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ABSTRACT: Olive Mill Solid Residue (OMSR) can be utilized as a bio-sorbent in wastewater treatment. Even though several studies on OMSR as a bio-sorbent were carried out, there is still a need to investigate a simple and relatively inexpensive OMSR treatment that increases pollutant removal. In this study; OMSR is used in batch experiments to remove toxic heavy metals from aqueous solutions including Cd^{2+}, Cu^{2+}, and Pb^{2+} ions. The effect of OMSR treatment (untreated; OMSR-U, treated with n-hexane; OMSR-H, and treated with water; OMSR-W) was investigated by chemical oxygen demand and cation exchange capacity. It was confirmed by both tests that OMSR-W was the best treatment. The same result was re-confirmed by batch uptake experiments of the heavy metal ions. Using OMSR-W as a bio-sorbent; the effect of several parameters such as pH, contact time, bio-sorbent concentration, metal ions concentration, and the presence of other metal species were studied to figure their influence on the metal ions uptake. The optimum conditions for single metal systems were found to occur at pH 5.5, an initial metal concentration of 50 mg/L, a shaking time of 60 minutes, a bio-sorbent concentration of 20 g/L. In binary metal ions solutions; Cd^{2+} uptake was increased in presence of Cu^{2+} or Pb^{2+}. However, the uptake of Cu^{2+} and Pb^{2+} was decreased in presence of other metals. The equilibrium sorption data for single metal systems were described by the Langmuir isotherm model. The highest value of maximum uptake was found for Pb^{2+} (4.587 mg/g) followed by Cd^{2+} (4.525 mg/g) and Cu^{2+} (4.367 mg/g). These results show that OMSR-W, which has a very low economical value, could be used for the treatment of wastewater contaminated with heavy metals.

KEYWORDS: Heavy metals, isotherm, wastewater treatment, adsorption capacity

Introduction

In terms of water availability, Jordan is rated among the poorest countries in the world.[1] Nowadays, its renewable water supply capacity covers half of its population's water demand.[2] A potential alternative resource for Jordan is the reuse of wastewater.[3] Wastewater reuse has the lowest marginal cost among the non-conventional water resources.[4] Although the possibility of wastewater reuse is huge; thus far, wastewater reclamation and reuse in Jordan are not high. The technologies applied in wastewater reuse include heavy metals removal; which consider as the most common chemical pollutants in wastewater.[1,5]

Heavy metals create crucial pollution issues. Their contamination and related risks are matters of increasing concern regarding the environment and human health.[6-10] For instance, the accumulation of heavy metals indicated cancerous breast biopsies.[11] Heavy metals are either being transferred to the environment naturally or by means of humans' activities. Table 1 shows a comparison between the worldwide emissions generated by the studied heavy metals from natural sources and the worldwide emissions generated by the studied heavy metals from synthetic sources.[12] This comparison shows that the emissions of heavy metals from the human activities exceed the emissions of heavy metals from natural sources. The U.S. Environmental Protection Agency (EPA)[13] revealed the

Maximum Contaminant Level (MCL) for the drinking water for these contaminants (Table 1).

To eliminate heavy metals from water, many treatment methods have been applied including; ion exchange,[14-18] adsorption,[19-22] coagulation,[23] electro-coagulation,[24] and biological processes.[25,26] The most efficient is the adsorption method using; sorbents that require little processing, abundant in nature or by-products or waste materials from industry.[27-33] For instance; palm coir and apricot shells waste were tested as bio-sorbent to remove heavy metals from wastewater.[34,35] Chicken bones were also used as a bio-sorbent for the removal of Cu (II) ions from aqueous solutions.[36]

Olive oil production is considered one of the major agricultural production in Jordan with an approximate annual production of 21.5 thousand tons per year.[37,38] The production process of olive oil generates 3 products: olive oil, solid waste, and aqueous waste.[39,40] According to Qdais and Alshraideh[41]; unless the environmental criteria given a very high priority, the co-combustion of Olive Mill Solid Residue (OMSR) remains the most favorable management option. However, OMSR could be converted to a commercially available by-product.[42,43]

Several attempts were carried out to utilize the OMSR as a bio-sorbent in wastewater treatment. The untreated OMSR cannot be used to remove all metal from aqueous solutions by

Table 1. Global emission and permissible levels of Cd^{2+}, Cu^{2+}, and Pb^{2+}.

ELEMENT	EMISSIONS TO ATMOSPHERE		PERMISSIBLE LEVEL
	NATURAL (KT/YEAR)	SYNTHETIC (KT/YEAR)	MCL (MG/L)
Cd^{2+}	0.15-2.6	3.1-12	0.005
Cu^{2+}	2.3-54	20-51	1.300
Pb^{2+}	0.97-23	289-376	0.015

Abbreviation: MCL, maximum contaminant level.

adsorption.[44,45] Hawari team[46] has found out that OMSR has an effective way to decrease Zn^{2+} concentration in wastewater. A combination of heavy metal sorbent and ethanol production from OMSR using microwave pre-treatment is suggested by Abu Tayeh et al[47] group. Biochar produced from OMSR was also tested and found useful adsorbents for removing heavy metals from water.[48,49]

Even though several studies on OMSR as a bio-sorbent in wastewater treatment were carried out; still there is a need to investigate a simple and relatively inexpensive OMSR treatment that increases the heavy metal removal. Therefore, the objective of this study was to investigate the effectiveness of simple and low-cost pre-treatment of OMSR on the removal of toxic heavy metals from wastewater. OMSR was treated by water and by n-hexane. The toxic heavy metals chosen for this multi-metal bio-sorption study were Cd^{2+}, Cu^{2+}, and Pb^{2+}. The selection of these metals had been made regarding their wide industrial use and potential impact. Exposure to intemperate levels of these metals remarkably increases the probability of nervous system damage, kidney damage, and renal dysfunction because they are non-biodegradable. These metals are considered the most common heavy metal contaminants.[50-53] Chemical Oxygen Demand (COD) and Cation Exchange Capacity (CEC) were used to indicate the effective bio-sorbent. Then; the most effective treatment was examined by uptake metal. Subsequently; the influence of some parameters on the bio-sorption process such as: the effect of pH, contact time, bio-sorbent concentration, initial concentration of the metal ions solutions, presence of other metals, and bio-sorption isotherms have been examined.

Materials and Methods

Preparation of OMSR

OMSR was collected from an olive oil production plant in Amman, Jordan.

Untreated OMSR (OMSR-U). The sample of the OMSR was dried by using direct sunlight in an open area for 2 weeks, and then dried in an oven at 50°C for 1 week to ensure complete dryness. The OMSR was then ground and sieved into 0.90 mm (see Figure 1a). The sieved samples were not sorted according
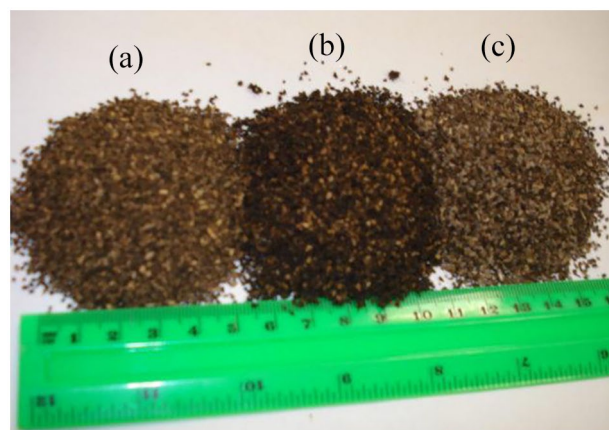
Figure 1. (a) OMSR-U, (b) OMSR-W, and (c) OMSR-H.

to sorbent particle size, sorting according to size from the point of view of industrial applications provides no additional benefit for the bio-sorption process yet causes additional costs.[45]

Treatment by distilled water (OMSR-W). About 50 g of dried OMSR-U was washed 6 times with distilled water until the dark color of the supernatant became clear, and then the sample was filtered and dried (Figure 1b).

Treatment by n-hexane (OMSR-H). About 50 g of dried OMSR-U was washed 6 times with n-hexane as organic solvent until the dark color of the supernatant became clear, and then the sample was filtered and dried (Figure 1c).

Characterization of OMSR

Chemical oxygen demand (COD). The COD represents the number of oxygen equivalents that are consumed in the oxidation of organic compounds by strong oxidizing agents, and it indicates the amount of organic pollutants present in the examined sample.[54] COD is measured in milligrams per liter (mg/L), which indicates the mass of oxygen consumed per liter of solution.[55] The closed reflux, titrimetric method was used in this measuring job. The 3 different OMSR dried samples were shacked with distilled water (100 g/L), then the solid suspensions were kept under magnetic stirring in a shaker at 150 rpm for 120 minutes. Solid-liquid separation was performed using
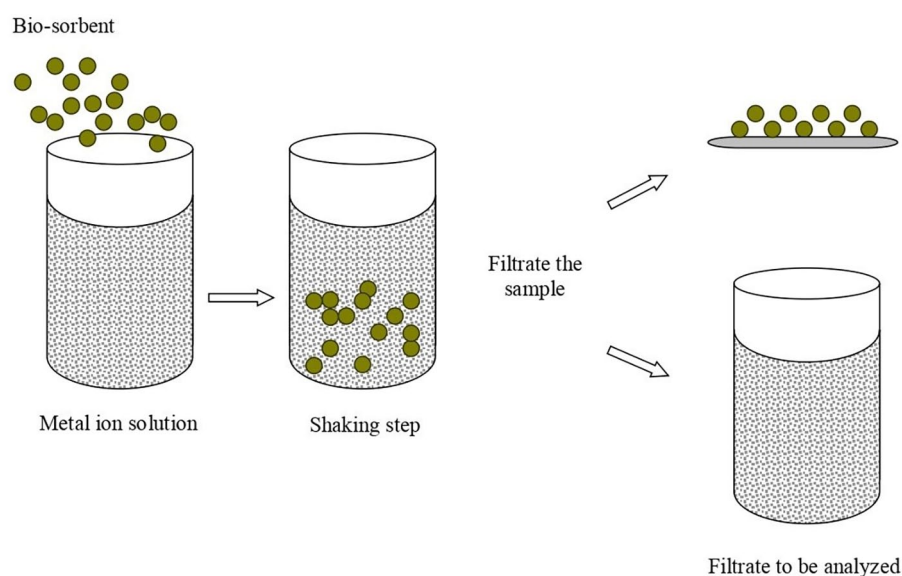
Figure 2. Batch experiment illustration.

centrifugation technique at 2000 rpm for 10 minutes, then the pH of the solutions was monitored, and it was found that the pH values were between 6 and 7. The supernatants samples were diluted 100 times, and then a volume of 2.5 mL of the diluted samples was added to the standard tube then mixed with a volume of 1.5 mL of 0.0167 M $K_2Cr_2O_7$ and a volume of 3.5 mL H_2SO_4. The tubes were tightly capped and were shook and turned several times to make sure that it is mixed completely, then the tubes were placed in a block digester at 150°C for 2 hours. The tubes were cooled to room temperature and transferred to a conical flask for titration; 1 to 2 drops of ferroin indicator were added and stirred rapidly while titrated with 0.1 M FAS (standard ferrous ammonium sulfate titrant). At the end point the color was changed from bluish green to reddish brown.

Cation exchange capacity (CEC). CEC is a measure of negatively charged sites on the surface that help in holding positively charged ions.[56] It is the quantity of exchangeable cations (in milliequivalents) per unit dry weight of substance.[57] In this study; the CEC for the OMSR samples was determined using the Ammonium Replacement Method, and the percent of ammonium ion in the samples was determined by the Kjeldahl method.[58] An amount of 200 mL of 6 N NH_4Cl was added to 2 g of the 3 different OMSR dried samples. The samples were shaken at 150 rpm for 1 week. The samples were filtered, and the filtrate was washed 3 times with distilled water then washed with 50 mL of ethanol to remove the excess ammonium ion. After that, the solid samples were air dried then added to an 800 mL Kjeldahl flask and mixed with 25 mL of 6 N NaOH, and 50 mL of 2% H_3BO_3. Then, 10 drops of bromocresol green methyl red mixed indicator were added to the mixture and stirred rapidly while titrated with 0.1 N H_2SO_4. At the end of this test, the color was changed from bluish green to pink.

Batch tests

Adsorption is a separation process that refers to the adhesion of molecules (adsorbate) to a solid surface (adsorbent) and is classified as either physical or chemical adsorption.[59] Examination and preliminary evaluation of a solid-liquid adsorption system is based on 2 kinds of investigation: (a) The equilibrium batch sorption tests (the one used in this study), and (b) Dynamic continuous-flow sorption.[60,61] The amount of metallic ion biosorbed by grams of the biomass (q; adsorption capacity) and the metal removal efficiency ($E\%$) are calculated using equations (1) and (2), respectively:

$$q = \frac{(C_i - C_f)V}{m} \qquad (1)$$

$$E\% = \frac{C_i - C_f}{C_i} \times 100\% \qquad (2)$$

where C_i is the initial concentration of the metallic ion (mg/L), C_f is the final (equilibrium) concentration of the metallic ion (mg/L), m is the mass of the bio-sorbent in the reaction mixture in gram, and V is the volume of the reaction mixture in liter.[53,62,63]

All adsorption tests in this study were performed by the batch technique (Figure 2).

Chemicals. Stock solutions of Cadmium Nitrate, Copper Chloride, and Lead Nitrate of 1000 mg/L were used as adsorbates, and solutions of various concentrations were obtained by diluting the stock solution with distilled water. The metal ions concentrations were determined by Flame Atomic Absorption Spectrometry (Perkin Elmer Model Analyst 100). All the chemicals used were of analytical reagent grade.

Effect of pre-treatment. Batch sorption experiments were carried out to investigate the uptake efficiency for the 3 OMSR samples. The experiments were carried out by mixing 1 g of a dry sample with 50 mL of 50 mg/L solution of Cd^{2+}, Cu^{2+}, or Pb^{2+}. The samples were shaken at 150 rpm at a temperature of 20°C. The solutions were then filtered using a syringe filter with 0.45 μm and the filtrate was analyzed by a flame atomic absorption spectrometry.

The optimum conditions. To enhance the uptake efficiency of the best-chosen bio-sorbent, the optimum condition was determined. The bio-sorption process was affected by several variables including: pH, contact time, bio-sorbent concentration, and initial concentration of the metal ions solutions.

To study and evaluate the significance of variables on the removal efficiency of metal ions, the adsorption experiments were carried out using a batch procedure. First, the pH values were studied from 2 to 8. To obtain the desired pH; the metal solution was adjusted with 0.1 M NaOH and 0.1 M HCl. The experiments' parameters were kept as above (see the effect of pre-treatment).

Then each variable (contact time, bio-sorbent concentration and initial concentration of the metal ions solutions) was changed keeping the other variables fixed to investigate the optimum value. The contact time was changed from 10 to 360 minutes, while the bio-sorbent concentration was varied from 10 to 80 g/L and the initial concentration of the metal ions solutions was between 20 and 200 mg/L.

Present of other metals. Batch experiments were carried out under the optimum conditions for single (Cd^{2+}, Cu^{2+}, and Pb^{2+}) and binary (Cd^{2+}/Cu^{2+}, Cd^{2+}/Pb^{2+}, and Cu^{2+}/Pb^{2+}) systems. A comparison between such experiments provides information on the competition between different metal ions for the active sites on the surface of the best-chosen bio-sorbent.

Bio-sorption isotherms. The equilibrium of the bio-sorption process is frequently described by fitting the experimental data with models usually used for the representation of isotherm adsorption equilibrium.[60,64]

Langmuir is one of the most widely accepted and linearized equilibrium adsorption isotherm models.[60] It is used to describe the equilibrium between adsorbate and adsorbent system. Langmuir assumes that the fractional surface coverage is directly proportional to the rate of desorption from the surface, and that the rates of adsorption and desorption are equal at equilibrium.[27,63] The Langmuir equation is expressed as:

$$q = \frac{q_{max}bC_f}{1 + bC_f} \qquad (3)$$

where q (adsorption capacity) is the amount of solute adsorbed per unit weight of sorbent at equilibrium measured in mg/g,

C_f is the adsorbate equilibrium concentration in solution measured in mg/L, q_{max} is the maximum adsorption capacity measured in mg/g, and b is Langmuir adsorption constant (L/mg).[65-67]

The term q_{max} is assumed to represent a fixed number of surface sites in the sorbent, and it should be constant and temperature-independent. It is determined merely by the nature of the sorbent. To facilitate fitting the model to the experimental data and its parameter evaluation, equation (3) can be transformed into an expression of linear form[68]:

$$\frac{C_f}{q} = \frac{C_f}{q_{max}} + \frac{1}{bq_{max}} \qquad (4)$$

A plot of (C_f/q) against C_f produces a linear graph with slope = ($1/q_{max}$), and intercept = ($1/bq_{max}$).[66]

In this work; the equilibrium of the bio-sorption process was described by fitting the experimental data for single metal systems (Cd^{2+}, Cu^{2+}, and Pb^{2+}) with the Langmuir isotherm model. The investigation of each single metal ion system was performed by varying the initial metal ion concentration in the range of 20 to 200 mg/L, and the batch experiments were carried out under the optimum conditions.

Results and Discussion

This study was carried out as an attempt to utilize Olive Mill Solid Residue (OMSR) as a bio-sorbent for heavy metals removal from wastewater. Although adsorption is a highly effective process with fast kinetics, it relatively has a high cost of materials.[69] In order to find a simple and cost-effective method; the effect of pre-treatment of OMSR (OMSR-W and OMSR-H) on the removal of Cd^{2+}, Cu^{2+}, and Pb^{2+} from wastewater was investigated. COD and CEC were used to indicate the effective bio-sorbent. The most effective treatment was then examined to uptake metal. Thereafter, the influence of some parameters on the uptake efficiency such as: the effect of pH, contact time, bio-sorbent concentration, initial concentration of the metal ions solutions, presence of other metals, and bio-sorption isotherms have been examined.

Characterization of OMSR

The COD and CEC values for the 3 OMSR samples are listed in Table 2. The results show that the values of COD decreased by treatment. This trend was expected because

Table 2. COD and CEC values of untreated and treated OMSR.

	COD (MG O$_2$/L)	CEC (EQ/G)
OMSR-U	35 200	29.83
OMSR-H	16 000	22.15
OMSR-W	4800	18.03
Blank	0	–

washing OMSR will lead to leaching the organic compounds. OMSR-W has the lowest COD value followed by OMSR-H then OMSR-U. CEC results show that OMSR-U has the highest value, whereas the values of the OMSR-W and OMSR-H were less and close. The best bio-sorbent is the one having the lowest COD and the highest CEC values. Although OMSR-U has the highest CEC value; still it cannot be considered as the best bio-sorbent as it increases the organic pollutant in the treated water since it has the highest COD value. On the other hand; the OMSR-W and OMSR-H have close CEC values, while OMSR-W has the lowest COD value compared to other treatments. Based on these results; it was concluded that OMSR-W is the material of choice for water purification, because it contaminates water with organic compounds in a smaller extent than OMSR-U or OMSR-H. The COD value of OMSR-W could be further reduced using microbial treatment method. The microbial treatment is an inexpensive, nontoxic, and non-polluting method. This will be investigated in future work.[70,71]
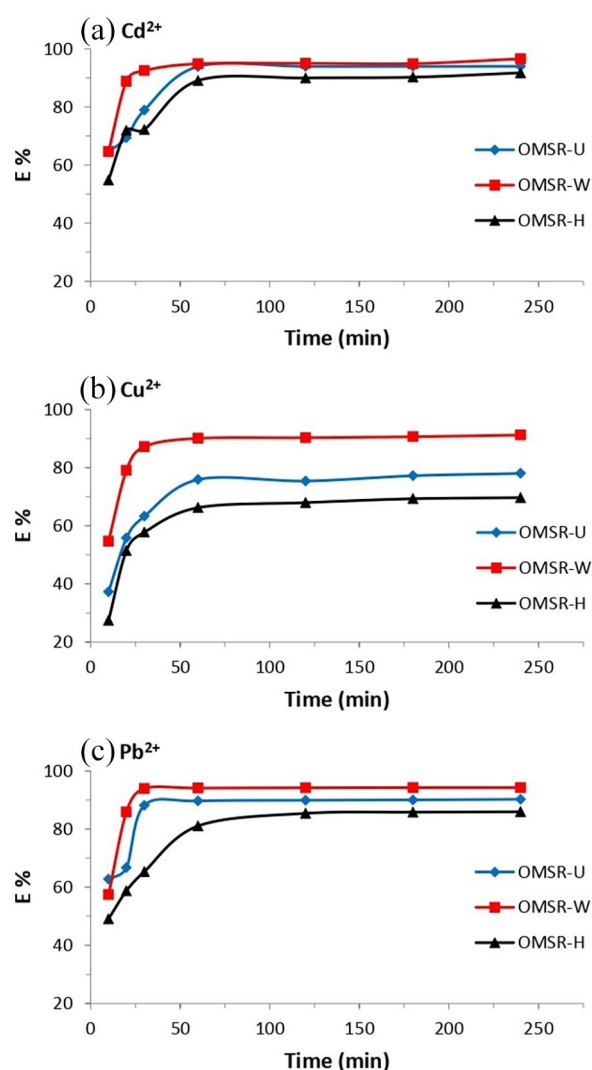
Effect of pre-treatment of OMSR

In this experiment, the batch tests were performed using 3 different bio-sorbents (OMSR-U, OMSR-W, and OMSR-H) with a concentration equal to 20 g/L for each bio-sorbents. The batch experiments are illustrated in Figure 2. The batch experiments were carried out under the influence of contact time for Cd^{2+}, Cu^{2+}, and Pb^{2+} with an initial concentration equal to 50 mg/L for each metal ion. Figure 3a and b indicate that Cd^{2+} and Cu^{2+} have the same equilibrium time which can be reached after 60 minutes using the 3 different OMSR bio-sorbents. Meanwhile; for Pb^{2+} (Figure 3c) the equilibrium stage reached after 30 minutes for both OMSR-W and OMSR-U, while for OMSR-H the equilibrium stage reached after 120 minutes. At equilibrium; all tested bio-sorbents were effective at removal of >80% of Cd^{2+} and Pb^{2+}, and >60% of Cu^{2+}.

Based on the metal removal efficiency, $E\%$ (Figure 3); the uptake using OMSR-W was the highest and the uptake using OMSR-H was the lowest for the 3 metals' ions (Cd^{2+}, Cu^{2+}, and Pb^{2+}). The pre-treatment of OMSR with water (OMSR-W) may expose more available binding sites for metal bio-sorption and may remove surface impurities from the biomass. These might be the reasons for the increase in the uptake capacity of the biomass.[72-74] Whereas; n-hexane as an organic solvent may dissolve or damage the binding sites. This could explain the decrease in the uptake capacity of the biomass after the treatment with n-hexane.

The optimum conditions of the batch experiments

According to our findings in the characterization of OMSR and the batch experiments; OMSR-W was found as the best bio-sorbent, and therefore it can be used to determine the

Figure 3. Effect of pre-treatment of OMSR on uptake of (a) Cd^{2+}, (b) Cu^{2+}, and (c) Pb^{2+}. The batch tests were performed using a concentration equal to 20 g/L for each bio-sorbents and an initial concentration equal to 50 mg/L for each metal ion.

optimum conditions in the batch experiments. The effect of solution pH, contact time, bio-sorbent (OMSR-W) concentration, and initial metal ions (Cd^{2+}, Cu^{2+}, and Pb^{2+}) concentration on batch experiments were investigated.

Effect of pH. The pH of the bio-sorption process is very important because it affects the metal uptake, the surface chemistry of the bio-sorbent and metal ions specification.[75] Batch experiments were carried out to assess the effect of the pH. The pH values from 2 to 8 were performed using OMSR-W with a concentration equal to 20 g/L. The solution's pH value is an important parameter affecting the adsorption process of heavy metals.[76] Bio-sorption data for Cd^{2+}, Cu^{2+}, and Pb^{2+} (with an initial concentration equal to 50 mg/L for each metal ion) using OMSR-W at pH from 2 to 8 are shown in Figure 4a. It was found that the removal of Cd^{2+}, Cu^{2+}, and Pb^{2+} at pH = 2 was less than that at pH = 3, however; the uptake mostly reaches the equilibrium at pH ≥ 3. According to Rahman and
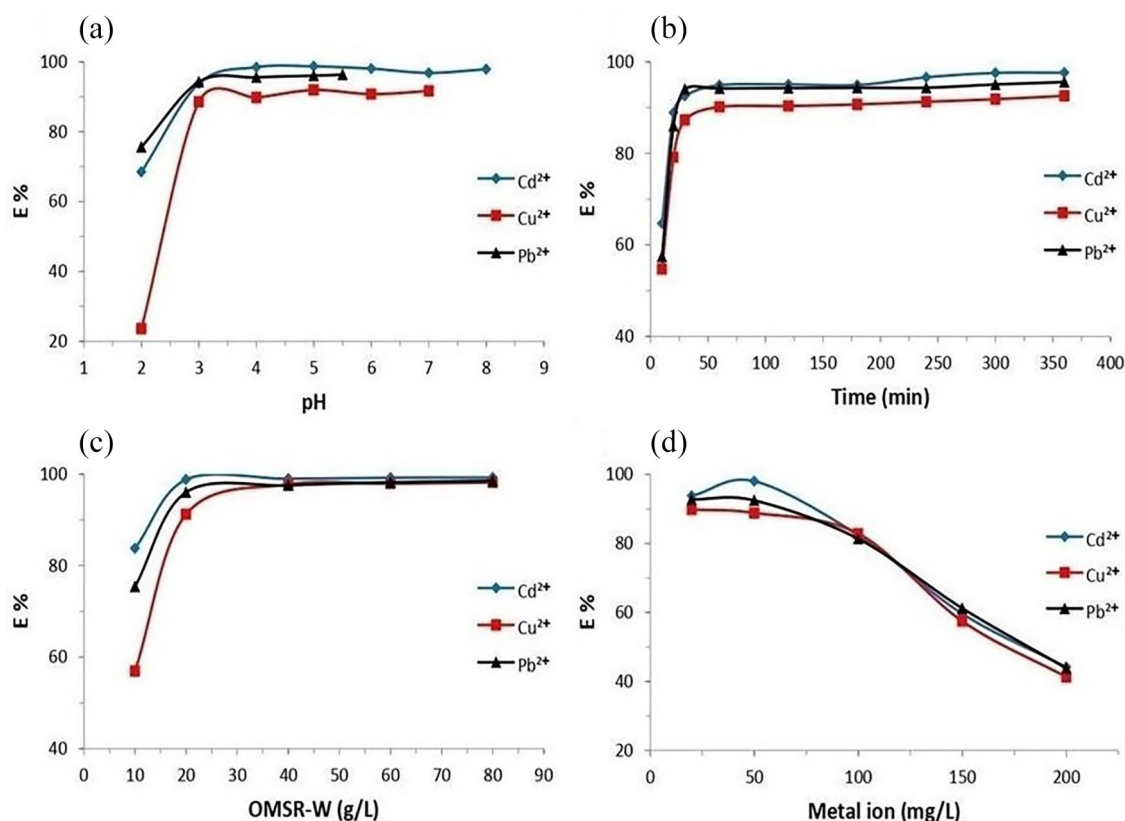
Figure 4. Effect of: (a) pH on OMSR-W uptake of Cd^{2+} (blue), Cu^{2+} (red), and Pb^{2+} (black). The batch tests were performed using a concentration equal to 20 g/L for OMSR-W and an initial concentration equal to 50 mg/L for each metal ion. (b) Contact time on OMSR-W uptake of Cd^{2+} (blue), Cu^{2+} (red), and Pb^{2+} (black). The batch tests were performed at pH = 5.5, OMSR-W concentration = 20 g/L, and an initial concentration equal to 50 mg/L for each metal ion. (c) Concentration of OMSR-W on the uptake of Cd^{2+} (blue), Cu^{2+} (red), and Pb^{2+} (black). The batch tests were performed at pH = 5.5, contact time = 60 minutes, and an initial concentration equal to 50 mg/L for each metal ion. (d) Initial metal ion concentration on OMSR-W uptake of Cd^{2+} (blue), Cu^{2+} (red), and Pb^{2+} (black). The batch tests were performed at pH = 5.5, contact time = 60 minutes, and OMSR-W concentration = 20 g/L.

Sathasivam[77] the low bio-sorption efficiency at low pH can be explained by the fact that positively charged functional groups increase the competition between protons and metal cations for binding active sites of biomass.

For each of the studied metal ions; the increase in the pH value of the solution will decrease the solubility of metal ions in a way causing their precipitation to occur.[78] Cd^{2+}, Cu^{2+}, and Pb^{2+} ions start to precipitate at pH higher than 8, 7, and 5.5 respectively (see Figure 4a). Therefore, the pH value of 5.5 was chosen to be used for the rest of the experiments for the 3 metal ions.

Effect of contact time. The contact time experiments were carried out at a pH value of 5.5 using the OMSR-W (20 g/L); the samples were shaken for different contact times. It is essential to evaluate the effect of contact time between the bio-sorbent and the metal ions solutions. As the bio-sorption process proceeds, the sorbent reaches the saturation state and then the sorbed solute tends to desorb back into the solution. Eventually, the adsorption and desorption rates will be equal and attain an equilibrium state. When the system reaches the sorption equilibrium, no further net adsorption occurs.[68,79]

This experiment was determined at varying contact time from 10 to 360 minutes. For an initial metal ions concentration equal to 50 mg/L; the results revealed similar behavior in the uptake of Cd^{2+}, Cu^{2+}, and Pb^{2+}, where the uptake of metal ions seems to occur in 2 steps: rapid step and slow step (Figure 4b). The first step involves rapid metal uptake within the first 10 minutes of contact time that is followed by the subsequent removal of the metal which continues with time until an equilibrium state is reached within almost 60 minutes. Yue et al[80] group was reported that Pb^{2+}, Fe^{2+}, and Cd^{2+} were rapidly adsorbed by infused tea leaves (*Camellia sinensis*) during the first 10 minutes. Similarly; Cd^{2+}, Cu^{2+}, and Pb^{2+} were adsorbed by the OMSR-W within <10 minutes.

The rapid step is probably due to the abundant availability of active sites on the material. With the gradual occupancy of these sites; the sorption becomes less efficient in the slower step. Based on these results, it was concluded that a shaking time of 60 minutes will be suitable for subsequent sorption experiments.

Effect of OMSR-W concentration. The adsorbent concentration is an important factor that influences the adsorption process and defines the adsorption capacity of the adsorbent for a given initial concentration of metal ions solution.[81,82] For the purpose of observing the effect of this parameter on the rate of metallic biosorption and determining the lower and upper levels of OMSR-W concentration for removing the metals efficiently; uptake experiments were carried out using different concentrations of
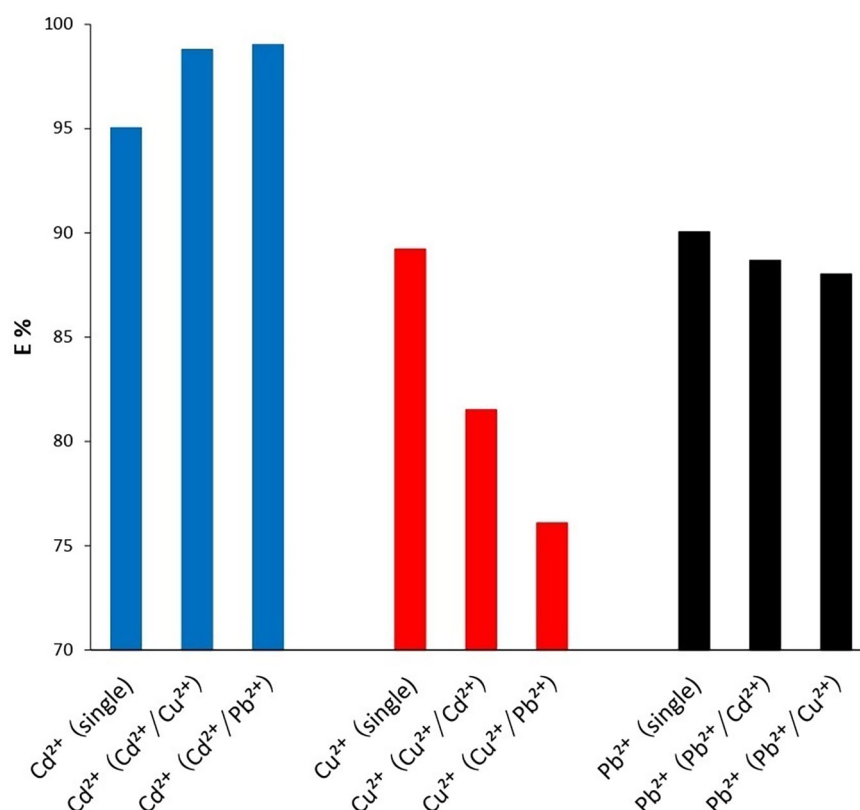
Figure 5. Comparison between OMSR-W uptake of metal ion in single and bi-metallic solutions; Cd^{2+} (blue), Cu^{2+} (red), and Pb^{2+} (black). The batch tests for single and bi-metallic solutions were performed at pH = 5.5, contact time = 60 minutes, OMSR-W concentration = 20 g/L, and an initial concentration equal to 50 mg/L for each metal ion.

OMSR-W at a pH value of 5.5. The results obtained are shown in Figure 4c. For a given initial concentration of metal ions solutions (50 mg/L); whenever there was an increase in OMSR-W concentration (g/L), there was an increase in the efficiency. Increasing the OMSR-W concentration will increase the number of sorption sites at the OMSR-W surface. This is basically what led to the increase in metal ions removal.[80,81] However; the adsorption will increase up to certain OMSR-W concentrations, after that, the effect of the increase in OMSR-W amount becomes insignificant. This is due to the inability of metal ions to reach to the adsorbent surface.[83] For an initial concentration of the metal ions used (50 mg/L); no change was observed in the bio-sorption efficiency at OMSR-W concentration >20 g/L for both Cd^{2+} and Pb^{2+}, and OMSR-W concentration >40 g/L for Cu^{2+}. Therefore, 10 and 20 g/L were defined as the lower and upper levels of OMSR-W concentration for Cd^{2+} (50 mg/L) and Pb^{2+} (50 mg/L). Whereas for Cu^{2+} (50 mg/L); the lower and upper levels of OMSR-W concentration were defined at 10 and 40 g/L. Therefore, the OMSR-W concentration equal to 20 g/L was chosen to be used for the rest of the experiments for the 3 metal ions.

Effect of initial concentration of the metal ions solutions. The effect of initial metal ions concentration on bio-sorption is shown in Figure 4d. The range of initial concentration was between 20 and 200 mg/L. The results show that sorption efficiency decreases when the initial concentration of all metal ions is >50 mg/L. The decrease in the removal efficiency at higher initial concentrations of metal ions is probably caused by the fact that all the adsorbents had a limited number of active sites. These sites could become saturated above a certain metal ions concentration. Similar results have been reported by Yue et al[80] group. Therefore; to achieve greater efficiency in the removal of the heavy metals at the given experimental conditions (pH = 5.5, contact time = 60 minutes, and OMSR-W concentration = 20 g/L), it is required to maintain the metal ions concentration ≤50 mg/L.

Effect of mixed metal ions solutions

To investigate the effect of the presence of >1 metal's ion species in solution on metals uptakes; batch experiments were carried out under the optimum conditions for single systems containing 1 metal ion (Cd^{2+}, Cu^{2+}, and Pb^{2+}) and binary systems containing 2 metal ions (Cd^{2+}/Cu^{2+}, Cd^{2+}/Pb^{2+}, and Cu^{2+}/Pb^{2+}). In batch experiments for each binary system; 1 g of dried OMSR-W was brought in contact with 50 mL of mixed solutions that contain 50 mg/L for each metal's ions. This experiment was carried out at a pH value of 5.5, and the samples were shaken for 60 minutes. The same batch experiments were carried out for every single system.

The adsorption of metal ions by OMSR-W from single and bi-metallic solutions is shown in Figure 5. For single systems; the metal uptake by OMSR-W followed the following order:

$Cd^{2+} > Pb^{2+} > Cu^{2+}$. In binary systems and in comparison to metal uptake in single systems; the uptake of Cu^{2+} was considerably reduced in the presence of Cd^{2+} or Pb^{2+}, the uptake of Pb^{2+} was inhibited slightly when mixed with Cd^{2+} or Cu^{2+}. However, in this study, there was an increase in Cd^{2+} uptake in the presence of Cu^{2+} or Pb^{2+} when compares to its uptake in a single system. The results in the binary systems can be explained by considering the properties of the metal ions present, such as ionic radius, electronegativity, potential, and redox potential of these metals. Therefore; the presence of other metal ions in the solution can affect the adsorption of a target metal ion.[84-86]

Bio-sorption isotherms

The equilibrium of the bio-sorption process was described with the Langmuir adsorption isotherm model. The bio-sorption isotherm experiments were studied for single metal systems (Cd^{2+}, Cu^{2+}, and Pb^{2+}) by varying the initial concentration of heavy metal ions in the range of 20 to 200 mg/L, and at the optimum experimental conditions (pH = 5.5, contact time = 60 minutes, and OMSR-W concentration = 20 g/L). A plot of (C_f/q) versus the various concentrations of the 3 metal ions at equilibrium (C_f) is shown in Figure 6. The maximum adsorption capacities (q_{max}) obtained from this model are 4.587, 4.525, and 4.367 mg/g for Pb^{2+}, Cd^{2+}, and Cu^{2+} respectively. This indicates that the adsorption capacity of the OMSR-W increased in the order of $Pb^{2+} > Cd^{2+} > Cu^{2+}$. The Langmuir constants and their correlation coefficient values (R^2) for the 3 metal ions calculated based on this isotherm model are summarized in Table 3. Very high correlation coefficient values were obtained for the 3 metal ions (.998 for Pb^{2+}, .999 for Cd^{2+}, and .996 for Cu^{2+}), indicating that there is a good agreement between the experimental data and the Langmuir isotherm parameters. The capacity difference of OMSR-W to remove Pb^{2+}, Cd^{2+}, and Cu^{2+} could be attributed to different adsorptive affinities of the metal ions which tentatively correlated to cation properties; such as hydrated radii, electronegativity, and softness.[53] The results obtained in this study are comparable (to some extent) with those found in the literature in which agricultural waste were used to remove heavy metals from wastewater (q_{max} [mg/g]: Pb^{2+}; 17.07, Cd^{2+}; 5.41, and Cu^{2+}; 4.55).[87]

Conclusion

This study has shown the possibility of using OMSR-W as a low-cost bio-sorbent for the removal of heavy metal ions (Cd^{2+}, Cu^{2+}, and Pb^{2+}) from aqueous solutions. OMSR-W (the most effective treatment) was found to have a higher metal uptake value in comparison to OMSR-U and OMSR-H. OMSR-W leaches the minimum amount of organic matter since it has the lowest COD value compared with other treatments. The treatment of OMSR-W may expose more available binding sites for metal bio-sorption and may remove surface
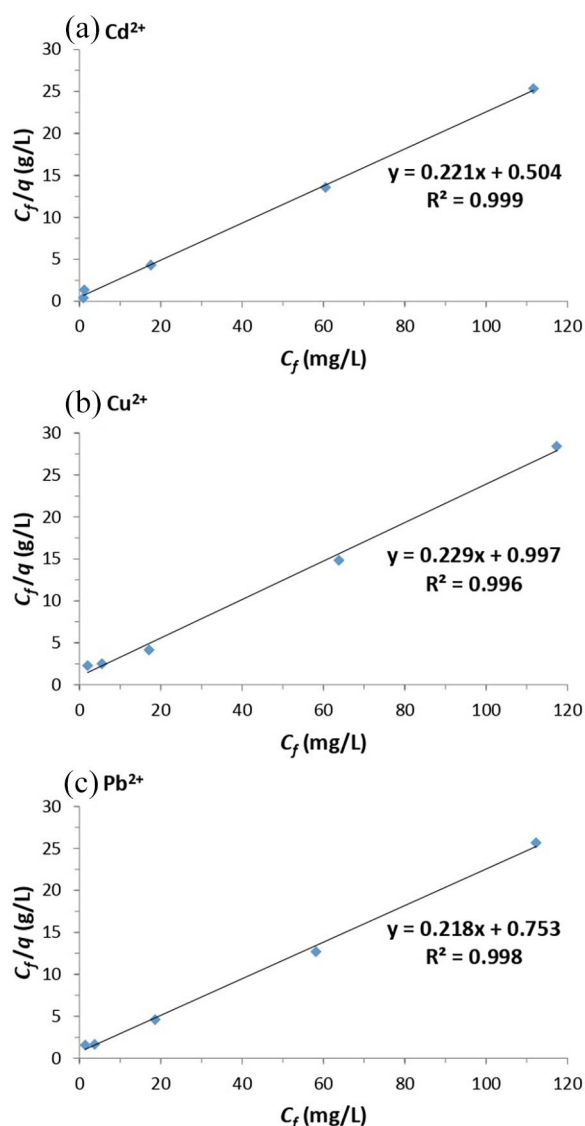
Figure 6. Langmuir adsorption isotherm of (a) Cd^{2+}, (b) Cu^{2+}, and (c) Pb^{2+} by OMSR-W. The bio-sorption isotherm models were studied for single metal systems and performed at pH = 5.5, contact time = 60 minutes, and OMSR-W concentration = 20 g/L.

Table 3. The Langmuir constants for Cd^{2+}, Cu^{2+}, and Pb^{2+} by OMSR-W.

METAL ION	Q_{MAX} (MG/G)	B (L/MG)	R^2
Cd^{2+}	4.525	.438	.999
Cu^{2+}	4.367	.230	.996
Pb^{2+}	4.587	.290	.998

impurities from the biomass. Several parameters were found to affect metal ions uptake by OMSR-W such as pH, contact time, bio-sorbent concentration, metal ions concentration, and the presence of other metal species. The equilibrium sorption data for single metal systems were investigated by the Langmuir isotherm model. The highest value of maximum uptake, q_{max},

was found for Pb^{2+} followed by Cd^{2+} and Cu^{2+}. A good agreement between the experimental data and the Langmuir isotherm parameters was obtained for the 3 metal ions.

The low cost and easily prepared OMSR-W shows an ability to adsorb one or more metal ions from solutions, which may increase its potential for application in the wastewater treatment. However; further investigations with real wastewater samples and the reuse of OMSR-W bio-sorbent are required to confirm the findings and to apply this method on an industrial scale.

Author Contributions

ENM: Methodology, Formal analysis, Visualization, Writing – Original Draft, Writing – Review & Editing, Literature review. FYF: Performed the experiments, Analysis and interpretation of data, Writing – Review & Editing, Literature review. Dr. KMI: Methodology, Formal analysis, Visualization, Writing – Review & Editing, Literature review. Dr. SJ: Analysis and interpretation of data, designed the figures, Writing – Review & Editing, Literature review.

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