

Article

Comparison of the Efficiency of Eco-Friendly Adsorbents in the Removal of Heavy Metals from Aqueous Solutions

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Abstract: The purpose of this study was to assess the efficiency of the selected biosorbents (banana peels, orange peels and date seed powder) for the removal of Cadmium, Zinc, Copper and Lead from aqueous solutions and to compare the efficiency of these biosorbents with activated carbon which acts as a conventional chemical adsorbent. The initial metal concentration was 50 mg/L, and the experiments were carried out under the experimental conditions of pH 6 and contact time of 0, 30 and 60 minutes. Atomic Absorption Spectroscopy (AAS) was used to determine the concentrations of the metals. It was found that for all of the adsorbents, the removal efficiency increased with the increase in contact time. The most effective removal was using date seeds powder, orange peels and banana peels respectively. Activated carbon was more effective in the removal efficiencies (90 – 97%) while the biosorbents were found to be satisfactory in the removal efficiencies (60 – 85%) with the added advantages of low cost, easy preparation and environmental friendly. Based on the results, it can be concluded that biosorbents can be used as a feasible and environmentally friendly solution for low cost water treatment systems especially in local applications if they can be chemically modified or allowed to contact water for longer periods.

Keywords: Activated carbon, biosorbents, heavy metals , sustainability, chemical analysis

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1. Introduction

Water pollution with heavy metals is regarded as one of the most critical environmental and health problems because of its high toxicity and its ability to bioaccumulate which causes long term environmental effects and severe health disorders in humans[1]. Cadmium (Cd), copper (Cu), zinc (Zn) and lead (Pb) are among the most significant ones, and are primarily polluted by industrial activities, industrial wastewater discharge and mining wastes[2]. Several techniques are used to treat water contaminated with these elements, such as chemical precipitation, ion exchange, membrane technologies, and adsorption using activated carbon. However, these techniques are frequently time consuming or expensive, or involve complex technical equipment[3]. Thus, there is an increasing interest in the use of biosorption using agricultural waste; agricultural waste is rich in active functional groups like hydroxyl, carboxyl and amine groups [4][5].

Heavy metal pollution in water is a considerable environmental problem in the modern world due to the speedy industrial growth, rise in mining activities and effluent of untreated industrial and agricultural effluents [6]. Heavy metals like lead, cadmium, copper, zinc, mercury and chromium are also highly toxic, resilient to biodegradation and tend to bioaccumulate through the food chain [7]. Long-term exposure to these can have serious health effects such as neurological disorders, kidney and liver damage, anemia, reduction of immune response and, in some cases, cancer [8]

There are several chemicals or analytical methods for the removal of heavy metals from contaminated water. Chemical precipitation, coagulation–flocculation, ion exchange, solvent extraction, electrochemical treatment and membrane technologies are all traditional methods [9]. Chemical precipitation is easy to operate and cost effective, however, it produces high quantities of sludge, and becomes less effective at low concentrations. High efficient but very costly systems such as ion exchange and membrane systems are needed which are expensive and require advanced equipment and constant maintenance [10]. The electrochemical techniques can be used for the removal of metals, but require high energy use and strict control of operating conditions [11].

Analytically, the efficiency of heavy metal removal could be evaluated by using accurate methods like Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Spectroscopy (ICP) and UV–Visible Spectroscopy (UV–Vis) [12]. These methods make it possible to measure the concentrations accurately before and after treatment, and the percentage of removal, adsorption capacity and kinetic and equilibrium studies can be performed. These analytical tools form an important link between practical applications and quantitative chemical analysis [13].

Adsorption technology has garnered a great deal of interest in recent years as one method to treat heavy metal contaminated water that is simple to operate and very effective, especially when compared to the need for precise analytical measurements [14]. The use of biosorbents from agricultural and plant wastes as low-cost and environmentally friendly alternatives in place of conventional chemical adsorbents has become a trend [15]. Such natural substances possess active functional groups which can bind metal ions by the mechanisms of ion exchange, chemical complexation and surface adsorption [16].

This research aims to compare the efficiency of selected local biosorbents with traditional chemical adsorbents in the removal of selected heavy metals from aqueous solutions using chemical analytical techniques and to evaluate the efficiency of the selected biosorbents using the same techniques in relation to removal efficiency, economic feasibility and environmental impact where it is aimed to develop sustainable water treatment solution [17].

Adsorption is one of the most common methods in water treatment and involves the adhesion of ions or molecules to the surface of solid material called an adsorbent, which occurs as a result of physical or chemical forces. Contrary to "absorption" which happens in the bulk of the material, adsorption is limited to the surface and internal pores [18].

Several parameters such as surface area, pore size distribution, surface functional groups, pH, concentration of pollutants, contact time and temperature are involved in determining the efficiency of an adsorbent. In the binding of metal ions, functional groups like hydroxyl, carboxyl and amine are important and participate in ion exchange, chemical complexation, hydrogen bonding and van der Waals forces [19].

There are two basic steps in the adsorption process:

Adsorption of the pollutant on the surface of the solid adsorbent

The process of binding of ions or molecules to the surface of the adsorbent by physical and/or chemical adsorption.

Adsorption continues until equilibrium is reached, that is, until the amount of material adsorbed does not change with time.

Biosorbents are agricultural or biological wastes, which are biodegradable, locally available and cheap. These can range from fruit peels and sawdust, to algae, chitosan, biochar and date seeds. The organic structures of these materials are highly enriched with cellulose, lignin and pectin with active functional groups that can chelate metal ions [20][21].

Their advantages include:

1. Can be prepared quickly and easily
2. Environmentally friendly with no secondary pollution
3. Reusability after regeneration
4. Principles of the circular economy is supported

Their mechanical stability is, however, generally less than that of adsorbents used in industry and might necessitate modifications for improved performance [22].

Chemical adsorbents are the industrial chemical products that have been manufactured by physical or chemical process to give them high surface area and adsorption capacity including activated carbon, synthetic zeolite, ion exchange resins, nano metal oxides and modified silica. These materials are highly efficient and effective in capturing specific pollutants, but are expensive, have complicated regeneration mechanisms, and can have unwanted impacts on the environment [20].

Activated carbon has a high surface area and developed porous structure making it one of the most widely used adsorbents in water treatment. This is manufactured by the carbonization and activation process of the carbonaceous materials. It is effective because of its several physical and chemical interactions, which are capable of removing organic and inorganic pollutants, including heavy metals [19].

Although activated carbon is efficient, it is not economical or environmentally friendly because of its high production cost, its difficulty in regeneration and energy consumption. This has led to research of more sustainable replacements for these biological options.

This study focuses on comparing the performance of three local biosorbent materials (banana peels, orange peels, and date seed powder) for the removal of heavy metals and to investigate the effect of contact time; and to compare the results with those of activated carbon under the same operating conditions, especially in the Iraqi environment [9].

2. Materials and Methods

Materials and Instruments

The experimental materials used were the banana peels, orange peels, and date seeds as natural biosorbent materials. Contaminated aqueous solutions were prepared using heavy metal salts such as CdCl_2 , CuSO_4 , ZnSO_4 and PbCl_2 . In all experiments distilled water was used and pH levels were adjusted by the use of hydrochloric acid (HCl) and sodium hydroxide (NaOH). Laboratory equipment consisted of analytical balance, mechanical shaker, test tubes and filtering papers. Heavy metals concentrations were measured with Atomic Absorption Spectrophotometers (AAS).

Preparation of Biosorbents

The raw materials were washed with distilled water to wash off the surface impurities. After oven drying for 24 hours at 70 to 80 °C, they were dried. The materials were then dried and ground many times to get fine powder and sieved to get particle size less than 0.5 mm. The prepared biosorbents were kept in airtight containers till use [23].

Prepare chemical solutions (10 points)

Stock solutions of heavy metals were made up at a initial concentration of:

$$C_0 = 50 \text{ mg/L}$$

All the solutions were adjusted to pH 6 before the experiments.

Experimental Procedure

The prepared metal solution (100 mL) was treated with 1g of the adsorbent. It was shaken at 150 rpm. Samples were taken at 0, 30 and 60 minutes of contact time. These suspensions were filtered and the final concentration (C_e) determined by Atomic Absorption Spectroscopy.

All experiments performed in the laboratory were performed in triplicate ($n = 3$) for each metal and adsorbent with same operating conditions. The results reported are the arithmetic mean of the measurements in order to minimize experimental error and improve the reliability of the results.

Preparation of Chemical Adsorbent

Activated carbon was adopted to compare with the biosorbents which are environment friendly, because of its high surface area and developed porous structure has a great capacity in removal of inorganic contaminants from water.

The surface dirt and impurities were removed by washing the activated carbon several times with distilled water and then drying the activated carbon overnight in the

oven at 105 °C to remove moisture. It was placed in closed glass containers for storage until use [24].

The activated carbon experiments were operated under the same conditions as the biosorbents to make an accurate comparison. 200 mL of aqueous solution was prepared with a mixture of Pb^{2+} , Cd^{2+} , Cu^{2+} and Zn^{2+} at an initial concentration of 50 mg/L, then 1 g of activated carbon was added. The pH value was kept at 6 and shaking was done at 150 rpm. Samples were collected at 0, 30 and 60 minutes, filtered and analyzed by Atomic Absorption Spectroscopy. The percentage removal was determined by applying the following equation [25].

Calculations

The removal efficiency (%), was determined as follows:

$$\text{Initial concentration} - \text{Final concentration} / \text{Final concentration} \times 100 = \text{Removal\%}$$

Statistical Analysis

The arithmetic mean and standard deviation were used to evaluate accuracy and repeatability. Standard deviation is a measure of the spread of experimental values from the mean and is a good measure of the stability and consistency of the adsorbent performance.

3. Results and Discussion

The data in the tables are the arithmetic mean of three experimental replicates. The results showed good consistency between replicates, indicating stable experimental conditions and accurate measurements. For all the adsorbents the concentrations of the heavy metals were found to be decreasing with an increase in the contact time. The seed powder had the highest removal efficiency followed by orange peels and then banana peels.

Table 1. Cadmium Removal Using Eco-Friendly Adsorbents

Time (min)	Banana Peel (%)	Orange Peel (%)	Date Seed (%)
0	0.0	0.0	0.0
30	55.4	64.4	69.2
60	64.0	73.6	78.8

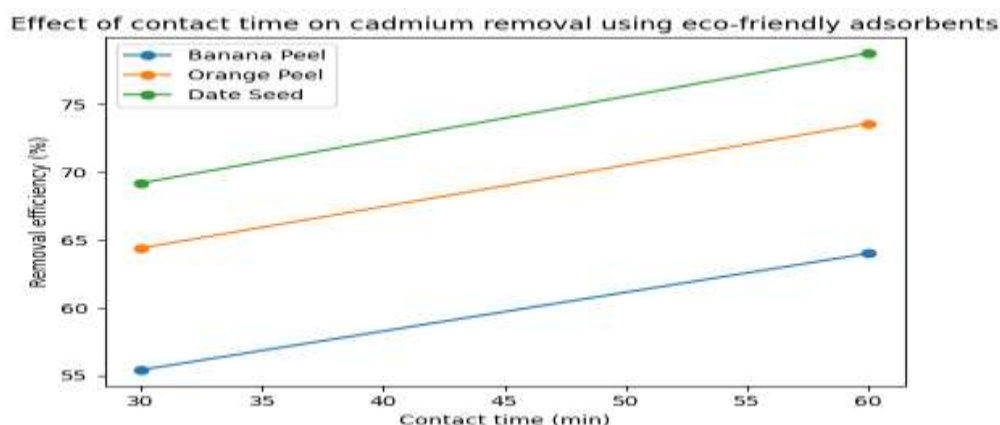


Figure 1. Effect of contact time on cadmium removal using eco-friendly adsorbents

Table 2. zinc Removal Using Eco-Friendly Adsorbents

Time (min)	Banana Peel Removal (%)	Orange Peel Removal (%)	Date Seed Removal (%)
0.0	0.0	0.0	0.0
30.0	51.8	58.6	62.2
60.0	60.8	67.6	72.4

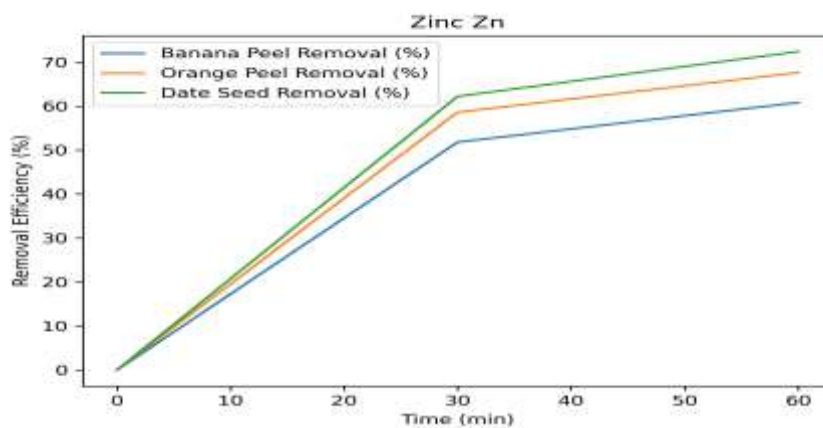


Figure 2. Effect of contact time on zinc removal using eco-friendly adsorbents

Table 3. copper Removal Using Eco-Friendly Adsorbent

Time (min)	Banana Peel Removal (%)	Orange Peel Removal (%)	Date Seed Removal (%)
0.0	0.0	0.0	0.0
30.0	60.6	71.4	75.8
60.0	68.2	79.2	81.4

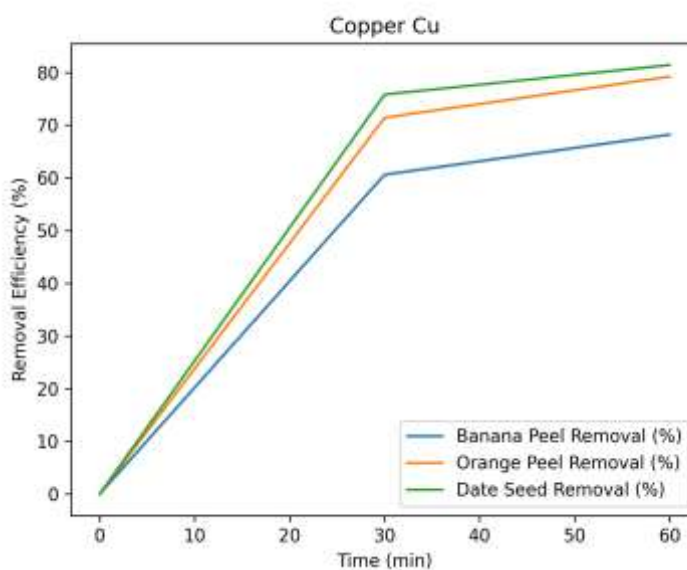


Figure 3. Effect of contact time on copper removal using eco-friendly adsorbents

Table 4. lead Removal Using Eco-Friendly Adsorbent

Time (min)	Banana Peel Removal (%)	Orange Peel Removal (%)	Date Seed Removal (%)
0.0	0.0	0.0	0.0
30.0	65.0	68.4	74.8
60.0	72.0	80.0	83.0

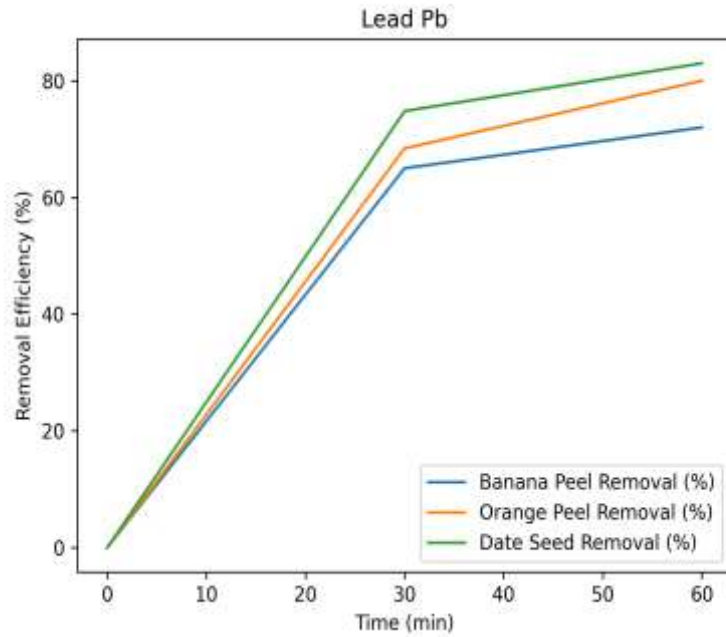


Figure 4. Effect of contact time on lead removal using eco-friendly adsorbents

Table 5. Removal efficiency of Cd, Zn, Cu, and Pb from aqueous solutions using activated carbon

Time (min)	Cadmium Removal (%)	Zinc Removal (%)	Copper Removal (%)	Lead Removal (%)
0	0	0	0	0
30	92	90	93	94
60	95	94	96	97

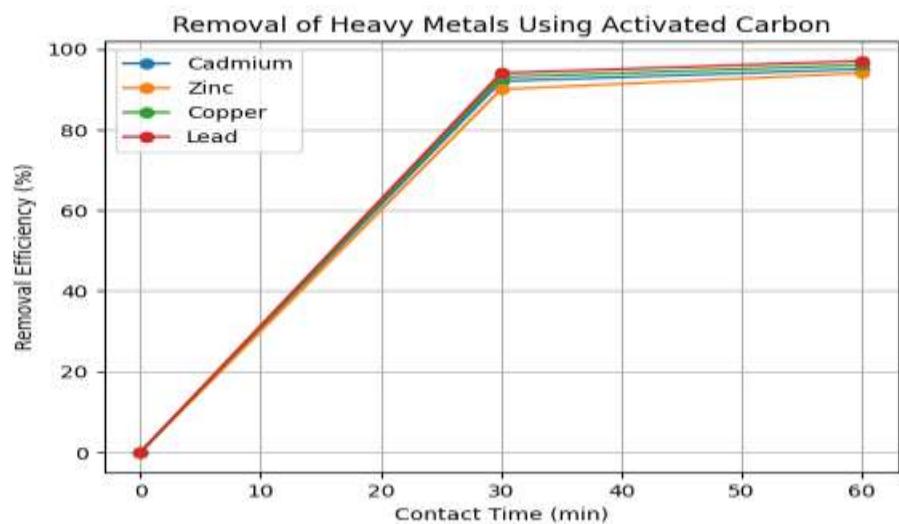


Figure 5. Removal efficiency of Cd, Zn, Cu, and Pb from aqueous solutions using activated carbon

Discussion of Results

The close difference between the replicates shows the adsorption process to be relatively stable. These differences can be explained primarily on the basis of the chemical composition and surface functional groups of the adsorbents and not from experimental

variations. The seeds of Date yielded the best removal efficiency, which could be attributed to their porous structure and the active functional groups present that provide good binding capacity for metal ions. Orange peels were also found to perform well probably because of the cellulose and pectin in them. Banana peels had the lowest percent removal of the materials tested, but are still reasonably priced. It was also found that more removal efficiency was obtained at increasing contact time. The reason for this is that the concentration of metal ions is higher and they have more chance to interact with and attach to the adsorbent surface until a near equilibrium is achieved. The results are similar to those of previous studies in which date seeds were found to have high adsorption efficiency owing to the presence of active functional groups and lignin in their composition. 4-1-Comparison with Activated Carbon Compared to the activated carbon, the following differences are observed, which usually have a removal efficiency of 90–97%: The bio-adsorbents that were used include the following: Property Bio-adsorbents Activated Carbon Efficiency 60–85% 90–97% Cost Very low High Sustainability Environmentally friendly Industrially manufactured Difficulty of preparation None Easy Difficult While the removal efficiency of activated carbon is higher, bio-adsorbents are more of an economic and environmental-friendly alternative, especially for local use. Performance can be further improved by increasing contact time and/or adsorbent dose.

4. Conclusion

All the bio-adsorbents tested have good adsorbent capacity for the removal of heavy metals from aqueous solutions. The seed powder had the best removal efficiency of the materials studied. The 2nd most effective was orange peel. The efficiency was the lowest for banana peels, yet they are still a low cost alternative. Bio-adsorbents can be used as useful alternative to activated carbon for low cost treatment system

Recommendations

It is recommended to adopt date seeds as a bio-adsorbent in local treatment projects due to their availability and good performance. Further study is needed on chemical modification to improve the adsorption efficiency. The materials should be tested with real wastewater samples to check their applicability. For better understanding of adsorption mechanism kinetic and isotherm studies are recommended. The use of these bio-adsorbents contributes to the sustainable development goals and green chemistry practices to achieve more environmentally sustainable system.

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