The effect of different organic fertilizers in the removal of heavy metals from the soil and water

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Abstract- Heavy metals pollution became a demanding issue globally due to its severe consequences such as water scarcity and lethal diseases spreading. Consequently, finding a low-cost and ecofriendly solution for this issue became essential. The study focused on reusing the agricultural wastewater and reclaiming the fields polluted with heavy metals. The adsorption process, which makes the pollutants insoluble in the water, was found to be a reliable solution which could achieve the defined requirements of the study. In fact, plants residues proved to be efficient, eco-friendly and low-cost biosorbers. Thus, four different types of modified crop wastes (Banana peel charcoal, orange peel Charcoal, mixed biochar and compost) were tested to determine which type of these materials is the most efficient in detoxifying heavy metals in the water under agricultural environment conditions which are relatively low TDS, low percentages of dissolved heavy metals ions and neutral pH. The study was conducted on soil samples brought from Al-Gabal Al-Asfar region in Al-Qalubiya governate, Egypt due to the high pollution levels of heavy metals in the area’s soil. In order to amplify the range of the study, the sustainability of the tested materials was examined through modifying the heavy metals percentages in a group of soil samples by adding 30 ppm of cadmium to the soil, thus simulating the estimated pollution increase in the next ten years. Eventually, orange peel charcoal was found to be the most efficient modifier with the tested substances.

Index Terms- Biosorption, Heavy metals ions, Organic substances, Pyrolysis reaction, Water parameters.

Abbreviations: AP: After pollution, TDS: Total dissolved solids, BP: Before pollution, rpm: revolutions per minute, ppm: parts per million, ICP: inductively coupled plasma, L: liter, mL: milliliter, C°: Celsius.

I. INTRODUCTION

In the past few decades, heavy metals pollution has increased drastically.1,2 Heavy metals pollution is a critical issue facing the globe at the moment. In fact, it could be a main reason in causing other kinds of pollution such as water and soil pollution. Heavy metals contamination is resulting mainly due to the ongoing spread of anthropogenic activities because of the increasing population and urbanization.3,4 Heavy metals are metallic elements with relatively high atomic weight and density at least 5 times greater than that of water. Heavy metals are non-degradable, so they are permanently toxic.5 The main heavy metals are Cadmium, Zinc, lead and Mercury. The presence of heavy metals in the environment profoundly affects the lithosphere, biosphere, hydrosphere, and atmosphere. The direct causes of heavy metal contamination are the anthropogenic activities2,3,4 represented in industrial mining activities, direct discharging of metal-containing effluents by the industries, emission of polluted air from vehicles engines and the release of toxic materials by sanitation in nearby forests and lakes. Indeed, it was reported that approximately 80% of the municipal wastewater is passed into the aquatic environment without treatment.6 In fact, heavy metals are hazardous to the soil, plants, and marine life7. They have several devastating consequences such as ecosystems devastation, wetlands disappearance, food shortage, water scarcity and the spread of deadly diseases such as cancer, Alzheimer, kidney and liver damage, and congenital malfunctions.8,9,10,11 In addition, heavy metals pollution contributes to other serious issues such as soil pollution, marine life toxification, and crops corruption. Not to mention, Heavy metals contamination of the soil can pose risks and hazardous effects to humans10 and the surrounding environment7 by direct ingestion or interaction with the soil and the food chain, contaminate groundwater, reduce food quality by photoxicity, and reduce land usability for agricultural production, causing food insecurity.10

Heavy metals are transported to the plants through direct absorption during irrigation processes due to being dissolved in the irrigation water. According to Wei and Chen2001), about 20% of China's agricultural lands were contaminated with heavy metals, which represents roughly 20 million hectares.11 In fact, many solutions were established to solve the issue of heavy metals contamination such as membrane processes, chemical precipitation, electrolytic processes, and the usage of microbiological bacteria. However, it was found that using such applications is inefficient due to some factors like the high operational costs or having limited removal efficiencies under agricultural environment’s conditions, which is inappropriate for the established requirements.12,13 Recently, the usage of biopolymers and organic substances derived from the agricultural wastes in the biosorption of heavy metals became an interesting field of study.14,15 Lignin is a one of the natural polymer that makes up the cell wall of the plants and represents about 16-33% of the plant’s biomass.16 Lignin has a three-dimensional complex aromatic structure that contains...
a number of functional groups, such as methoxyl, carboxyl, hydroxyl and aldehyde groups.\textsuperscript{[17][18][19]} Not to mention, cellulose and hemicellulose, which are polysaccharide polymers found in the cell wall of the plant, play a role in the biosorption of heavy metals due to their special physical and chemical structure that contains functional groups like methoxyl, just as lignin.\textsuperscript{[19][20]}

Using the residues of several crops is a very efficient solution, especially under the agricultural circumstances, due to many factors such as the low cost, ease of usage and production, sustainability and high efficiency. In fact, previous studies were done on substances such as papa wood\textsuperscript{[21]}, coconut coripirth\textsuperscript{[22]}, pine park\textsuperscript{[23]} and moss\textsuperscript{[24]}. Nonetheless, the research aimed to find a solution using substances that are available in Egypt, the country where the study was conducted, in addition to having high potential as an efficient bioadsorbents due to the presence of high percentages of cellulose, hemicellulose and lignin\textsuperscript{[25]}. Consequently, four substances were found to be available in Egypt especially and globally in general which are orange peel, compost, banana peel and biochar. In 2013, it was estimated that Egypt produces approximately 12.33 million tons of biomass that could be used for biosorption such as rice ash annually\textsuperscript{[26]}. Moreover, in 2012, Egypt produced 1.585 million tons of orange\textsuperscript{[27]}. In fact, Egypt suffers from water scarcity according to the United Nations standards which states that an area is experiencing water stress when annual water supplies drop below 1,700 m\textsuperscript{3} per person and water scarcity when annual water supplies drop below 1,000 m\textsuperscript{3} per person\textsuperscript{[28]}. In Egypt, the annual capita of water is 610 m\textsuperscript{3}.\textsuperscript{[29]}

In 2014, 7.3 million people did not have access to fresh water sources.\textsuperscript{[30]}

II. LITERATURE REVIEW

According to previous studies, the agricultural residues of different plants such as coconut and pine could be an efficient heavy metals bioadsorbent after undergoing specific chemical reaction, known as pyrolysis, due to their chemical characteristics.\textsuperscript{[17-24]}

Pyrolysis reaction, which is a thermal decomposition reaction that occurs in the absence of oxygen so that the reactants are not burned, converts the plant wastes into an efficient bioadsorbents known as charcoal or biochar. Pyrolysis reaction can be done under various temperature ranges (200-1000°C). Moreover, the pyrolysis reaction can last for about 10-240 minutes (step 3). On the other side, pre pyrolysis reaction can last for duration that can reach 48 hours (step 1,2). Depending on the quantity and the type of the organic substance that undergoes the reaction, the temperature and the time of the reaction are determined. In fact, the relationship between the amount of charcoal produced from pyrolysis of the biomass samples and the pyrolysis temperature is inverse relationship.\textsuperscript{[31]}

The best temperature range of pyrolysis is between 377 - 527°C.\textsuperscript{[31]} The pyrolysis reaction undergoes three different stages:

1- Vaporization of the moisture (water vapor).
2- Degasification of different gases like nitrogen, hydrogen, carbon monoxide and carbon dioxide producing a volatilized carbon rich black residue known as the primary biochar.

3- The carbonization of the organic residue and the disappearance of the fibrous structure which improves the grinding ability and yields the final product known as the secondary biochar.

The volatilized by product gases of the pyrolysis could be liquified and used as a power source known as a biofuel which is current field of research.\textsuperscript{[33]}

III. MATERIALS AND METHODS

3.1 Area of study

The study was conducted on soil samples brought from Al-Gabal Al-Asfar region located at 30°12'00.0"N and 31°22'00.0"E in Al-Qalyubia governate. Al-Gabal Al-Asfar region is characterized by being one of the most polluted regions in Egypt due to being irrigated by effluent water from factories and sanitation sewage water for more than 50 years.\textsuperscript{[34]} such a practice made the soil polluted with heavy metals such as Zn, Cd, and Pb which polluted the cultivated crops threatening the health of the consumers as well as the inhabitants of the area.

3.2 Organic modifiers preparation

The orange peel was prepared by exposing 1200 grams of orange peel to 100°C inside an oxygen-isolated oven for 12 hours to undergo the pyrolysis process. Then, the pyrolysis reaction was initiated by subjecting the orange peel to 500°C for 2 hours. At the end, the orange peel charcoal was prepared. The banana peel charcoal and the mixed biochar were prepared using the same method. Indeed, the difference between the mixed biochar and banana or orange-peel charcoal is the components of the biochar. The raw material of the used biochar consisted of various plants residues of several crops. Some of the components of the biochar were rice ash and different trees leaves. Similarly, the compost is a mix of plant residues and organic wastes, but it does not undergo pyrolysis reaction. Instead, the residues are collected, mased and mixed with the soil without undergoing any further reactions. Eventually, 1 Kg of each modifier was prepared. In fact, the used modifiers were prepared and brought from the lab of faculty of agriculture in Ain Shams university.

3.3 Soil sample preparation

90 kilograms of polluted soil were brought from Al-Gabal Al-Asfar. First, the soil was sieved to remove any additional wastes such as ash residues and plastic remnants. Afterwards, the soil was mixed with the soil without undergoing any further reactions. As far, 1 Kg of each modifier was prepared. In fact, the used modifiers were prepared and brought from the lab of faculty of agriculture in Ain Shams university.

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long term. To simulate the future pollution, 30 ppm of cadmium were added to each soil sample that consisted of 3 Kg. The final number of the test samples is 30 samples. The soil was put in a plastic pot of 17 cm height and base that have a radius of 7 centimeter. The base had 4 holes, to discharge excessive water, each had radius of 2 centimeter.

3.4 Plants selection
In order to test the efficiency of the project, plants were cultivated in the polluted soil after mixing the modifiers with the soil to analyze the physical and the chemical changes that occurred to the plants (Figure 1). The requirements of the chosen plant were being fast-growing plant with long and big leaves. Long leaves are reliable indicators for pollution in the soil as the least amount of pollutants appears clearly as it changes the color of the leaves from green into dark blue or black. Furthermore, a fast-growing plant was needed to determine the efficiency of the project quickly to analyze the results and develop the solution if needed. The final choice was the red radish plant due to its fast-growing speed (3-5 weeks) and its long leaves. Each sample contained four seeds of radish.

3.5 Test plan design
A test plan was designed to meet the defined requirements of the study (Figure 2). The test plan consisted of 30 pots divided into two groups: Current pollution group (normal) and Future pollution group. Four modifiers were used in the test plan: orange peel charcoal, banana peel charcoal, mixed biochar and compost. Each modifier was used in three samples to guarantee the precision of the results. Eventually, six control samples (three in each group) were added to be a standard that will be compared with the results of the test samples to determine the efficiency of the modifiers.

3.6 Water samples collection
After 2 weeks of mixing the modifiers with the soil, each soil sample was irrigated with 1.5 L of water. The field capacity is a concept which defines the maximum amount of water which the soil will absorb. The tested soil samples had field capacity of 1 L. Consequently, 0.5 L of the irrigated water will not be absorbed and will be used as a measurement sample to determine the parameters of the sewage water of the polluted soil and whether it could be reused in the process of irrigation again or not. After 2 hours of irrigating the soil, 50 mL of water were collected from each sample through plates that were placed under the pots.

3.7 Water samples preparation
After collecting the water samples, the pH and the TDS of each sample was measured and recorded. Afterwards, the water samples entered the ICP device to be analyzed and to calculate the amount of heavy metals in the water samples.

IV. RESULTS AND DISCUSSION

4.1 Effect on pH
pH is the measurement of the concentrations of hydrogen ions in the solution which measures the acidity or the basicity of the solution on scale of 0-14. The recommended pH of irrigation water is 6.5-8.4. From the results, it is obvious that the acidity of all the samples, whether under current pollution conditions or future pollution conditions, is neutral or slightly basic which is within the defined range of pH for irrigation water.

4.2 Effects on TDS
TDS or total dissolved solids is the measurement of the combined organic or inorganic substances dissolved in the solution. The suitable TDS of irrigation water must be between 525-1400 ppm.

<table>
<thead>
<tr>
<th>The sample</th>
<th>Control sample</th>
<th>Banana peels sample</th>
<th>Orange peels sample</th>
<th>Bio char sample</th>
<th>Compost sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>TDS (FP)</td>
<td>918.3</td>
<td>1510</td>
<td>891</td>
<td>1416</td>
<td>1790</td>
</tr>
<tr>
<td>TDS (CP)</td>
<td>1270</td>
<td>1248</td>
<td>836.6</td>
<td>1443</td>
<td>2303</td>
</tr>
</tbody>
</table>

Table 1. The TDS values of the samples in ppm

4.2.1 Banana peel sample
Under current pollution conditions, banana peel sample had high TDS which is 1510 ppm (larger than the control sample by about 40%). Under current pollution conditions, the TDS reached 1248 ppm which indicates the efficiency of banana peel in rich soil. The TDS under future pollution conditions was lower compared to the control sample by about 2% which is an unsignificant percentage.

4.2.2 Orange peel sample
From all the samples, orange peel presented high efficiency in reducing TDS whether under current or future pollution conditions. Before applying pollution simulation, the TDS of the...
orange peel sample reached 891 ppm which is less than the control sample by 4%. After applying pollution, the TDS reached 836.6 ppm which is less than control sample by 34%.

4.2.3 Compost Sample
Compost sample had the worst percentages of TDS which were 1790 ppm under current pollution conditions (greater by 51% compared to control sample) and 2303 ppm under future pollution conditions (greater by 55% compared to control sample).

4.2.4 Bio char sample
Bio char sample showed intermediate results between the results of banana peel and compost samples which were 1416 ppm under current pollution conditions (greater than the control sample by 20%) and 1443 ppm under future pollution conditions (greater than the control sample by 12%).

4.3 Effect on metals
Based on the results, All the used modifiers could reduce arsenic, cadmium, lead and chromium to negligible percentages (less than 0.001 ppm). Before analyzing the results, it is important to mention the maximum safety percentages of heavy metals in irrigation water [39][40][41]:

<table>
<thead>
<tr>
<th>The element</th>
<th>As</th>
<th>Cd</th>
<th>Fe</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Safe range (ppm)</td>
<td>0.01</td>
<td>0.01</td>
<td>5</td>
<td>0.2</td>
<td>0.02</td>
<td>5</td>
<td>0.2</td>
<td>5</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 2. The safe percentages of heavy metals in irrigation water

4.3.1 Control sample
The control sample showed relatively high percentages of heavy metals, especially cadmium. However, the percentages of As and Pb were insignificant.

<table>
<thead>
<tr>
<th>The sample</th>
<th>As</th>
<th>Cd</th>
<th>Fe</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control sample (CP)</td>
<td>&lt;0.001</td>
<td>0.05</td>
<td>0.067</td>
<td>0.07</td>
<td>0.001</td>
<td>0.01</td>
<td>0.02</td>
<td>&lt;0.001</td>
<td>0.026</td>
</tr>
<tr>
<td>Control sample (FP)</td>
<td>&lt;0.001</td>
<td>0.35</td>
<td>0.41</td>
<td>0.11</td>
<td>0.02</td>
<td>0.11</td>
<td>0.023</td>
<td>&lt;0.001</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 3. The heavy metals profile of the control samples

4.2.2 Banana peel sample
Under current pollution conditions, banana peel could increase the percentage of micro elements which are Cu and Fe. For Fe, the percentage increased by about 36% under current pollution conditions and 54.4% under future pollution conditions. For Cu, it increased by 12.5% under current pollution conditions and decreased by 20% under future pollution conditions. Not to mention, the increase in micro elements percentages is important for the fertility of soil as long as it is still below the safe range. Moreover, the percentages of Zn were the same under current and future pollution conditions compared to the control sample.

<table>
<thead>
<tr>
<th>The sample</th>
<th>As</th>
<th>Cd</th>
<th>Fe</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Banana peels sample (BP)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.13</td>
<td>0.08</td>
<td>&lt;0.001</td>
<td>0.02</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.023</td>
</tr>
<tr>
<td>Banana peels sample (AP)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.9</td>
<td>0.089</td>
<td>&lt;0.001</td>
<td>0.02</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 4. The heavy metals profile of the banana peel samples

4.3.3 Orange peel sample
For Fe, the percentage increased by about 88% under current pollution conditions and it was the same as control sample under future pollution conditions. For Cu, it decreased by 30 % under current pollution conditions and decreased by 20% under future pollution conditions. On the other side, the percentages of Mn increased by 75% under current and future pollution conditions (about 0.03 ppm). Moreover, the percentage of Zn was the same under current and future pollution conditions which was equal to the control sample.

<table>
<thead>
<tr>
<th>The sample</th>
<th>As</th>
<th>Cd</th>
<th>Fe</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orange peels sample (BP)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.4</td>
<td>0.049</td>
<td>&lt;0.001</td>
<td>0.04</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.03</td>
</tr>
<tr>
<td>Orange peels sample (AP)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.41</td>
<td>0.09</td>
<td>&lt;0.001</td>
<td>0.04</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.026</td>
</tr>
</tbody>
</table>

Table 5. The heavy metals profile of the orange peel samples

4.3.4 Compost Sample
For Fe, the percentage increased by about 64% under current pollution conditions and decreased by 71% under future pollution conditions. For Cu, it decreased by 22 % under current pollution conditions and decreased by 20% under future pollution conditions. On the other side, the percentages of Mn increased by 50% under current pollution conditions and decreased by about 20% under future pollution conditions. Moreover, the percentages of Zn were the same under current and future pollution conditions (the same as the control sample).

<table>
<thead>
<tr>
<th>The sample</th>
<th>As</th>
<th>Cd</th>
<th>Fe</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compost Sample (BP)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.08</td>
<td>0.09</td>
<td>&lt;0.001</td>
<td>0.01</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.02</td>
</tr>
<tr>
<td>Compost sample (AP)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.25</td>
<td>0.12</td>
<td>&lt;0.001</td>
<td>0.03</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Table 6. The heavy metals profile of the compost samples

4.3.5 Bio char sample
For Fe, the percentage increased by about 41% under current pollution conditions and decreased by 41% under future pollution conditions. For Cu, it increased by 22 % under current pollution conditions and increased by 9% under future pollution conditions. On the other side, the percentages of Mn were the same under current and future pollution conditions and it was the same as control sample. Moreover, the percentages of Zn were the same under current and future pollution conditions which were equal to the control sample (increased by 33%).

<table>
<thead>
<tr>
<th>The sample</th>
<th>As</th>
<th>Cd</th>
<th>Fe</th>
<th>Cu</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bio char sample (BP)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.13</td>
<td>0.089</td>
<td>0.02</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Bio char sample (AP)</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.13</td>
<td>0.089</td>
<td>&lt;0.001</td>
<td>0.02</td>
<td>&lt;0.001</td>
<td>&lt;0.001</td>
<td>0.03</td>
</tr>
</tbody>
</table>

Table 7. The heavy metals profile of the bio char samples

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From the results, some deductions were reached:
1- In a soil that have high TDS, banana peel and orange peel are more efficient in adsorption than in normal soil.
2- Compost and biochar are more efficient in poor soil (low TDS) than in rich soil.
3- Most of the samples of water will not be favorable to be used as irrigation water, especially the compost sample, due to the high TDS of the sewage water of the samples. However, orange peel was the only substance that showed high efficiency in reducing the TDS in addition to banana peel under future pollution conditions “High TDS”. In fact, they were the only samples that could be used to purify the sewage water and reuse it in the irrigation process.

V. CONCLUSION
The study could successfully find the most suitable modifiers to purify agricultural wasted water form heavy metals under agricultural environment conditions which were orange peel charcoal and banana peel charcoal based on the TDS and pH results in addition to the heavy metals profile of the wastewater samples. The orange peel showed high efficiency and sustainability in detoxifying heavy metals under current and future pollution conditions. In fact, the sewage water of soil mixed with banana peel could be used in the irrigation of specific crops which needs relatively high TDS. On the other side, orange peel is better for crops that need low TDS and intermediate fertility. Eventually, compost could be defined as the least favorable substance to be used because of the high TDS of the wastewater of its sample, especially under the future pollution conditions, which makes the sewage water unusable for the irrigation process.

VI. REFERENCES

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