Estimated of Pomegranate Peel Waste for Biosorption of Cu (II) & Pb(II) Ions From Aqueous Solutions

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ABSTRACT
This study intends to explore the waste natural materials' adsorption capability. The use of pomegranate peels was investigated to see the chances of eradicating Pb(II) and Cu(II) ions from the aqueous solutions. Adsorption capability was evaluated using batch adsorption experiments, which also evaluated the impact of solution pH and initial metal concentration. The ideal biosorption conditions included a pH of 6.0, a dose of 0.1 g of biomass, and an equilibrium duration of 90 minutes. The adsorption data fit in a way that was comparable to the isotherm models by Freundlich and Langmuir. Pomegranate peel (PGP) was tested for its affinity and adsorption capability. Based on the values of the separation factor (RL) and Freundlich constant (n), it seems that the metal ions were taken up onto biosorbents in a preferred manner. According to this study's conclusions, the equilibrium data suit the Freundlich and Langmuir isotherms rather nicely. According to correlation coefficient data, the maximal sorption capacity of the produced pomegranate peel is 5000 mg/g. The Fourier Transform Infrared Spectrometer (FTIR), Energy Dispersive X-ray Spectrometer (EDX), and Scanning Electron Microscope (SEM) were utilised in the characterisation examinations. As a result, distinct aggregates formed on the surface of the biosorbent. In the characterisation experiments, an energy-dispersive X-ray spectrometer (EDX) and a scanning electron microscope (SEM) were employed. Different aggregates developed on the biosorbent surface as a result of contact with metal ions. On the surface of the biosorbent, distinct aggregates formed as a result of interaction with metal ions. Either via complexation or electrostatic attraction, the metal ions attached themselves to the biosorbents' active sites.

1. Introduction

Nowadays, a sizable portion of the world's organic resource production is wasted and not recycled (Billa, Angwafo, & Ngome, 2019). Water poisoning by metal ions has garnered international attention recently because of its extreme toxicity and hazardous potential for both people and the surroundings (Mousavi et al., 2019). A major issue is the heavy metals since they may be harmful and carcinogenic even in small amounts, especially lead and cadmium. Their non-biodegradable nature and high solubility allow them to readily circulate and bioaccumulate from sources, such as industry, agriculture, and the military into aquatic ecosystems including blood, water, and the food chain (Mousavi et al., 2019). The remediation techniques used to remove or immobilise metal from water include membrane filtration, electrochemical treatment, chemical precipitation, ion exchange, and electrodialysis. Shakoor et al. (2020) also found that biosorption is an economical and feasible way to eliminate heavy metals from water. Many people consume pomegranate fruits both raw or processed, such as juice or jam. Hence, the peel of the pomegranate is a byproduct of the pomegranate juice and it is reasonably priced. The peel of the pomegranate contains lower amounts of e
llagic acid (EA), gallagic acid, EA-glycosides, and punicalagin and its isomers, which are all known ellagannins (ETs) (El-Ashtoukhy, Amin, & Abdelwahab, 2008). The components of pomegranate peel include polyphenols, ellagic tannins, and gallic and ellagic acids. According to Adetokun, Uba, and Garba (2019), several heavy metals such as Fe and Cu are important for sustaining healthy metabolic processes in living beings, whereas others—like As and Cd—are unnecessary and have no biological importance. Human exposure to cadmium has been shown to have carcinogenic effects as well as many harmful consequences on the kidney, skeletal system, and respiratory system (Cadmiuma, 2018). Studies on workers exposed to chromium compounds in the workplace have revealed lung cancer as well as genotoxic consequences such as sister chromatid exchange and chromosomal abnormality (Adetokun et al., 2019). Lead is a poison that damages several bodily systems and bioaccumulates tannis and gallic and ellagic acids. According to Adetokun, Uba, and

Garba (2019), certain heavy metals—like Cu and Fe—are important for preserving healthy metabolic processes in living organisms, whereas others—like As and Cd—are unnecessary and have no biological importance. Human exposure to cadmium has been linked to cancer and has several harmful consequences on the kidney, skeletal system, and respiratory systems (Cadmiuma, 2018). Studies on workers exposed to chromium compounds in the workplace have revealed lung cancer as well as genotoxic consequences such sister chromatid exchange and chromosomal abnormality (Adetokun et al., 2019). Lead is a poison that damages several bodily systems and bioaccumulates. Lead may cause permanent brain damage even at low concentrations, and children are particularly vulnerable to its neurotoxic effects (Lead, 2018).

In this study, the use of pomegranate peels as a cost-effective biosorbent was examined to see its potential in removing metal ions from the aqueous solution. The initial meta and solution pH were the subjects of the adsorption studies. The equilibrium findings were obtained by utilising the Freundlich and Langmuir isotherm models, and SEM, EDX, and FTIR examinations were utilised to determine the adsorption mechanisms. Adsorption tests were conducted with care to preserve the solution's pH and starting metal content.

2. Materials and Methods

2.1. Preparing the Biosorbents

Pomegranate peel (PGP) was gathered from Dhi Qar, a Nasiriyah grocery. After repeatedly washing the materials with distilled water, they were left to dry overnight at 70˚C in the oven. A laboratory mill was used to grind the dry materials, and a standard sieve of the American Society for Testing and Materials (ASTM) was used to filter them through a 150–250 µm size fraction.

2.2. Preparation of Solutions

The metal solution was diluted to the appropriate ratios to create the solutions employed in the tests. Metal stock solutions of Pb (II) and Cu (II) with a concentration of 1000 mg/L were prepared by dissolving Pb (NO3)2 and Cu (NO3)2−3H2O salts in 0.1 mol/L KNO3. In this study, 0.1 mol/L KNO3 was used as the electrolyte to control the electrical conductivity of metal ions and also to diminish the stock solutions to the necessary amounts. To determine the quantity of lead present in wastewater, an atomic absorption spectrophotometer was employed.

2.3. Characterization Studies

Employing the method from Brunauer-Emmett-Teller (BET) facilitates the total pore distribution surface area of pomegranate peel. Electron Diffraction X-ray Spectroscopy and an Ultra High-Resolution Scanning Electron Microscope (FESEM) were used to analyse the materials' structure. The samples were made by utilising a carbon tap to distribute a tiny amount of adsorbents on a metallic sample container that resembled a cylinder. Afterwards, a thin layer of gold was applied to the preparations using a Bio-Ras Sputter coater (Rave Scientific, Somerset, New Jersey). When the electron beams incidentally crossed the sample surface, signals were recorded. The image in FESEM was achieved by using secondary electrons (the ejected electron from the sample surface) to obtain fine surface topographical features, known as back-scattered electrons, which gave contrast based on atomic number. Using an EDX Oxford-affixed HITACHI SU8020 FESEM, the samples were coated and analysed. To discover the functional groups on the adsorbent surface, the FTIR was used. Meanwhile, a Thermo Scientific NICOLET 6700FT-IR Spectrometer was employed to examine the FTIR spectra. Using KBr, the samples that were in powder form were detected. The range of the observed spectra was 4000–282 cm^{-1}.

2. 4. Batch Adsorption Studies

In a conical flask, 0.1g of biosorbent and 100 mL metal ion liquid were mixed to conduct adsorption experiments. At 200 rpm, the mixture was shaken for an hour. The optimal pH range for a solution was 2.0–8.0. Either HCl or

NaOH was used to change the solution's pH. Between 10 to 80 mg/L, the impact of starting metal concentration was investigated. Meanwhile, the concentration of metal ions in the supernatant was determined by employing an Atomic Absorption Spectrometer (AAS). The employment of Equation 1 determines the quantity of metal ions taken up by the biosorbent.

$$\mathbf{q} = \frac{(C0 - Ce)\,V}{W} \text{ .... Equation (1)}$$

q is the quantity of adsorbed metal ions, *Co* is the initial concentration of metal ions, *Ce* is the equilibrium of metal ion concentration, and *V* is the volume of metal ion solution. For the adsorption test, triplicate experiments were conducted.

3. Results and Discussion

3.1 Adsorption Studies

3.1.1 pH Effects

The adsorption process is significantly influenced by the pH of metal aqueous solutions. It assesses both the metal speciation and the charge type of the adsorbent surface. In Figure 3.1, the adsorption capacity of PGP is shown to contradict the initial pH. The pH value between 2-4 was selected to demonstrate that adsorption is the sole mechanism that removes metal, as at pH values more than 6, Cu(II) ions may be precipitated out as copper hydroxide compounds such as Cu(OH)+, Cu(OH)2, Cu2(OH)2 2+, and Cu(OH)3. Remarkably, PGP's adsorption capabilities tend to rise as pH levels rise. Adsorption capacities (qe) rise sharply when pH rises in the pH range of 2 to 6, then gradually between 6 and 8. The lower adsorption capacity at low pH levels may result from hydrogen and metal ions competing for the same adsorption locations.

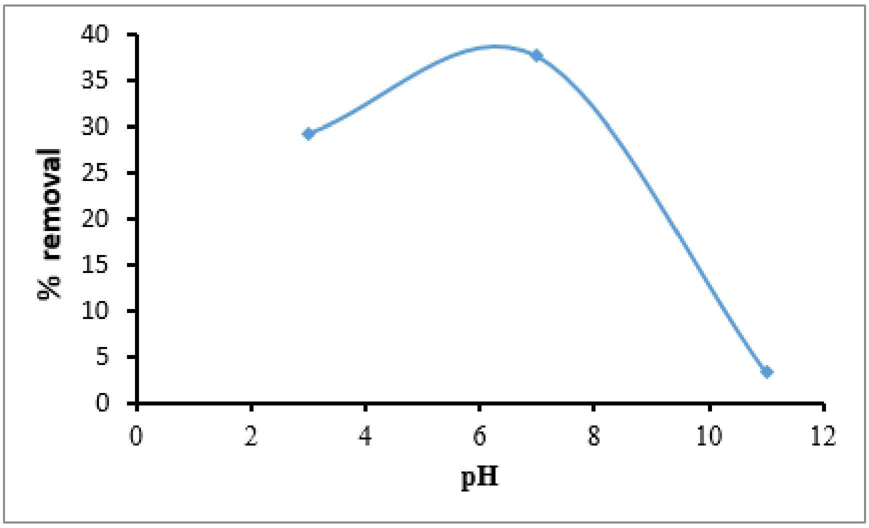

Figure 4. 1 Impact of the pH initial solution on the adsorption of PGP adsorption
(Test condition: 100 mg/L)

3.1.2 Impact of the Initial Metal Concentration

Figure 3 illustrates how starting concentration affects Cu(II) & Pb(II) ion adsorption onto biosorbents. 2. When initial metal concentration increased, so did the quantity of metal ions adsorbed by pomegranate peel (PGP). Cu(II) and Pb(II) adsorbed onto PGP, for instance, rose from 98.3 to 97.5 mg/g and 99.8 mg/g to 99.7 mg/g. The high probability of metal ions interacting with the biosorbent surface and the quick rate of metal ions diffusion onto the biosorbent surface are the two main reasons for a significant amount of metal ions taken in with a high initial metal concentration (Wang et al., 2013). The ratio of metal ions to productive sites is low at low starting metal concentrations. In contrast, the ratio of metal ions to active sites is low at low initial metal concentrations. On the other hand, with large starting metal concentrations, this ratio is comparatively high. Stated differently, there were much more metal ions than there were active sites available for adsorption (Putra, W. P. et al., 2014).

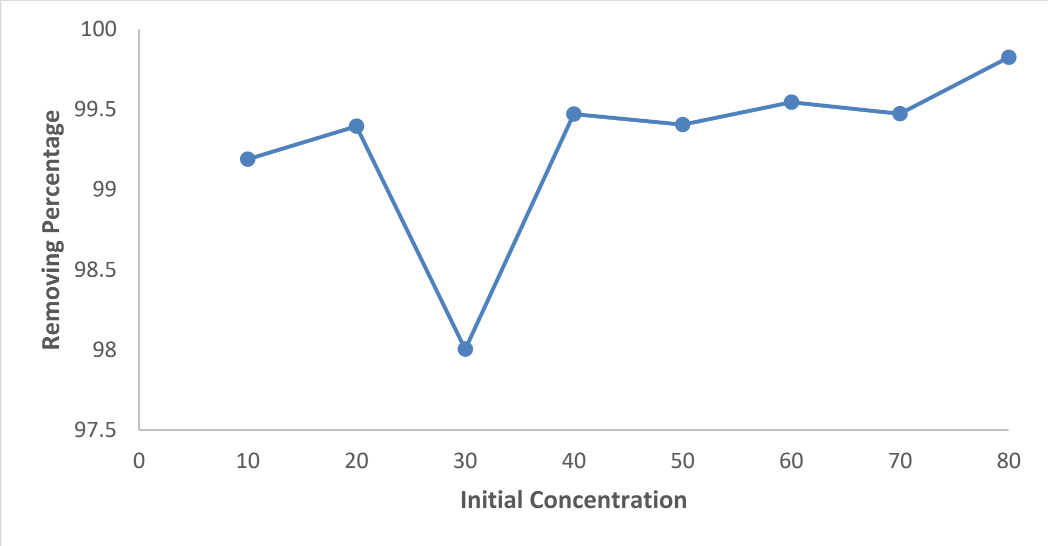

Figure 3.2. Effect of Initial Metal Concentration on PGP adsorption

3.1.3. Isotherm Models

It is believed that adsorption processes occur on heterogeneous surfaces, and the isotherm, an empirical equation, links the adsorption capacity with the concentration of (PGP) at equilibrium. To get fit to (PGP) adsorption, these two adsorption isotherm models were used, and the outcome is shown in Figure 3.3. Figures 3.3a and b show the plot for the Freundlich and Langmuir adsorption isotherms (PGP) uptake data, respectively. The separation factor (RL), a crucial Langmuir parameter, ranged in average value from 0.0002 to 0.043. This indicated that the (PGP) system had good adsorption. The multilayer adsorption and physical process are beneficial, as evidenced by the value of (1.78). The finding is supported by Li and Gondal (2014). Li and Gondal (2014) observed that the Freundlich model suited greater than the Langmuir model using identical experimental methodologies. They suggest this is due to the monolayer coverage adsorption process of (PGP) molecules on the adsorbents not occurring. These authors claimed that the Freundlich equation accurately predicted an increase in the (PGP) concentration on the adsorbent providing there was an associated increase in the (PGP) concentration in the liquid Values of the Freundlich exponent larger than one was recorded. This indicates ideal adsorption circumstances. This implies ideal adsorption circumstances. The results showed how well the equilibrium data suited the Freundlich and Langmuir isotherms based on the experiment. The prepared pomegranate peel has a maximum sorption capacity of 5000 mg/g.

The process of PGP adsorption was adequately characterized by both isotherm models, as indicated by the correlation coefficient () values (Table 3.1). As suggested by Bhatnagar and Anastopoulos (2017), and Sadaf et al. (2015), the correlation coefficient values imply that the PGP is chemically adsorbed at specific, fixed and well-defined sites. In addition, adsorption also occurs during heterogeneous surface interactions.

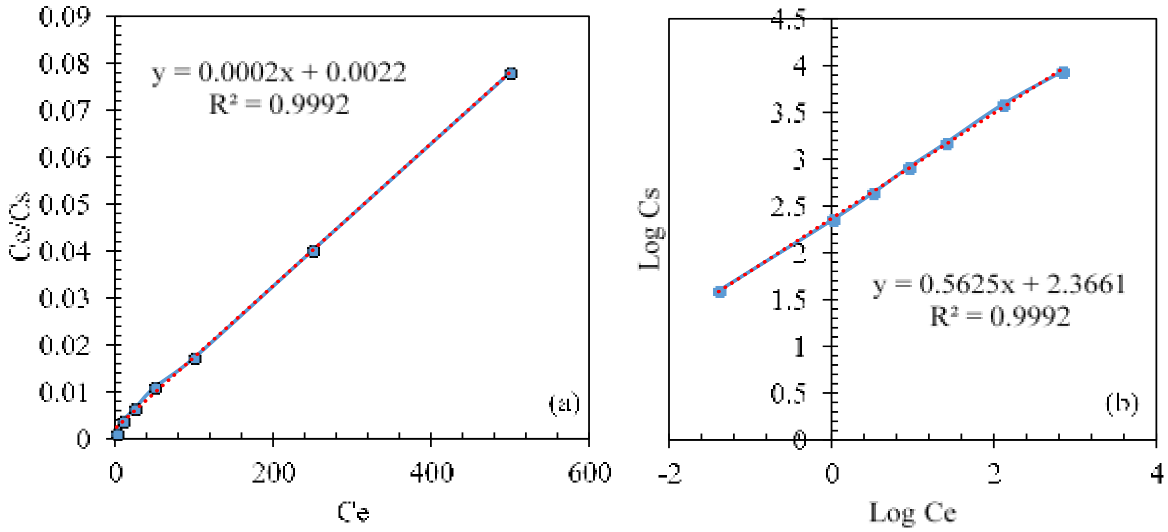

Figure 3.3 (a) Langmuir isotherm and (b) Freundlich isotherm

Table 3 .1. *Parameters of the Langmuir and Freundlich adsorption models.*

Adsorbent	Langmuir model			Freundlich model		
	Q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	n	R^2
PGP	5000	11	0.9992	10.66	1.78	0.9992

4.Conclusion

Based on the result, it is concluded that pomegranate peel may be used as an inexpensive substitute for biosorbent to eliminate heavy metals in aqueous solutions such as the Pb (II) and Cu(II) ions. Metal ion binding is facilitated by the biosorbents' functional groups. However, characterisation and adsorption studies are only a preliminary assessment of this kind of use in water treatment.

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