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Bio-adsorbents for the Removal of Heavy Metals from Water

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Abstract

The work represents the bio-adsorption of arsenic(III) from standard solutions and real water samples using a powdered avocado seed as a bio-adsorbent. The adsorbent was synthesized, demineralized, and characterized by X-ray diffraction (XRD), scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS), Fourier transformation infrared spectroscopy (FTIR), and Brunauer-Emmett-Teller (BET) theory. Batch adsorption studies were carried out by using avocado seed, and As$^{III}$ was analyzed by using inductively coupled plasma optical emission spectroscopy (ICPOES) after optimizing the following parameters: pH 6, analyte concentration 2 mg L$^{-1}$, bio-adsorbent dosage 0.8 g, contact time 120 min between analyte and adsorbent, and temperature from 22 to 40°C. The adsorption capacity of 93.75 mg/g was obtained, and the Langmuir isotherm was adopted by the adsorbent due to the chemisorption that occurs on the surface between the functional groups of the bio-adsorbent and As$^{III}$.

Keywords: arsenic(III), bio-adsorption, inductively coupled plasma optical emission spectroscopy
1. Introduction

Arsenic (As) is the 20th most abundant element in the earth’s crust, and its concentration on the soil level is about 5–13 mg/kg [1]. Naturally, arsenic is found in different oxidation states: V (arsenate), III (arsenite), 0 (arsenic), and -III (arsine) [2, 3]. Arsenic (As) is one of the elements that occur naturally and commonly found as an impurity in metal ores, and it is in abundance. It can be found in the soil, water, and living organisms. It is produced commercially for use in wood preservatives, metal alloys, and pesticides.

Both As\(^{III}\) and As\(^{V}\) exist in the pH range of 6–9, and when comparing As\(^{III}\) and As\(^{V}\), it is known that As\(^{III}\) is more toxic than As\(^{V}\) and also in terms of mobility [4]. Depending on the pH, Arsenite (As\(^{III}\)) exists in four forms in aqueous solution, such as H\(_2\)AsO\(_3\), H\(_2\)AsO\(_3\)^{−}, HAsO\(_3^{2−}\), and AsO\(_3^{3−}\). In a reductive environment, below pH 9.1 As(III) exists in the form of inorganic arsenite (H\(_3\)AsO\(_3\)) and is thermodynamically stable [5].

Since arsenic is one the most well-known poisonous elements in the periodic table, it is known to be carcinogenic in many parts of the world [6]. Long-term exposure to arsenic, through water and food, can lead to serious health problems like neurological effects, hypertension and cardiovascular diseases, and skin and lung cancer [7]. The kidney is the major source for regulation of water and electrolytes, waste, and chemical compounds, and arsenic(III) can affect the role of the proximal tubules and glomerulus of the kidney [8].

Arsenic(III) is the one that is known to be toxic [4]. The World Health Organization (WHO) recommended a more rigid limit of 10 μg/L as the maximum acceptable arsenic level [9]. Commercial methods for removing arsenic involve technologies such as precipitation, membranes, and adsorption. But adsorption is the most easy, flexible, inexpensive method to be applied by using mineral oxides [10], polymer resins [11], and activated carbons [12]. According to literature, waste materials such as rice husks, tea, and agricultural waste have been applied as inexpensive adsorbents [13].

It is well known that South Africa is a developing country with limited resources for water purification; therefore, the aim of this work is to develop a cheaper, easy-to-use method of treating water especially in the rural areas where the water treatment stations are not yet established.

The most crucial aim of the work is that the bio-adsorbent must be manufactured from a locally available material that is reusable in order to save the rural area’s people from daily expenses.

2. Materials and experimental method

2.1. Reagents and standards

Potassium carbonate and arsenic standard employed in the synthetic application procedures of this work were of analytical grade and obtained from Sigma-Aldrich (St. Louis, MO, USA). Millipore water (Merck, Darmstadt, Germany) of 18 MΩ cm\(^{-1}\) was used throughout the experiments. Concentrated nitric acid (HNO\(_3\)) (70%) was also purchased from (St. Louis, MO,
USA, www.sigmaaldrich.com). All materials especially plastics and glassware prior to use were cleansed by soaking in dilute HNO$_3$ and rinsed with copious deionized water. The stock standard solutions of As(III) at a concentration of 1000 mgL$^{-1}$ was obtained by dissolving an appropriate amount of arsenic oxide. The working standards were prepared daily by stepwise dilution of stock solution. Avocado fruit waste seeds (AFWS) were locally sourced from fruit and vegetable shop outlet around the city of Johannesburg (Gauteng Province, South Africa).

2.2. Instrumentation

The As quantification was performed using inductively coupled plasma optical emission spectroscopy (ICPOES) (iCAP 6500 Duo, Thermo Fisher Scientific, UK) equipped with a charge injection device (CID) detector. The sample injection application was done through a concentric nebulizer and a cyclonic spray chamber. A Mettler Toledo pH meter model 120 (Greifensee, Switzerland) was employed for all pH measurements. The active carbon material production, i.e., activation, was performed in a tubular furnace (Gallenkamp, Germany). The AFWS and ACM were characterized for porosity, pore structures, surface area, and pore volume using N$_2$ gas adsorption BET (Brunauer, Emmett, and Teller) method for surface area, while the crystallinity of the material was determined by X-ray diffraction (XRD, Rigaku, UHMa IV, Japan). Surface morphology and surface functional groups were determined by scanning electron microscopy (SEM, TECAN VEGA 3 XMU, Czech Republic) coupled with energy dispersive spectroscopy (EDS) (TECAN VEGA 3 XMU, Czech Republic) and Fourier transmission infrared spectroscopy (FTIR, PerkinElmer FTIR, UK), respectively.

2.3. Adsorbent preparation and application

The precursor for the active carbon material was acquired by collecting avocado seeds. The avocado fruit waste seeds (AFWS) were air-dried and thoroughly washed before rinsing with deionized water. The washed seed residues were then oven-dried overnight at 100°C. The seeds were then pulverized by ball milling it with laboratory hammer mill (Janke and Kunkel Micro-hammer Mill, Staufen IM Breisgau, Germany) to obtain fine powder. The bulky powdered material was later fractionated to diverse particle size using laboratory sieves. The resultant particles of different miniature diameters ranging from 38 to 150 μm were obtained in which 75 μm particle size was subsequently employed in production of active carbon material. The powdered form of avocado seed was then stored inside desiccator until application.

The adsorption studies were carried out to evaluate the efficiency of the avocado peel (bio-adsorbent) for the removal of As$^{III}$ from the aqueous solution using the batch adsorption method. The batch adsorption experiments were carried out in 50 mL plastic bottles by shaking a constant mass of a predetermined size of adsorbent with arsenic standard solutions. The pH of the solutions was adjusted accordingly by adding either ammonium hydroxide or acetic acid solution. Each flask was sealed and kept in a state of agitation (200 rpm) using a mechanical laboratory shaker for the material to reach equilibrium. Upon equilibrium, the samples were filtered and analyzed using inductively coupled plasma optical emission spectroscopy (ICPOES). Parameters such as pH, concentration of solution, mass of adsorbent, contact time, and temperature were optimized.
The percentage removal of As(III) in solution was calculated using Eq. (1):

$$R\% = \frac{C_o - C_e}{C_o} \times 100$$  \hspace{1cm} (1)

where $R$ is the percentage (%) removal and $C_o$ and $C_e$ are the initial and equilibrium concentrations of the analyte, respectively.

The amount of metal adsorbed by adsorbent was calculated from the difference of metal quantity added to the biomass and metal content of the supernatant (Eq. (2) [14, 15]):

$$q_e = \frac{(C_o - C_e)}{M} \times V$$  \hspace{1cm} (2)

where $q_e$ is the metal uptake (mg g$^{-1}$), $C_0$ and $C_e$ are the initial and equilibrium metal concentration (mg L$^{-1}$), $V$ is the volume of the solution (mL), and $M$ is the mass of the adsorbent (g).

3. Results and discussion

3.1. Characterization of the raw avocado seed and activated carbon material

The FTIR spectrum is an important technique which provides the surface functional groups that significantly contribute in the enhanced adsorption efficiency of the adsorbent. FTIR was used to determine the surface functional groups of raw avocado fruit waste seed. In Figure 1, the spectrum of the powdered avocado seed is represented, where the band located at 3259 cm$^{-1}$ corresponds to $\nu$(O–H) vibrations in the hydroxyl group, while the strong peaks

![Figure 1. FTIR spectrum of avocado fruit waste seed (AFWS).]
at 2913 and 2848 cm\(^{-1}\) bands correspond to \(\nu(C-H)\) vibration in the alkane/alkyl aliphatic group which could be methylene [16–20]. The presence of alcohols and carbonyl groups was confirmed by the bond vibrations observed at 1633 cm\(^{-1}\). This confirms that avocado seed is composed of carboxylic group which is responsible for adsorption; similar results were reported in the literature [21, 22].

The surface morphology and the chemical composition of raw avocado seed was studied with scanning electron microscope coupled with energy dispersive spectroscopy (SEM-EDS). The image in Figure 2(a) showed that raw avocado seed material had a smooth surface with long ridges and a series of graphitic layers with various pores.

The EDS analyses performed on avocado seed revealed that the surface contained different mineral particles, such as carbon, oxygen, potassium, phosphorus, and chlorine (Figure 2b). The highest content of oxygen may assist in adsorption due to electron lone pairs.

### 3.2. Optimization of adsorption parameters

pH is one of the most important parameters that influence the adsorption of the analyte. In this study, the amount of As\(^{\text{III}}\) adsorbed on avocado seed was the highest at pH 6 and gradually decreased as the pH increased up to 9 (Figure 3a) [7]. However, the highest removal was observed with avocado seed due to the presence of carboxylic group on the surface which increased the affinity toward arsenic to the adsorbent (Figure 1). Oxygen of the carbonyl group easily formed the complex with the arsenic [23]. Arsenic(III) adsorption decreased as the pH goes below 6 due to the increasing ionic strength [24].

The effect of the concentration was carried out by increasing the initial concentration from 5 to 30 mg L\(^{-1}\), and the solutions were adjusted to pH 6 at 25°C. It was observed that the percentage removal increased with the increasing concentration of the analyte; this is due to
the fact that as the concentration increased more ions were available in the solution for adsorption [25]. It was observed from the results in Figure 3b that the highest removal (65%) was reached using 20 mg L\(^{-1}\) and after there was no significant increase in the percentage (%) removal of As\(^{III}\).

The amount of adsorbent is one of the important factors that affects the adsorption capacity. The adsorbent amount of raw avocado seed on the efficiency of adsorption was investigated, and adsorbent amount was varied from 0.025 to 0.8 g. The results observed indicated that the adsorption increased with increasing adsorbent dosage till 0.8 g (Figure 3c). The increase in the percentage removal is due to the availability of active sites for adsorption [26]. It was found that after the dosage of 0.4 g there is no significant change in the percentage removal of arsenic. Then, 0.8 g was used throughout the experiments.

Figure 3. Optimization of (a) pH of the solution, (b) concentration of the analyte, (c) bio-adsorbent dosage, (d) contact time between the bio-adsorbent and the analyte, and (e) temperature of the solution.
The effect of contact time is an important factor in adsorption because it affects the adsorption kinetics of an adsorbent at the given initial concentration of the adsorbate [26]. The batch adsorption experiments were carried out to investigate the effect of agitation time on the adsorption of As(III). Adsorption rate initially increased rapidly, and the highest removal was reached at 120 min (Figure 3d). Further increase in contact time did not show a significant change in the percentage (%) removal of arsenic.

Temperature is one of the parameters that affect the equilibrium and solubility and can also initiate the chemical reaction. This is because temperature can either increase or decrease the activation energy of the analyte. The effect of temperature on the adsorption of arsenic was investigated from room temperature of 40°C. From the results obtained in Figure 3e, the temperature did not have any effects since there is no significant increase or decrease in the percentage (%) removal of arsenic.

Under optimized conditions, 2 mg L\(^{-1}\) As\(^{III}\) standard solution was adsorbed by the avocado peels, and 75% As\(^{III}\) was removed (Figure 4). The adsorption capacity was 93.75 mg/g when Eq. (2) was applied.

3.3. Adsorption kinetics

Adsorption is described by the functions which connect the amount of adsorbate on the adsorbent.

The distribution of metal ions between the liquid phase and the solid phase is described by several isotherm models such as Langmuir and Freundlich [27].

The Langmuir equation can be written in the form of Eq. (3):

\[
\frac{C_e}{q_e} = \frac{1}{q_{max}} C_e + \frac{1}{K_L q_{max}}
\]

where \(C_e\) is the equilibrium concentration (mg/L), \(q_e\) is the amount of arsenic adsorbed onto the solid phase (mg/g), \(b\) is the equilibrium adsorption constant related to the affinity of binding.
sites (L/mg), and $q_{\text{max}}$ is the maximum amount of arsenic per unit weight of adsorbent for complete monolayer coverage.

Freundlich equation is represented as shown in Eq. (4):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$  \hspace{1cm} (4)

where $C_e$ is the equilibrium concentration (mg/L), $q_e$ is the amount of arsenic adsorbed onto the solid phase (mg/g), $K_f$ is an indicator of the adsorption capacity, and $n$ is the heterogeneity factor.

The results in Figure 5(a and b) and Table 1 showed that the correlation coefficient for linear Langmuir model ($R^2$, 0.97) was higher than the Freundlich model ($R^2$, 0.72). The data was best fitted in Langmuir model, and this signified that the adsorbent had high affinity for arsenic(III)
due to the carboxylic groups that are the surface of the avocado seed [28], meaning that the chemisorption took place. To prove that the data belonged to Langmuir isotherm, the separation value, \( R_L \) value from Eq. (5) was calculated. \( R_L \) proves whether the Langmuir adsorption nature is favorable if \( R_L > 0 \), unfavorable if \( R_L > 1 \), and irreversible if \( R_L = 0 \):

\[
R_L = \frac{1}{1 + (1 + K_L \times C_0)}
\]

(5)

where \( C_0 \) is the initial concentration and \( K_L \) is a Langmuir constant obtained from plotting \( 1/q_e \) versus \( 1/C_e \). The results in Table 1 indicated that the equilibrium sorption was favorable for Langmuir isotherm.

3.4. Analytical figures of merit

Analytical figures of merit for the quantitative analysis of arsenic(III) such as limit of detection (LOD), limit of quantification (LOQ), correlation coefficient \( (R^2) \), and the relative standard deviation (RSD) were calculated. In order to determine the LOD, the blank solution was subjected to the optimum experimental conditions, and the signals for ten blank samples were measured \((n = 10)\). The limit of detection (LOD), calculated based on \( 3S/m \) (where \( S \) is the standard deviation of the blank and \( m \) is the slope of the calibration curve) was 0.10 mg L\(^{-1}\). The limit of quantification \( (LOQ = 10S/m) \) was 0.20 mg L\(^{-1}\) for arsenic(III). The linear calibration curve was plotted with a correlation coefficient of 0.98.

The precision (repeatability) of the batch adsorption method was studied by measurements of eight replicates of 2.0 mg L\(^{-1}\) standard solution of As\(^{III}\) as shown in Table 2. The precision, expressed in terms of standard deviation (%RSD), was 2.1.

3.5. Application of the avocado seed adsorbent in real water samples

A water sample from East London municipality was adsorbed by the raw avocado seed under the optimized conditions. It is shown in Figure 6(a) and b that the bio-adsorbent is removed (54 and 55%) from sampling area A and B, respectively. During the adsorption of As\(^{III}\) from environmental water samples, an interference can be experienced from metal ions such as Fe\(^{III}\), Fe\(^{II}\), Zn\(^{II}\), Cd\(^{II}\), Ni\(^{II}\), Mn\(^{II}\), Al\(^{III}\), Pb\(^{II}\), and Cu\(^{II}\) [10].

This indicated that avocado seed has the great potential in removing heavy metals like As\(^{III}\) in environmental water samples without being modified.

<table>
<thead>
<tr>
<th>Adsorption isotherm</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>( k_L )</td>
<td>0.0022 L/mg</td>
</tr>
<tr>
<td></td>
<td>( R_L )</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>( R^2 )</td>
<td>0.97</td>
</tr>
<tr>
<td>Freundlich</td>
<td>( R^2 )</td>
<td>0.72</td>
</tr>
</tbody>
</table>

Table 1. Adsorption isotherms for As\(^{III}\) adsorption by a bio-adsorbent.
Figure 6. The determination of the percentage (%) of As\textsuperscript{III} removed by the bio-adsorbent from (a) Sample A to (b) Sample B using ICPOES.

<table>
<thead>
<tr>
<th>As\textsuperscript{III} standard solution adsorbed by avocado seed</th>
<th>Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before adsorption</td>
<td>2.0 mg L\textsuperscript{-1}</td>
</tr>
<tr>
<td>After adsorption</td>
<td>(0.50; 0.50; 0.50; 0.50; 0.49; 0.49; 0.49; 0.47) mg L\textsuperscript{-1}</td>
</tr>
<tr>
<td>Mean</td>
<td>0.49 mg L\textsuperscript{-1}</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>± 0.010 mg L\textsuperscript{-1}</td>
</tr>
<tr>
<td>Relative standard deviation</td>
<td>2.1%</td>
</tr>
</tbody>
</table>

Table 2. The repeatability of As\textsuperscript{III} concentration during the adsorption by avocado seed obtained from a local shop in Johannesburg.
4. Conclusions

This work focused on removal of arsenic from aqueous solution using a powdered raw avocado seed. Important parameters that affect adsorption were optimized accordingly, pH 6, analyte 2 mg L⁻¹, dosage mass 0.8 g, and contact time 120 min, and temperature was constant from room temperature of 40°C. It was observed that raw avocado fruit seed can remove more than 50% of arsenic(III) from real water sample without any modification. The advantages of this bio-adsorbent is that it requires less preparation time and is readily available. The use of avocado seeds as a bio-adsorbent will also reduce the waste that is normally discarded in the streets, and it does not affect the food security issues since it is not edible. Due to the advantages that it possesses, it is strongly recommended that it should be incorporated in the removal of toxic heavy metals such as As^{III}. The adsorption isotherm data were tested for both Langmuir and Freundlich models. The regression coefficient and $R_L$ values, best fitted Langmuir model ($R^2 = 0.97$), and the adsorption capacity was 93.75 mg/g. The Langmuir model means that chemisorption took place at the monolayer of the bio-adsorbent due to the availability of functional groups such as carboxylic acids that have high affinity for metal ions such as As^{III}.

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