



Adsorption of *Pb (II)* and *Cd (II)* Ions from Their Aqueous Solutions unto Carbonised Orange Peels

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Abstract: The presence of heavy metals in the environment and especially water is known to both cause severe harm to marine organisms, and also to terrestrial plants and animals including human beings. In an attempt to minimize environmental pollution caused by agricultural wastes and maximize agricultural by-products, the adsorption of Pb^{2+} and Cd^{2+} using carbonized orange peel as adsorbent was studied using batch adsorption method. The initial physico-chemical properties of the prepared adsorbent were 6.14, 10%, 12%, 2.0%, and 0.5mg/L for pH, attrition, ash content, moisture content and bulk density respectively. Atomic adsorption spectrophotometer was used to monitor the Pb^{2+} and Cd^{2+} concentrations of the simulated test solutions. The optimum values obtained were 97.34% at concentration of 40mg/L for Pb^{2+} and 93.45% at concentration of 20mg/L for Cd^{2+} , 99.46% at a pH of 7 for Pb^{2+} and 97.48% at a pH of 6 for Cd^{2+} , 96.76% at a contact time of 80 mins for Pb^{2+} and 50.05% at a contact time of 100 mins for Cd^{2+} and 97.36% at an adsorbent dosage of 1.2g for Pb^{2+} and 91.55% at an adsorbent dosage of 1.2g for Cd^{2+} . The results indicated that carbonized orange peel is a good adsorbent for the removal Pb^{2+} and Cd^{2+} from simulated waste water.

Keywords: Adsorption, Heavy Metals, Orange Peels, Carbonized

1. Introduction

Heavy metal contamination has in recent years become of great ecological and global public health concern. There has been a dramatic rise in human exposure as a result of exponential increase in the use of heavy metals in several industrial, agricultural, domestic and technological applications [1]. Some reported sources of heavy metals in the environment include geogenic, pharmaceutical industrial, agricultural, domestic effluents and atmospheric sources [2]. Areas that harbour mining, foundries and smelters, and other metal based industrial operations are notably point sources of environmental pollution [1-3]. Heavy metals are a major concern because they are extremely toxic with a tendency to bio accumulate in foods even at low concentrations, which translates to a great danger to living organisms [4].

The removal of Cd and Pb has become very imperative because low concentrations are toxic, coupled with their

damaging effects on the environment [5]. Lead affects all steps in the process of haemoglobin synthesis and porphyrin metabolism by forming complexes with oxo-groups in enzymes. Toxic levels of Pb in man have been associated with seizures and mental obstruction [6]. Cd poisoning affects many organs and, in some cases causes deaths and so making it of concern. Long-term exposure to Cd in air, water, soil, and food leads to cancer and organ system toxicity. This may include effects on respiratory, skeletal, urinary, reproductive, cardiovascular, central and peripheral nervous systems [7].

Researchers have employed several techniques for the removal of heavy metals from the environment. Adsorption is however a favoured technique compared to others like ion exchange, liquid extraction, precipitation, membrane extraction and electrolysis. This is so because most of these methods have a high cost and, in some cases, show inefficiency with long periods required to achieve optimal removal of the metals. In light of this, adsorption using

adsorbent from cheap materials has been the most favoured method employed [8].

Lately, biodegradable materials such as agricultural wastes are in trend for the removal of heavy metals from waste water. This is so because they are almost ubiquitous, non-hazardous and available at low cost. Modern agricultural industries produce tons by-products and wastes every year that have useful potential in adsorption [1]. Agricultural waste materials are also eco-friendly due to their unique chemical composition and renewability. The current study explores the use of orange peels for the removal of Pb and Cd ions from aqueous solutions. From literature, orange peels are recognized as an agro-industrial residue with adsorptive properties and have been used in adsorption process [9-11]. Orange peels are normally treated as waste especially in industries where oranges are a raw material. Studies have indicated that orange peels contain many functional groups such as hydroxyl and carbonyl groups. These functional group makes it a potential adsorbent for removing heavy metal ions [12].

2. Methodology

2.1. Sample Collection and Preparation of Adsorbent

Orange peels were collected from a fruit market in Makurdi, Benue State, Nigeria. They were properly washed with distilled water to remove sand particles and dirt, before being sundried and oven dried at 100°C for 24 hrs in each case. A porcelain mortar and pestle were used to pulverize the samples after which it was sieved through a 2 mm mesh sieve. The powdered orange peel was carbonized at 350°C in a muffle furnace for 15 mins before being washed with distilled water and later with 0.1 M HCl at pH of 6.5. The resulting adsorbent was then dried and kept for further analysis.

2.2. Preparation of Simulated Wastewater

Aqueous solutions of Cd and Pb ions was prepared from Analar grade $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ and PbNO_3 respectively. The stock solutions of the salts were prepared before serial dilution was done to obtain concentrations of 5ppm, 10 ppm, 25 ppm, 50 ppm, 75 ppm, 100 ppm and 150 ppm.

2.3. Measurement of Physical Properties of Adsorbent

2.3.1. Bulk Density Determination

A 10 mL measuring cylinder dried and pre-weighed (w_1) was packed with 3 g of the adsorbent, leveled and weighed (w_2). The volume (v) of the packed material was then measured and bulk density calculated in g/mL as follows:

$$\text{Bulk density} = \frac{w_2 - w_1}{v}$$

2.3.2. Ash Content

An empty clean crucible was preheated in a furnace at 500°C for an hour and left to cool in a desiccator and weighed (w_1). Exactly 2 g of the adsorbent was weighed into the cooled crucible (w_2) before it was placed in a muffle

furnace and the temperature raised to 500°C for 1 hour. It was removed and allowed to cool in a desiccator before weighing (w_3). The ash content was expressed as follows:

$$\text{Ash content (\%)} = \frac{w_3 - w_1}{w_2 - w_1} \times 100$$

Where: W_1 = Weight of empty crucible (g); W_2 = Weight of crucible + sample (g); W_3 = weight after ashing (g).

2.3.3. Moisture Content

A 2g sample of the adsorbent was transferred into an empty crucible and the total weight noted as m_2 . After being heated at 100°C in an oven, it was cooled in a desiccator and weighed m_1 . The sample was repeatedly heated until a constant weight was obtained. The moisture content was calculated as follows:

$$\text{Moisture content} = \frac{m_2 - m_1}{m_2} \times 100$$

Where: M_2 = Weight of crucible + sample (g) and M_1 = Constant weight obtained (g).

2.3.4. Attrition

One gram of the adsorbent was steeped in 50 mL distilled water and stirred for 2 hrs using a magnetic stirrer. The solution was filtered and the residue was dried off and the weight noted. The attrition was calculated based on the weight loss by as follows:

$$\text{Attrition (\%)} = \frac{\text{Initialweight (g)} - \text{Finalweight (g)}}{\text{Initialweight (g)}} \times 100$$

2.4. Batch Adsorption Studies

Batch adsorption studies was performed at different concentrations, adsorption dosage, contact time and varying pH to obtain the rate of adsorption and equilibrium data.

2.4.1. Contact Time

The effect of contact time was studied at time intervals of 20, 40, 60, 80, 100, and 120 mins at room temperature using 0.2g of the adsorbent in 20 mL of 15 mg/L of lead (II) nitrate solution in a container placed on a mechanical shaker at 130 rotation per minutes (rpm). The same process was carried out for cadmium chloride solution using 20 mL of 40 mg/L. They were later filtered and analyzed using atomic absorption spectrophotometer.

2.4.2. Adsorbent Dosage

Sample of carbonized orange peel of masses 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 were added to 20 mL of 15 mg/L of lead (II) nitrate solution. The same process was carried out for hydrated cadmium chloride solution using 20 mL of 40 mg/L. They were stirred by a mechanical shaker for 1hr then filtered and analyzed using atomic absorption spectrophotometer.

2.4.3. pH Variation

Adsorption was done at various pH; 2, 4, 6, 7, 9, and 12. The acidic and alkaline pH of the medium was adjusted using hydrochloric acid and sodium hydroxide solution. It was placed in a mechanical shaker for 1 hour and then filtered

and the filtrate was taken for analysis using atomic absorption spectrophotometer.

2.4.4. Effect of Concentration

Exactly 0.2g of the adsorbent was contacted with 20 mL of lead (II) nitrate solution of concentration 2.5, 5, 7.5, 10, 12.5, 15 mg/L and with 20 mL of hydrated cadmium chloride solution of concentration 20, 25, 30, 35, 40 mg/L respectively. They were placed in a mechanical shaker for 1 hour before they were filtered. The filtrates were taken for analysis using atomic absorption spectrophotometer.

2.5. Data Analysis

The adsorptive capacity per unit adsorbent (mg/g) by the ions was calculated as follows:

$$Q_e = \frac{C_i - C_e}{M} \times V$$

While percentage removal of heavy metal ions from initial solution concentration was calculated as follows:

$$\text{Percentage adsorption} = \frac{C_i - C_e}{C_i} \times 100$$

Where: Q_e = amount of metal removed per unit of the adsorbent (mg/g); V = volume of metal solution (litres); C_i = initial concentration of metal ions in the solution (mg/L); C_e = final concentration of metal ions in the solution; M = dry weight of adsorbent.

2.6. Kinetics Modeling

Equilibrium data for the adsorption of Pb (II) and Cd (II) ions from aqueous solution were fitted into the linearized form of the Langmuir model at a constant temperature of 293K. Langmuir adsorption is used to quantify and contrast the adsorptive capacity of adsorbent. It accounts for the surface coverage by balancing the relative rates of adsorption and desorption.

3. Results and Discussion

3.1. Physico - Chemical Characterization

Table 1 shows the physico-chemical properties of the adsorbent. The pH of the carbonized orange peel was moderately acidic with a value of 6.14. This value is good as a pH range of 5–6 is acceptable. The bulk density of the carbonized orange peel was 0.5mg/L while the attrition was 10% suggesting a low wearing property [13]. The moisture content of 2% implied that it was the sample possesses a large surface area for adsorption since it was reasonably dry. The ash content was also determined to be 12%. The physico-chemical characteristics obtained are acceptable for use as a good adsorbent for the removal of heavy metals.

Table 1. Physico-chemical characteristics of carbonized orange peel.

Parameters	Value
pH	6.14
Ash content	12%
Moisture content	2.0%
Bulk density	0.5 g/L
Attrition	10%

3.2. Effect of Adsorbent Dosage

Figure 1 shows the variation of adsorption efficiency with varying adsorbent dosage. Adsorbent dosage study determines the capacity of adsorbent for a given initial concentration of metal ion solution. The effect of adsorbent dosage on the removal of Pb (II) ions and Cd (II) ions from aqueous solutions at $C_0 = 20\text{mg/L}$ and 40mg/L was studied. The removal of Pb (II) ions and Cd (II) ions increased steadily with increase in adsorbent dosage from 0.2g to 1.2g with percentage removal efficiency from 91.52% to 97.36% for Pb (II) ions and 18.64% to 91.55% for Cd (II) ions respectively. Mass balance relationship may be responsible for this phenomenon. Increase in adsorption with increase in adsorbent dosage is attributed to the availability of larger surface area and more adsorption sites [14].

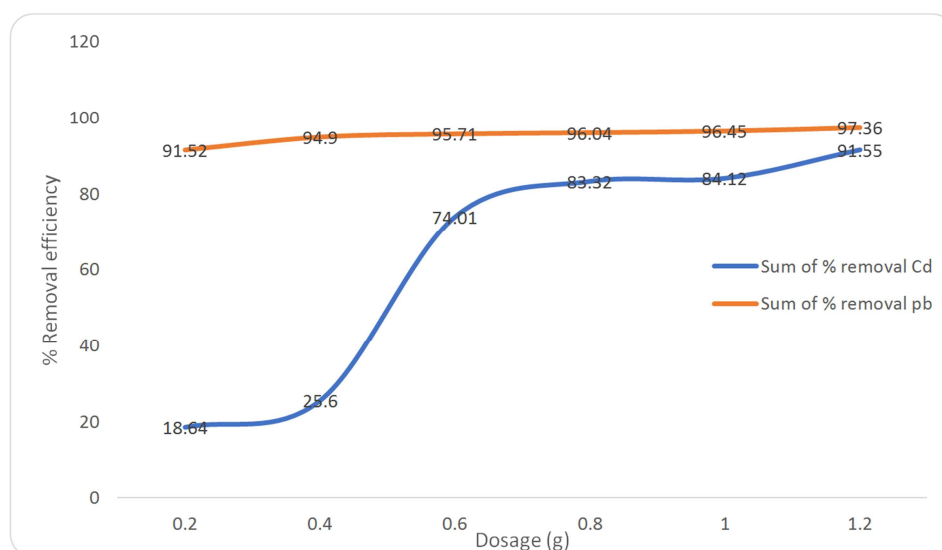


Figure 1. Effect of adsorbent dosage.

3.3. Effect of Concentration

The results of the effect of concentration of Pb (II) ions and Cd (II) ions as represented in Figure 2 shows that the percentage removal efficiency for both metal ions increases steadily from 95.69% to 97.34% for Pb (II) ions and 77.67% to 93.45% for Cd (II) ions with an increase in initial Pb (II) ion concentration from 15mg/L to 40 mg/L

and initial Cd (II) ion concentration from 5 mg/L to 20 mg/L. The removal of Cd (II) ion takes a relatively shorter time to reach equilibrium. This is due to the fact that with increase in concentration of both metal ions, there will be increase for active adsorption sites and the prices will increase. Hence, adsorption increases with increasing concentration [15].

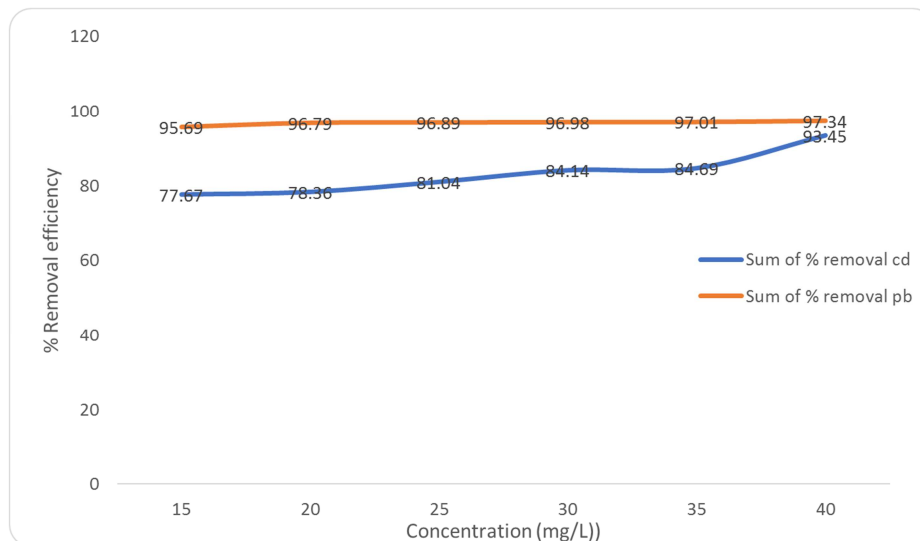


Figure 2. Effect of concentration.

3.4. Effect of Contact Time

Figure 3 gives the variation between absorption efficiency in terms of percentage removal of both Pb (II) ion and Cd (II) ions and time. It is observed that at contact time of 80 mins the percentage removal of Pb (II) ion is highest (96.76%) while the percentage removal of Cd (II) ion is highest at a contact time of 100 mins (50.05%). The adsorption of Pb (II) ions increased with increasing contact time from 89.67% to 96.76% at contact period of 20–80mins. Similarly, the adsorption of Cd (II) ion increased with increasing contact time from 19.86%–50.05% at contact period of 20–100 mins. Thus, the rate of adsorption

of both metal ions increased with increase in time. However, the rate of adsorption was found to be fairly constant and decreased after 80mins (between 20–80 mins.) for Pb (II) ions and 100 mins (between 20–100 mins.) for Cd (II) ions which is suggestive that the adsorption process was faster within the first 80 mins for Pb (II) ions and faster within the first 100 mins for Cd (II) ions as the largest amount of both metal ions were attached to the adsorbent within those periods. Higher adsorption efficiency of carbonized orange peels is attributed to available adsorption sites including the functional groups on the adsorbent surface [16].

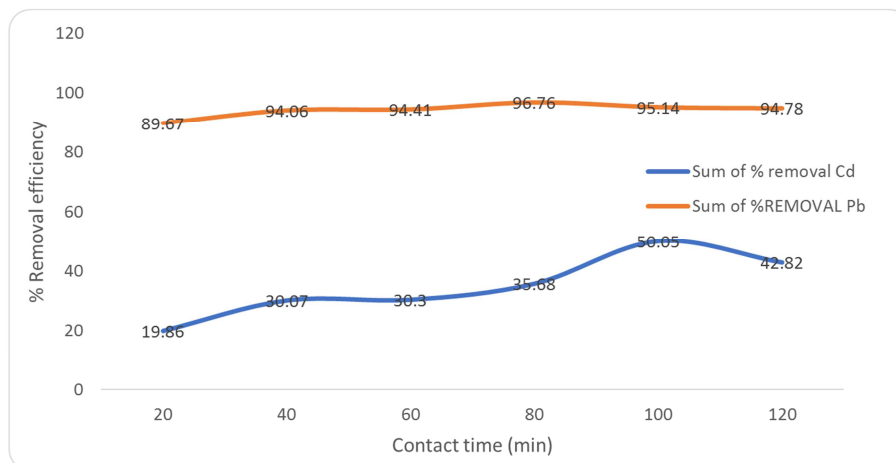


Figure 3. Effect of contact time.

3.5. Effect of pH

The effects of pH on adsorption of Pb (II) and Cd (II) ions for the batch equilibrium studies was done at pH values in the range of 3–8 for both metal ions and is given in Figure 4. The pH of the solution has been identified as an important variable governing metal adsorption. The fact that (H^+) are strong competing ions in the solution letting pH influence the chemical speciation of the functional group onto the

adsorbent surface is partly responsible for this. According to Akinhami *et al.* [17] the uptake of Cd(II) by orange peel depends on the solution pH, which they observed to be increasing. It can be further observed that the removal of Pb (II) ions and Cd (II) ions from the solutions increased with increasing pH. A maximum value was reached at equilibrium pH of 7 for Pb (II) ions and 6 for Cd (II) ions [18].

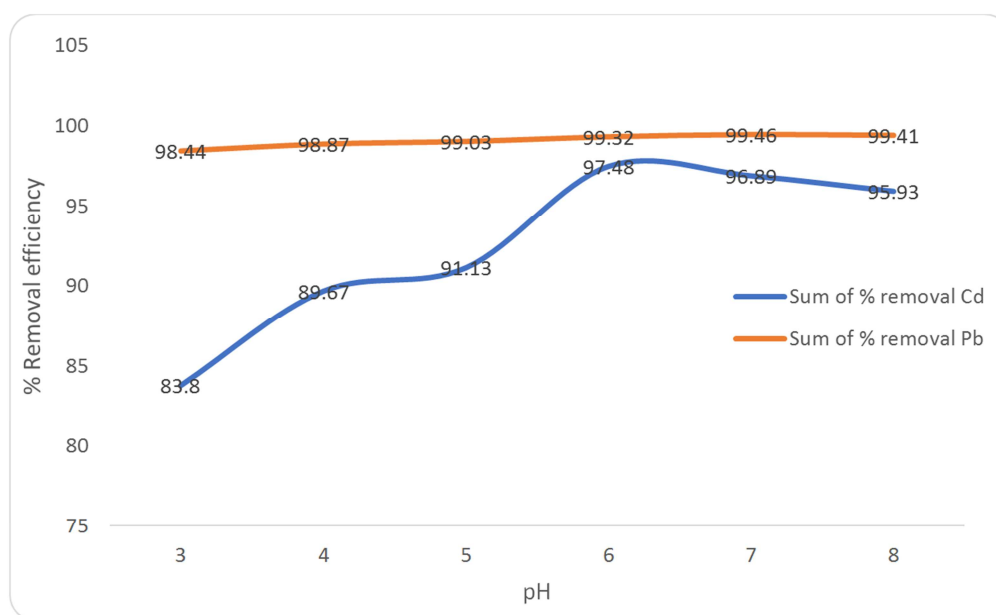


Figure 4. Effect of pH.

3.6. Adsorption Isotherm

The Langmuir isotherm constants for Pb (II) ions and Cd (II) ions are shown in Figures 5 and 6 respectively. The regression correlation coefficient (R^2) of Langmuir isotherm of Cd (II) ion is, $R^2=0.7196$ while the observed regression

correlation coefficient (R^2) of Langmuir isotherm for Pb (II) ion is $R^2=0.7389$. Consequently, the Langmuir isotherm of Pb (II) ion is found to be the best fit as compared to the Langmuir isotherm of Cd (II) ions.

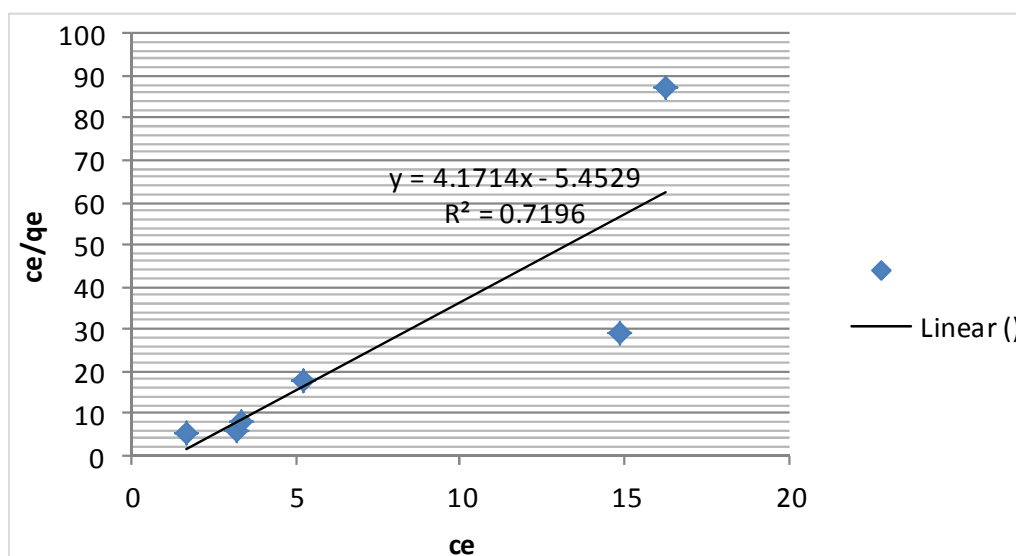


Figure 5. Langmuir isotherm for Cd (II) ions.

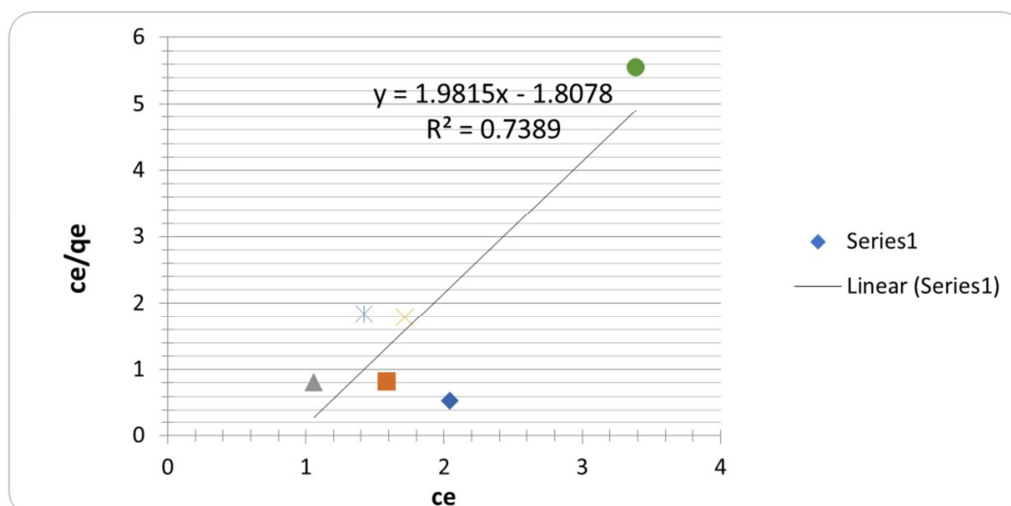


Figure 6. Langmuir isotherm for Pb (II) ions.

4. Conclusion

This study shows that the carbonized orange peel is an effective adsorbent for the removal of Pb (II) and Cd (II) ions from aqueous solutions. From the study, it can be inferred that orange peels, an abundantly available agricultural waste can be used as low-cost adsorbent. The higher adsorption capacity is favored by higher number of active binding sites, improved ion exchange properties and enhancement functional groups after chemical treatment. Overall, Pb (II) ions and Cd (II) ions are effectively adsorbed from simulated waste water by carbonized orange peels.

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