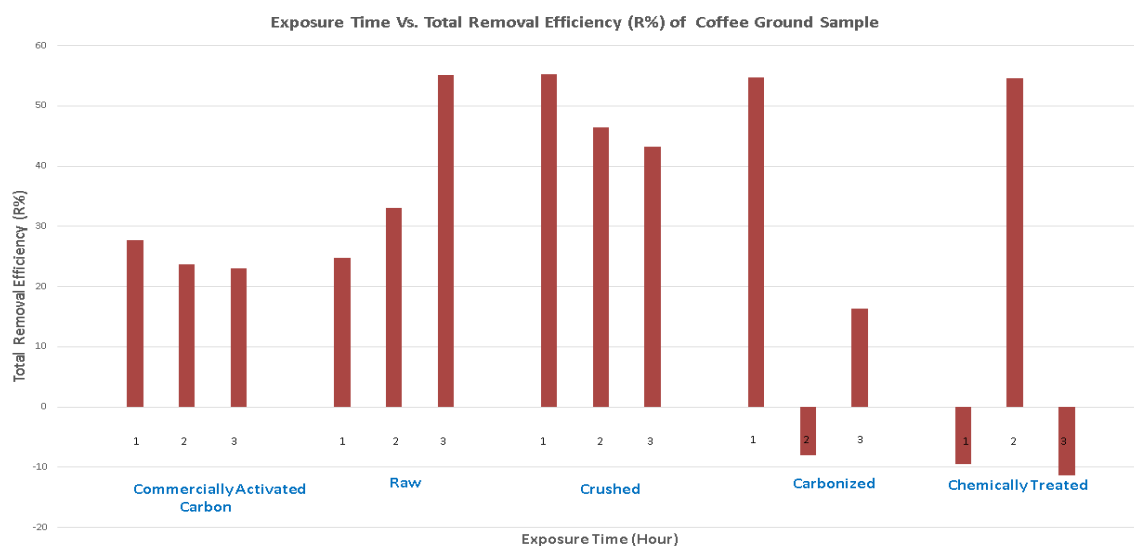


Figure 4. Total Removal Efficiency (R%) of commercial activated carbon and coffee samples at various contact times.

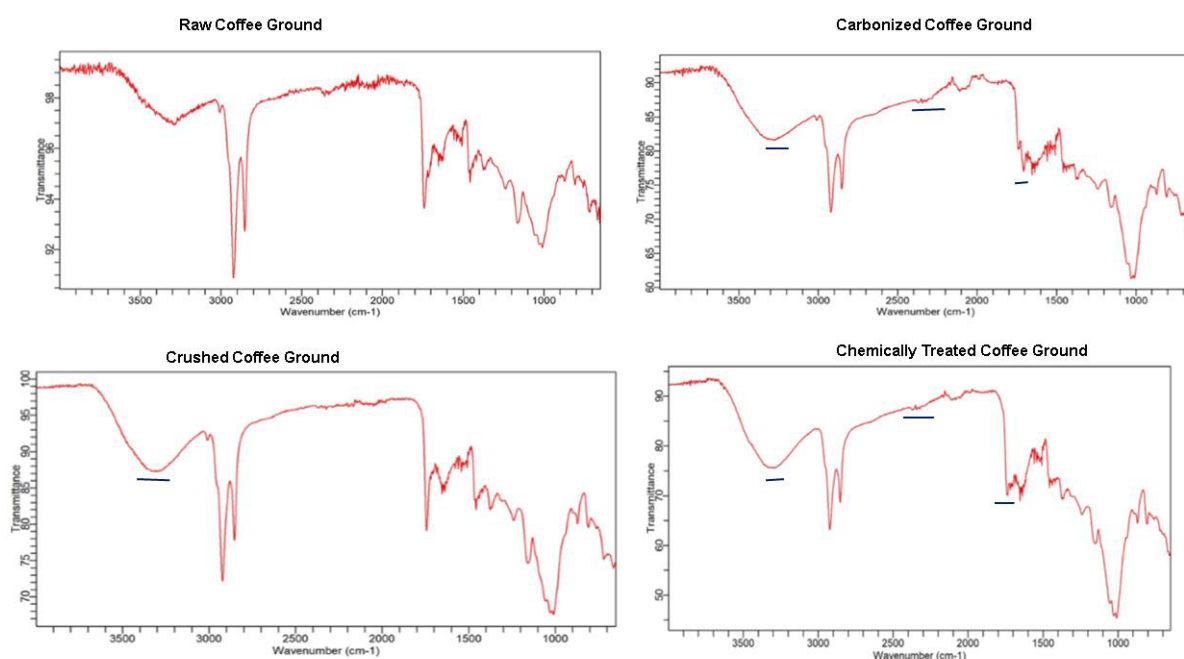


Figure 5. FTIR spectra of raw coffee ground, crushed coffee ground with broad and prominent O-H stretching, carbonized coffee ground and chemically treated coffee ground samples which both exhibit a broad and prominent O-H stretching, presence of charged amines, and shorter C=O peaks.

3.2 FTIR analysis

The FTIR spectra of the coffee samples are characteristics of a very good adsorbent with the following functional groups present: -OH stretching of alcohol at around $3,400\text{ cm}^{-1}$, charged amines ($\text{C}=\text{NH}^+$) at around $2,400\text{ cm}^{-1}$, C=O stretching at around $1,740\text{ cm}^{-1}$, and -COOH stretching at around $1,450\text{ cm}^{-1}$. The FTIR peaks were also identified by Mariana, et al. where coffee grounds used as bio sorbents can perform well in the adsorption process [15].

The FTIR spectra of the different coffee ground samples are shown in Figure 5. Comparing the O-H stretching due to the inter- and intra-molecular hydrogen bonding of phenolic compounds, such as alcohol, and carboxylic acid at around $3,200\text{ to }3400\text{ cm}^{-1}$, the samples exhibited a broad and prominent peak except for the raw coffee ground sample. This may explain why there is a need for more exposure time for the raw coffee ground sample to reach an optimum removal efficiency as previously discussed. The appearance of a peak from $2,200\text{--}2,400\text{ cm}^{-1}$ for charged amines ($\text{C}=\text{NH}^+$) in the carbonized and chemically treated samples are seen in the spectra. The absence of charged amines in the raw and crushed samples and its presence in the carbonized and chemically treated samples might have caused the faster adsorption of Pb^{2+} on the coffee ground surface as evidenced by the optimum removal efficiency at 1 hour and 2 hours of contact time. On the other hand, the carboxyl linkage, C=O derived from xanthine derivatives, such as caffeine at $1,700\text{--}1750\text{ cm}^{-1}$ became smaller and shorter for the carbonized and chemically treated samples. The better adsorption capacity of the coffee grounds was due to the presence of

O-H bonds and charged amines that allowed forces of attraction between the coffee ground surface and lead (Pb^{2+}).

3.3 SEM-EDS analysis

Table 1 presents the Atomic % of the elements present in the coffee ground samples. For the chemically treated sample, the presence of Chlorine came from the soaking of the sample to 0.1 M HCl as an attempt to chemically activate the coffee ground. The good performance of the crushed sample in terms of Total Removal Efficiency (R%) at a shorter contact time may be due to the presence of more carbon atoms, $77.67 \pm 0.61\%$ among the prepared samples. According to Zhou and Wang, the high efficiency of bio-based material for metal ion adsorption is due to its high carbon and low ash content [16]. The processing parameters for carbonization and chemical treatment of the coffee grounds might be further investigated and improved to optimize their adsorption capacity. There is a possibility that the temperature used burned more of the carbon in the coffee ground sample.

Table 1. Atomic percentage (%) of elements present in the coffee ground samples and their corresponding uncertainties.

Element	Sample			
	Raw	Crushed	Carbonized	Chemically treated
C	66.13 ± 0.59	77.67 ± 0.61	69.45 ± 0.64	67.56 ± 0.54
O	33.87 ± 0.87	22.33 ± 0.78	30.55 ± 0.92	32.20 ± 0.76
Cl				0.24 ± 0.03

Figure 6 presents the SEM micrographs of the coffee ground samples. It can be seen that the raw sample has lesser pores or openings on the surface. This may explain the longer exposure time it needs to adsorb the Pb^{2+} on its surface. For the crushed sample, there is the presence of open pores and deeper crevices that looks like cages. This may explain the faster adsorption of Pb^{2+} on the coffee ground surface. For the carbonized and chemically treated samples, it can be seen that there is the presence of smaller surfaces with open pores and smaller cages. The open pores and cages increased the surface area of the coffee grounds that were able to trap and adsorb more lead (Pb^{2+}) from the aqueous solution.

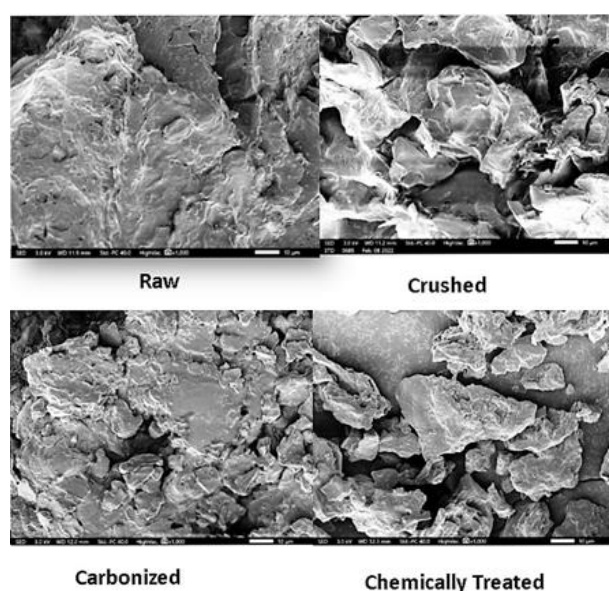


Figure 6. SEM micrographs of coffee ground samples at 1000 X.

4 Conclusion

In this study, it can be implied that low-cost and abundant bio-materials can exceed the adsorption performance of commercially available activated carbon. Spent Arabica coffee grounds have a strong potential in removing metals such as lead (Pb^{2+}) in water when processing parameters are optimized. Raw coffee samples can be able to adsorb lead (Pb^{2+}) in water but there is a need for a longer contact time for it to be more efficient. Decreasing the particle size by crushing increases the surface area for lead (Pb^{2+}) adsorption and opens deeper crevices and cage-like structures for further interaction between the functional groups on the coffee ground surface. Thus, more lead (Pb^{2+}) is adsorbed at a shorter contact time. Carbonization and chemical treatment may even be better in removing metals such as lead (Pb^{2+}) in water if processing parameters such as carbonization temperature and activating reagents are further investigated. Despite the low Total Removal Efficiency (R%) in some samples, it can be seen that spent Arabica coffee grounds can be better than that of the commercial activated carbon. The Arabica coffee ground's Total Removal Efficiency (R%) on lead (Pb^{2+})

can be attributed to the presence of an increased surface area and the presence of functional groups such as $-OH$, $C=NH^+$, $C=O$, and $-COOH$ which are characteristics of good adsorbent. Moreover, the crushing and carbonization of a spent coffee ground sample can be explored in further studies for its capacity to adsorb pollutants present in water.

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