

Removal Of Pb^{2+} Ions From Aqueous Solution Using Posdonia Oceanica Collected From Tajora Beach (Libya)

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Abstract – The seagrass posdonia oceanic (P.O) was collected from Tajora Beach and employed to remove Pb ions from aqueous solutions. The P.O samples were dried, ground and characterized by SEM, POM and FTIR analysis. The batch mode study showed the removal percentage of Pb^{2+} increases up to 88.1 % at 6 hrs using P.O. The maximum capacity of lead removal was found to be 28.82 mg/g. The adsorbed amounts of Pb^{2+} have decreased from 3.71 to 0.22 mg/g as pH increased from 4 to 10. The removals of Pb have positive relationship with temperature and the mass of P.O. The activation energy of Pb^{2+} removal is + 4.1 kJ/mole which suggests the endothermic nature of reaction.

Keywords – Removal, Pb^{2+} Ions, Posdoina Oceanica.

I. INTRODUCTION

Water pollution has become a serious concern worldwide. Water turn polluted with the accumulation of many pollutants including heavy metals. Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations and tanneries(1). Some metals associated with these activities are cadmium, chromium, iron, nickel, lead and mercury. At the low concentrations these metals excite some biological processes where become toxic at threshold concentration. They cause physical distress, life-threatening illness and damage to vital body system. Hence, remediation of contaminated effluents before their discharge into the aquatic system is essential (1).

Many attempts have been done on the removal of heavy metal from wastewater using conserved technologies such as ion exchange, flocculation, oxidation or chemical precipitation. Such methods are sometimes inefficient and expensive, particularly for removal of low concentrated heavy metal ions, and usually lead to produce toxic sludge that adverse the economical feasibility of

the treatment methods (2, 3). However, biosorption technique has shown positive results in sequestering heavy metals. It is stated that biosorption is a potential effective and alternative to traditional treatment processes of metal ions removal. It is a technically feasible and economically viable sustainable technology for the treatment of wastewater streams (2).

Biosorption is a property of certain types of inactive, dead biomass to bind and concentrate heavy metals from even very dilute aqueous solutions. It appears as a complex phenomenon where the metallic species could be deposited in the solid biosorbent through different sorption processes of ion exchange, complexation, chelation and precipitation (4, 5). Several adsorbents were being produced and utilized from agriculture and industries such as seagrasses, molds, yeast, bacteria, crabshells, wool, rice, straw, peat moss, tea leaves and coconut fibre (6). The role of dried seagrass in removal of toxic metal ions from water has attracted great attention due to its high area to volume ratio that provides a large contact area for metal binding. The ability of such substances to adsorb metals depends on various factors such as the bioavailability of metals and their uptake capacity (4, 5). The uptake of metals in adsorbents depends on the surface reaction in which metals absorbed through electrostatic attraction to negative sites. For instance, metal cations with high electro-negativity and small ionic radii are preferably absorbed by algae biomass. Metal accumulation capacity of biomass is sometimes higher than chemical sorbents (7).

An example of seagrass is *Posidonia oceanica* which an endemic marine magnoliophyta found in the Mediterranean Sea. It forms large underwater meadows from the surface to depths of 40 m, which are an important part of the ecosystem (8, 9). The seagrass forms structures known as Mats which are monumental constructions that result from the horizontal and vertical growth of the rhizomes with their entangled roots and the entrapped sediment. The fibers accumulate in considerable quantities, reaching a thickness of 1–2 m or more on the most Mediterranean beaches. This seagrass is very sensitive to human disturbance, such as coastal development, pollution, trawling and high water turbidity (9, 10). Huge quantities of these wastes are either transported (or possibly buried) in landfills, or piled up in adjacent areas to beaches or even re-immersed in the sea. This study presents the removal of Pb²⁺ from aqueous solutions using dried *Posidonia oceanica* is collected from Tajora Beach in Libya. The effects of contact time, pH, adsorbent mass and temperature were studied for metal sorption procedure.

II. EXPERIMENTAL

Sample preparation

Posidonia oceanica grasses were collected from Tajora beach (North western coast of Libya). The samples are manually separated, washed several times with distilled water to remove the surface-adhered particles and then dried in air for 48 h, to a constant weight. This step allows desiccation of the material without affecting its structural and functional characteristics. The dried grasses were reduced to a fine powder and sieved to get a size fraction around 100 µm.

The stock solutions of Pb²⁺ ions with concentration (10 mg/L) were prepared by diluting analytical grade solution (1000 mg/L) with distilled water. The initial pH was adjusted to the desired value using value using 0.1 N HCl or NaOH.

Instrumentations

The measure of Pb²⁺ concentrations in the samples determined by flame atomic absorption spectroscopy (GF95 – AAS) located in marine research centre Tajora-Libya. The pH measurements were carried out on a WTW720 pH meter model CT16 2AA (LTD Dover Kent, UK) and equipped with a combined glass electrode. The Fourier Trans Infrared (FTIR) spectroscopy was used to give a qualitative analysis of the main chemical groups present on the sample and responsible of the adsorption. The translucent samples disks were prepared by mixing the P.O powder with KBr; the spectra were recorded with a PerkinElmer Spectrum Tow. Scanning electron microscopy (SEM, JEOL JSM – 5610LV) and polarization optical microscope (POM) provide a view of the morphological structure of the sample.

Batch mode

Batch mode removal studies were carried out by varying several parameters such as contact time, pH, temperature and mass of grass (adsorbent). Essentially, a 50 ml of stock solution with concentration of 10 ppm was taken in a 250 ml conical flask in which the initial pH was adjusted using HCl/NaOH. Optimized amount of adsorbent was added to the solution and stirred using magnetic stirrer for specific time. The oxide samples were separated from solutions using centrifuge 4000 CPM for 5 minutes.

III. RESULT AND DISCUSSIONS:

3.1. Characterization of sample

The morphology plays an important role in the adsorption and precipitation of M(II) on the external surface. Scanning electron microscope and polarization optical microscope images of P.O are presented in Figure 1. The P.O sample exhibit well defined lignocellulosic fibrous structure with cylindrical fibers shape which is favourable for metal ions adsorption.

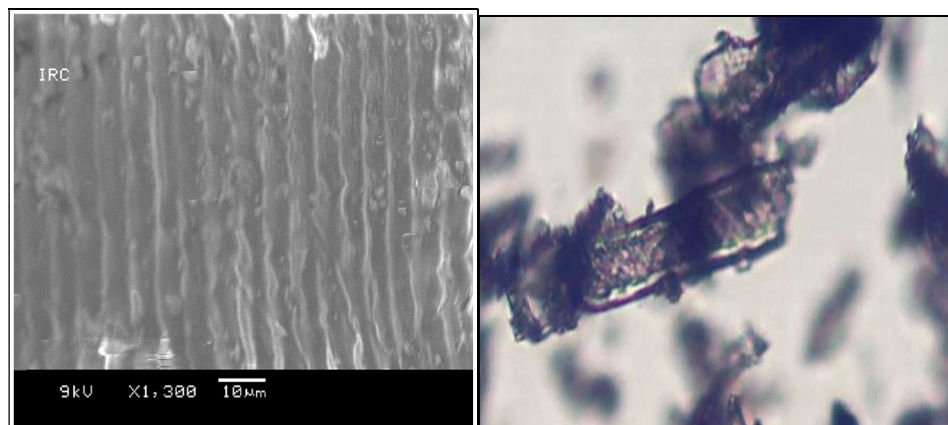


Figure 1 SEM and POM images for P.O

The FTIR spectra of P.O after the adsorption process (Figure 2) show a peak at 3331 cm⁻¹ due to (–OH) or amine groups (–NH), while the band at 2917 cm⁻¹ represents the stretching of –CH groups. The bands 1424 and 699 cm⁻¹ are attributed to –CH bending, and that observed at 1600 cm⁻¹ is assigned to C=O stretching groups. The peak at 1600 cm⁻¹ could be attributed to N–H bending, while those at 1423 and 1030 cm⁻¹ are assigned to –CN stretching. Similar results are reported on Pb²⁺ removal by P. O (11).

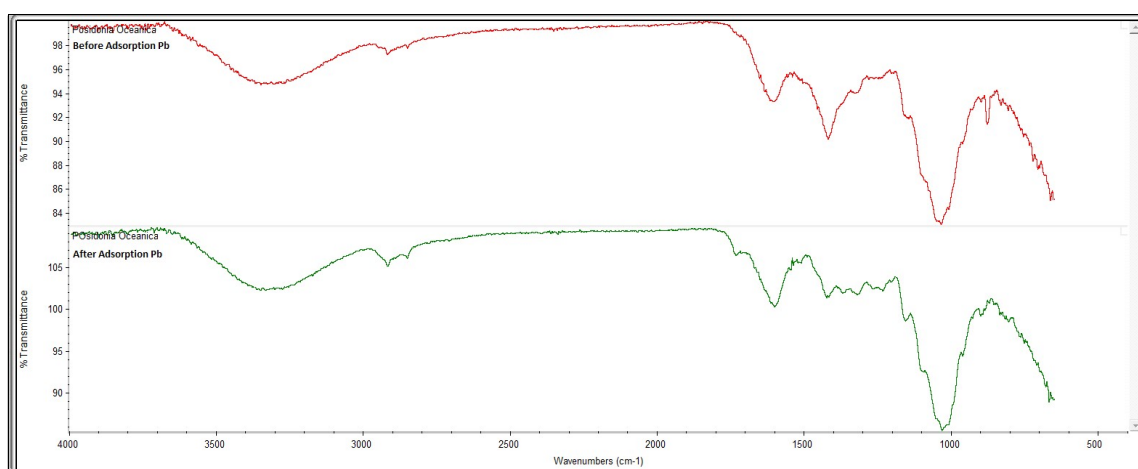


Figure 2 FTIR spectra of P.O before and after the adsorption process

3.2. Batch mode

3.2.1 Effect of Time.

The removal percentage of dyes over the adsorbents can be calculated as: $R\% = [(C_i - C_t)/C_i] \times 100$ (12, 13) where R% is the removal percentage, $C_i = 10$ ppm is initial concentration of dye solution, C_t is the concentration of Pb ions at contact time estimated from the concentration dependence of absorbance fit. Figure 3. shows the time dependence of Pb²⁺ removal at room temperature. The removal of the Pb²⁺ increase as the contact time increases. There is no finite time was observed for the removal up to at 6 hrs. The removal percentages of Pb²⁺ on the surface of P.O were found to be 48.1%, 58.1% and 88.1 % at 1, 2 and 6 hrs. The inserted

equations in Figure 2 describe the removal percentage (R%) as function of time (t) for the ion. The initial removal rate (dR/dt) could be derived from the equations when t=0. The initial removal rate for Pb²⁺ was found to be 23.9 hr⁻¹ using P.O.

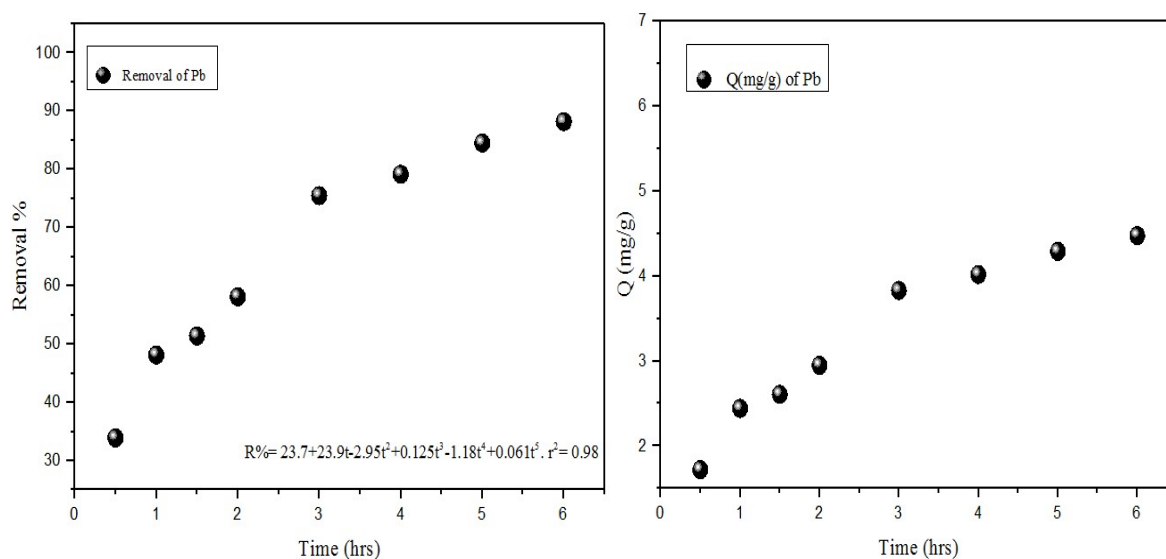


Figure 3. the time dependence of removal percentages and capacities at room temperature. The volume, concentration and pH of the dyes solution are 50ml, 10ppm and 4 respectively.

3.2.2: Effect of adsorbent mass:

The amount of the dye adsorbed by one gram of the oxides (Q) was calculated as following: $Q \text{ (mg/g)} = [(C_i - C_f) \times V] / W$ (12,13), where t= 2 hrs is the contact time, V= 50 ml is the volume of Pb²⁺ ions solution and W is the mass of oxides. The contact time is evidently chosen as 2 hrs to display the changes in the removal percentages. As shown in Figure 4, Q decreases from 7.4 to 2 mg/g as the mass of adsorbents increased 0.05 to 0.25 g. The maximum capacity of adsorbent $Q_{\max}$ can be estimated from the intercept of the liner fit of $1/Q_t$ at Y axis. $Q_{\max}$ of Pb²⁺ is 28.81 mg/g. This amount is lower than those observed by Wassila, etal for the divalent metal ions Pb(48.33 mg/g), Cu(43.9 mg/g), Ni(41.02 mg/g), Zn(37.90 mg/g) and Cd(30.22 mg/g) at pH 6 (11).

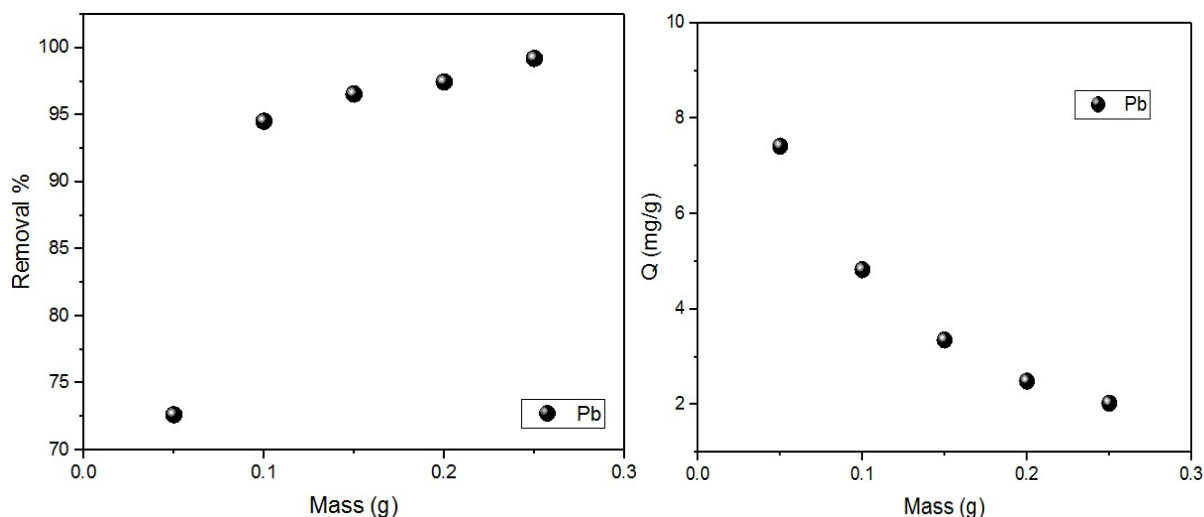


Figure 4. The effect of adsorbent mass on the removal percentages and capacities. The time, volume, concentration and pH of Pb²⁺ solutions are 2hrs, 50ml, 10ppm and 4 respectively.

3.2.4: Effect of temperature:

Temperature has an important impact on the adsorption process. An increase in temperature helps the reaction to compete more efficiently with e^-/H^+ recombination. The removal of Pb²⁺ was investigated at 25, 30, 40 and 60 °C. The obtained results are

illustrated below in Figure 5. The removal of Pb increased as temperature increased. For instance, the removal of Pb increased from (~86 %, 4.4 mg/g) at 25°C to (~96%, 4.9 mg/g) at 60°C. This result is agreed with normal expectations, and is a consequence of the increase of adsorption strength and the concentration of active intermediates with temperature. The energy of activation (E_a), was calculated from the Arrhenius plot of $\ln R$ vs $1000/T$. Arrhenius plot shows that the activation energy of the removal is positive and equal to 4.1 kJ/mole. This suggested that the Pb²⁺ removal by P.O is spontaneous with an endothermic nature.

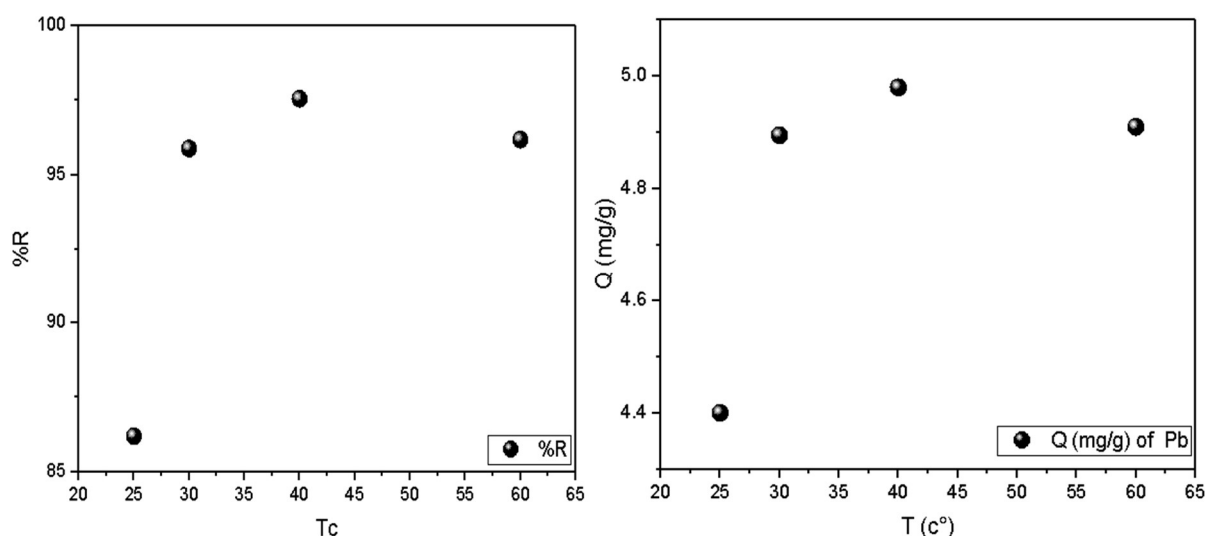


Figure 5. the effect of temperature on the removal percentages and capacities. The time, volume, pH and concentration solutions are 2hrs, 50ml, 4 and 10ppm respectively

3.2.4: Effect of pH:

The pH of solutions is a key parameter in dye adsorption. The magnitude of electrostatic charges which are impacted by the ionised molecules is controlled by the solution pH. As a result, the rate of adsorption will vary with the pH of the medium used. In general, at low solution pH, the percentage of removal will decrease for cations adsorption, while for anions the percentage of removal will increase. This is due to the increase in the positive charge on the solution interface and the adsorbent surface. In contrast, high solution pH is preferable for cation adsorption but shows a lower efficiency for anion adsorption. The positive charge at the solution interface will decrease while the adsorbent surface appears negatively charged.

To study the effect of pH, experiments were carried out at various pH values, ranging from 2 to 10 for constant Pb²⁺ ions concentration (10 ppm) and adsorbent mass (0.1g). Figure 6 presents the removal of Pb²⁺ as a function of pH. It was observed that the removal of Pb using the P.O decreases as pH increased. The highest removal of Pb was recorded at pH= 4 around (78.1 %, 3.71 mg/g) whereas the lowest removal of Pb was recorded at pH= 10 around (4.6 %, 0.22 mg/g). The removal efficiency of the adsorbents is clearly decreases as the acidity decreased. Similar trend was observed by Allouche in which Q_{max} for lead was found to 140 and 109 mg/g at pH 4 and 5 respectively (14). Unexpectedly, the removal percentage of Pb²⁺ was found to be (34.3 %, 1.63 mg/g) at pH 2.

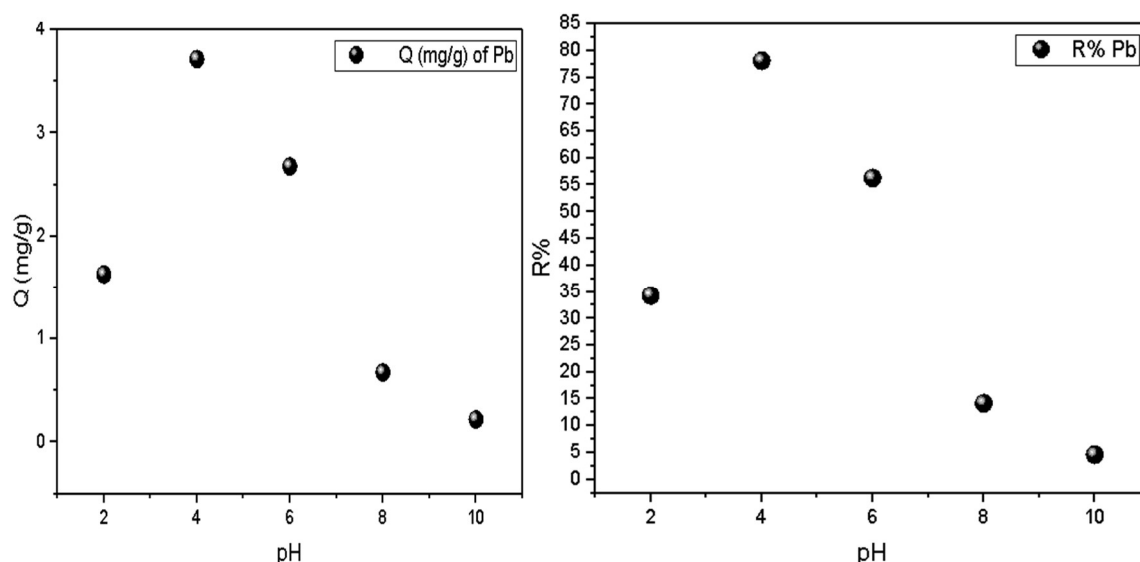


Figure 6. the effect of pH on the removal of removal percentages and capacities. The time, volume and concentration of solution are 2hrs, 50ml and 10ppm respectively.

IV. CONCLUSION

The removal of Pb²⁺ ions from aqueous solution using the posidonia oceanica has been reported. The seagrass were collected, dried and characterized by SEM, POM and FTIR measurements. The removal of Pb increases as the physical parameters: time, temperature, adsorbent mass increased. The initial rate of Pb²⁺ removal was determent to be 23.9 hr⁻¹. The maximum capacity of P.O is 28.82 mg/g. The highest removal efficiency was recorded at pH=4 (78 %, 3.71 mg/g) where the lowest removal was observed at pH=10 (9.1%, 0.22 mg/g). The study showed the nature of removal reaction is endothermic and its activation energy is positive and equal to 4.1 kJ/mole.

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