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Adsorption and thermodynamics of lead (II) using seeds of watermelon (SWM) as a low cost sorbent

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***Abstract*— The removal of lead(II) ions from aqueous solutions using seeds of watermelon (SWM) by adsorption technique has been studied. The adsorption % of Pb^{2+} at pH 6 and 120 min is ~ 97%. Solution pH, initial concentrations of Pb^{2+} ions and seeds of watermelon, shaking time and temperature were optimized. The Freundlich and Langmuir equations were applied. The thermodynamic parameters *viz.* the change in Gibbs free energy change (ΔG°, - 20.96 kJ mol^{-1} at 333 K), enthalpy (ΔH°, 18.51 $Jmol^{-1}$) and entropy (ΔS°, 63.00 $Jmol^{-1} K^{-1}$) were also evaluated. The negative ΔG° value indicates that the adsorption is spontaneous thermodynamically. The removal of ~97% of Pb^{2+} ions was attained using 2 g/L SWM applying the suggested optimum experimental conditions. The procedure was successfully applied to remove Pb^{2+} from aqueous and different natural water samples.**

***Index Terms*— Seeds of watermelon; lead, adsorption, thermodynamic parameters, EDX.**

I. INTRODUCTION

The toxicity of metals in solution at high concentrations affects human, animal and vegetation [1, 2]. Water and soil pollution with heavy metals has increased and spreading throughout the world in the last five decades as a result of industrial activities. Some metals are toxic and dangerous to environment due to their strong tendency to accumulate in food chains [2-8]. Cd, Pb, Cr, As, and Se are constantly released into the environment. Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations and tanning, metal finishing industries, chemical and battery manufacturing, paints and metal extraction [2, 8-9]. Wastewaters from a chemical industry polluted by heavy metal ions represent a hazard for all living organisms especially for human [10, 11]. These heavy metals can cause danger for ecosystems and human health if they are discharged into natural water resources and may pose finally a serious health hazard [12-14]. These toxic metals accumulate by living organisms producing diseases and disorders [15]. Our present work aims to study the adsorption characteristic of Pb^{2+} on the concentrating of seeds of watermelon, pH, contact time, initial Pb^{2+} concentration. The data have been analyzed by adsorption isotherms, kinetics and thermodynamic parameters and compared with other studies on Pb^{2+} [16-25]. Also, seeds of watermelon as a cheap sorbent and may represent an environmental problem was used for the removal of Pb^{2+} ions from aqueous solutions.

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II. EXPERIMENTAL

2.1- Chemicals and solutions

Unless otherwise stated, all chemical reagents used in this study were of analytical grade. Pb^{2+} stock solution, (1000±2 mg l^{-1}) was prepared from Merck CRM (Germany), $Pb(NO_3)_2$ in HNO_3. The working solutions were made by diluting with deionized water. Standard aqueous solutions of HNO_3 and/or NaOH were used for controlling the pH.

The seeds of watermelon sample used in this study were obtained from watermelon (Aljorma melon or Citrullus lanatus) which cultivate for the purpose of the production of seeds in Mansoura city, Egypt. The sample was washed, dried for 2 h in large trays in an oven maintained at 125 °C, allowed to cool to room temperature (25 °C) and crushed. The sample was sieved and that with size (25 - 63 µm) was used in the experiments and stored in a desiccator.

The waste materials of plants have the same chemical compositions which are usually composed of lignin and cellulose as the main constituents. Other components are hemicellulose, lipids, proteins, simple sugar, starches, water and hydrocarbons [26]. The IR spectrum of seeds of watermelon is similar to these compounds.

2.2. Natural water samples

Sea water was collected handly from Red sea at Sharm El- Sheikh, Nile water from Mansoura City, ground water from Mansoura City. The samples were filtered before use.

2.3. Apparatus

Varian AA240FS Atomic Absorption Spectrometer (AAS)- Australian, was used for the determination of lead concentration at 217 nm. The IR was recorded on a Mattson 5000 FT-IR Spectrophotometer and 8201 PC Shimadzu FT-IR Spectrophotometer, Japan using KBr disc. The X-ray diffraction was recorded *on* a XRD Bruker, Germany. The scan electron microscope analysis was undertaken on a SEM-

JEO/JSMS 410, Japan with energy dispersive X- ray EDX unit oxford, and England. The pH was measured using a Symphony pH meter, USA, provided with a glass electrode. The shaking of solutions was carried out with a 3500 VWR, USA digital shaker. Stirring of solutions was carried out with a magnetic stirrer Model Jenway 1000, England. Sartorius digital balance, Germany was used for weighting. Also, Milli-Q A10/ Elix Millipore- deionizer- France was used for deionized water.

2.4. General procedure

Known volumes of Pb^{2+} solution with different concentrations were pipetted into a quick fit glass bottles containing sorbent and completed to 50 ml with bidistilled water at the optimum pH. The resulting solutions were then stirred with a magnetic stirrer or shaker at 250 rpm for stirrer and 270 rpm for shaker. The samples were taken at fixed time intervals to enable the study of kinetics of the adsorption process. The samples were subsequently filtered off and the residual Pb^{2+} content in the filtrate was analyzed. The adsorption percentage of Pb^{2+} from its solutions was calculated from the relationship:

$$\% \text{ Adsorption} = (C_i - C_r) / C_i \times 100$$

Where C_i is the initial concentration of Pb^{2+} and C_r is the residual concentration. The metal uptake q (mg g^{-1}) was calculated as:

$$q = [(C_i - C_r) / m] . V$$

Where m is the quantity of adsorbent (mg) and V is the volume of the suspension (ml).

1.5. *Application*

To assess the applicability of the procedure, another series of experiments was conducted on 50 ml suspension of clear and pre-filtered natural water samples with an initial pH adjusted to the optimum value. These suspensions were placed in a glass beaker containing definite concentration of metal ion and the optimum concentration of the sorbent at 25 °C and stirred magnetically for the optimum time at 250 rpm of Pb^{2+} ions or shaking at 270 rpm. Unless otherwise stated, the experiments were conducted at room temperature.

III. Results and Discussion

(a) 3.1. Factors affecting the adsorption technique

(b) 3.1.1. Effect of pH

In order to study the effect of pH on Pb^{2+} adsorption by seeds of watermelon, experiments were carried out at pH 3, 6, 7 and 9. From Fig. 1, it is observed that there is no significant increase in percentage of Pb^{2+} adsorbed with change in pH (7-9). Similar observation was reported by Gilbert et al. [27]. This suggests that adsorption of Pb^{2+} is not largely influenced by pH. This could mean that ion-exchange mechanism is not strictly the mechanism by which the metal ions are being adsorbed onto the surface of seeds of watermelon. It is possible that the lone pair of electrons on some of the functional groups may play a major role in the removal of Pb^{2+} ions. It is thought the formation of complexes between Pb^{2+} and watermelon seeds. The pH 6.0 was selected for further experiments.

3.1.2. Effect of Pb^{2+} concentration and sorbent dose

The effect of initial Pb^{2+} concentration (1 - 150 mg L^{-1}) on its adsorption by 0.1 g seeds of watermelon after shaking (1 - 120 min) was shown in Fig. 2 which illustrates the increase of uptake as the Pb^{2+} concentration increases. The effect of varying amounts of seeds of watermelon (0.025- 0.3 g), on the adsorption of 5 mg L^{-1} Pb^{2+} from aqueous solutions was depicted in Fig. 3. The data showed that the adsorption increases as the amount of seeds of watermelon increases. Moreover, 2 g L^{-1} dose of watermelon seeds was optimum one for further experiments.

3.2. Kinetics of the adsorption process

The data of the adsorption of Pb^{2+} indicate that the adsorption is quite rapid firstly, which may be attributed to higher collision between Pb^{2+} and sorbent. On the basis of the results, 60 min of shaking was found suitable for maximum adsorption and were used in all subsequent measurements. The data in Fig. 1 were re-plotted against the square root of the shaking time; the linear correlation may verify the Morris-Weber equation. Fig. 4 shows that two distinct regions were observed, linear portion due to the boundary layer effect and a second portion due to the intra-particle diffusion effect [28]. However, the line is not linear indicating that intra-pore diffusion is not the limiting step in sorption of Pb^{2+} by watermelon seeds.

The initial rate of intra particle diffusion (K_d) was evaluated as 0.060 mg g^{-1} $min^{-0.5}$, which give indication about the mobility of the Pb^{2+} toward the watermelon seeds.

The kinetic for the adsorption of Pb^{2+} onto watermelon seeds was examined by Bangham equation [29]:

$$\text{Log log } [C_i /(C_i - qm)] = \log (K_o\, m/2.303V) + \alpha \log t,$$

where C_i corresponds to the initial concentration of Ni(II) ions, q is the amount of Ni(II) ions adsorbed (mg g^{-1}), m is the quantity of sorbent (mg) and V the volume of the suspension (ml), t is the time (min), K_o is the proportionality constant, and α is Bangham equation constant. Plotting of Log log [C_i / (C_i - q_m)] vs. log t gave a straight line. The results show that the diffusion of Pb^{2+} into watermelon seeds pores played a role in the adsorption process. The deduced values of K_o and α were 0.003 and 0.185, respectively.

Also, the kinetics data for Pb^{2+} adsorption by watermelon seeds were tested by Lagergren equation. The linear plot of log (q_e - q) versus shaking time (t) shows the conformity of the first-order. The value of K_{ads} was calculated to be 0.0602 g $mg^{-1}min^{-1}$.

The adsorption of Pb^{2+} onto watermelon seeds was examined by pseudo second order kinetic model. The plot of t/q_t versus time (t) gives straight line as shown in Fig. 4. The value of k_2 was 0.411 g mg^{-1} min^{-1}.

Also, the adsorption of Pb^{2+} onto watermelon seeds was examined by linear form of Elovich model which gave a straight line as shown in Fig. 5 by plotting q_t vs. ln t. Also The Elovich coefficients related to initial adsorption rate (a) and surface coverage (b) were calculated to be 10.308 mg g^{-1} min^{-1} and 6.821 mg g^{-1} min^{-1}, respectively.

3.4. Adsorption isotherms

A straight line is formed applying the Langmuir equation to the Pb^{2+} adsorption by watermelon seeds by plotting of $1/q_e$ *vs.* $1/C_e$ suggesting the applicability of the Langmuir model. The values of $q_{max,}$ k_L and the correlation coefficient (r) were 9.643 mg g^{-1}, 5.926 L mg^{-1} and 0.9591, respectively and the value of equilibrium parameter (R_L) was 0.01 indicating the favorability of the adsorption.

The Freundlich equation based on adsorption on a heterogeneous surface showed a linear plot of lnq_e vs. lnc_e. The parameters k_F and n were 11.927 mg g^{-1} and 1.603 respectively.

Temkin isotherm was applied by plotting q_e versus C_e which gave a straight line as shown in Fig. 6. Both Temkin isotherm constant (b) and equilibrium binding constant (k_t) were determined from the slop and the intercept to be 1.809 kJ mol^{-1} and 150.11 Lg^{-1}, respectively.

The Dubinin-Radushkevich (D–R) isotherm equation was applied. The linear form (Fig. 7) gives a straight line. From this figure, we determined the activity-coefficient (β) which evaluated as (0.0597 mol^2 kJ^{-2}) and the mean sorption energy (E) (2.894 kJ mol^{-1}) were determined.

3.5. Effect of temperature and thermodynamic parameters

In this study, a series of experiments were conducted on the adsorption of 5 mg L^{-1} Pb^{2+} onto 0.1 g of SPW at 278, 283, 298, 313 and 333 K to investigate the effect of temperature on the sorption dynamics at different stirring times. Such results may either be attributed to the creation of some new active sites on the sorbent or to the acceleration of some originally slow adsorption steps. Moreover, the enhancement of mobility of Pb^{2+} from the bulk of solution towards the adsorbent surface should also be taken into consideration. There was a decrease in the equilibration time to reach to a 100% for lead adsorption. Accordingly, complexation may occur between Pb^{2+} and oxygen atoms on the watermelon seeds surface. The simple adsorption procedure presents here may find application in the industrial wastewater treatment for the removal of Pb^{2+}.

In order to investigate the thermodynamic parameters for the adsorption of Pb^{2+} by seeds of watermelon, the distribution coefficient K_d was calculated at 278, 283, 313, 333 K give 0.636, 0.948, 0.889, and 3.532 L g^{-1} respectively. These results show that the K_d increases with temperature and revealing that the sorption of Pb^{2+} by SPW may be endothermic. The ΔHº and ΔSº were calculated by plotting of ln K_d against 1/T (Fig. 8). The calculated ΔH° was found to be 18.51 $Jmol^{-1}$. The positive value of ΔH° clarified that the sorption process is endothermic. The ΔS° was 63.00 $Jmol^{-1}$ K^{-1}. Moreover, the ΔG° values were -17.50, -17.81, -19.70, and -20.96 kJ mol^{-1} at 278, 283, 313 and 333. The negative ΔG° values indicate that the adsorption is feasible and spontaneous thermodynamically.

3.6. Application

To investigate the applicability of the recommended procedure, a series of experiments were performed to recover 5 mg L^{-1} of Pb^{2+} added to aqueous and some natural water samples. The adsorption experiments were carried out using 50 mL sample solutions with their initial pH values. The results obtained in Table 1 showed that the recovery was satisfactory and quantitative.

Table 1 Recovery of Pb^{2+} added to some water samples using 0.1 g of SWM sorbent.

Sample (location)	Added (mg l^{-1})	Adsorbed (mg l^{-1})	Re %
Distilled water	5	4.84	96.8
Tap water (our laboratory)	5	4.76	95.2
Nile water (Mansoura City)	5	4.82	96.4
Underground water (Mansoura City)	5	4.68	93.6
Sea water (Sharm El-Sheikh)	5	4.72	94.4

3.7. XRD, EDX and SEM studies

The lead sorption by SWM is interpreted by XRD, EDX and SEM analyses. Powered XRD studies help in understanding the changes occur on the structure of SPW sorption. Figure 9 a, b provided clear evidence of modification in the surface morphologies in form of cleavage. EDX technique shows the effective mass concentration of different elements involved in the investigated solids on their top surface layers. The EDX graph (Fig. 10 a, b) showed the presence of Pb^{2+} after treatment. The SEM image of SWM before and after lead adsorption (Fig. 11 a, b) is corresponding to the morphological changes in the surface of the adsorbents in the coverage of pores of SPW due to the adsorption of lead. It is seen from this figure that the adsorbed solid have high lead particles.

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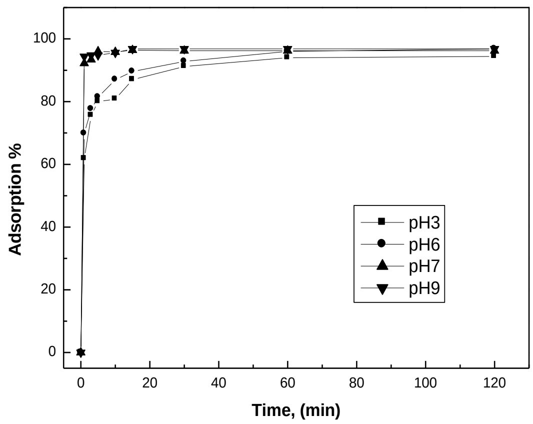


Fig. 1: Adsorption % of 5 mg l^{-1} Pb^{2+} by 0.1 g SWM *vs* shaking time at different pH's.

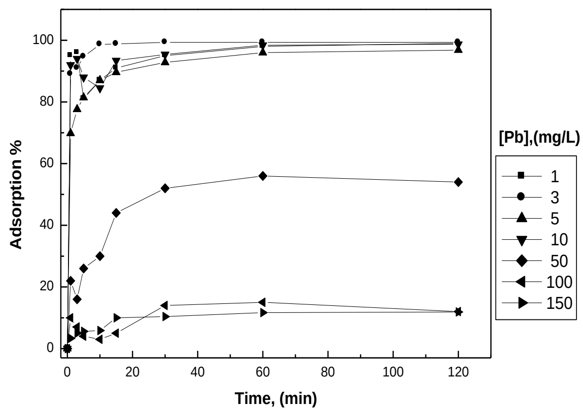


Fig. 2: Adsorption % of Pb^{2+} concentration (mg l^{-1}) on SWM at different shaking times.

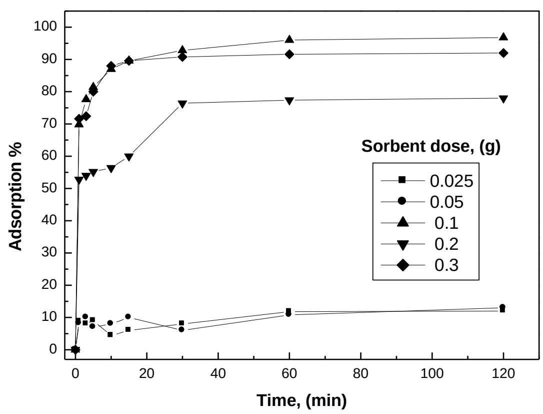


Fig. 3: Effect of SWM dose on adsorption % of Pb^{2+} at

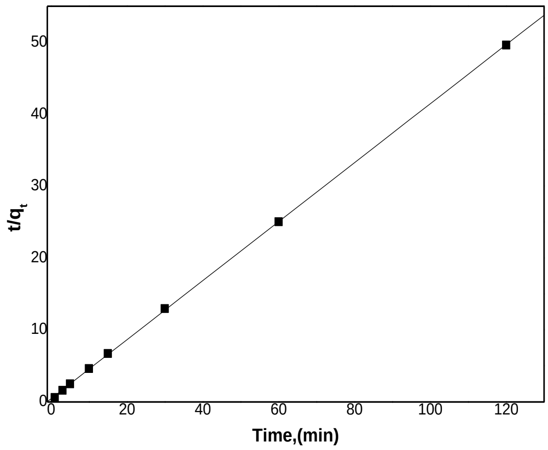


Fig. 4: Plot of (t/q_t) vs. stirring time (t) for the adsorption of Pb^{2+} by 0.1 g SWM at pH 6.

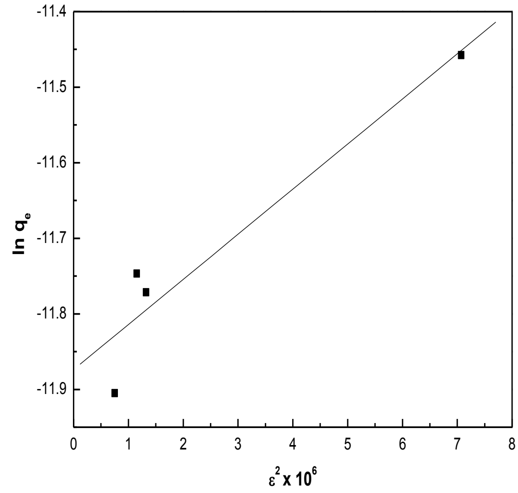


Fig. 7: D-R isotherm for Pb^{2+} adsorption onto SWM

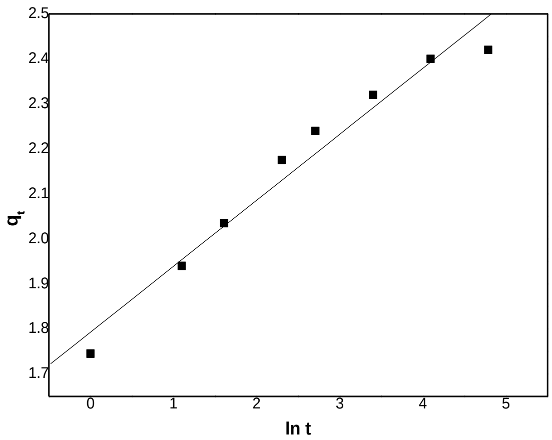


Fig. 5: Plot of q_t vs ln t for the adsorption of Pb^{2+} by 0.1 g SWM at pH 6.

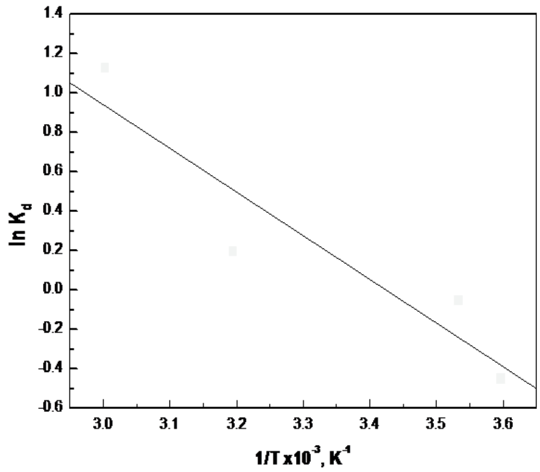


Fig. 8: Thermodynamic distribution coefficient (K_d) calculated for the adsorption of Pb^{2+} on SWM as a function of temperature.

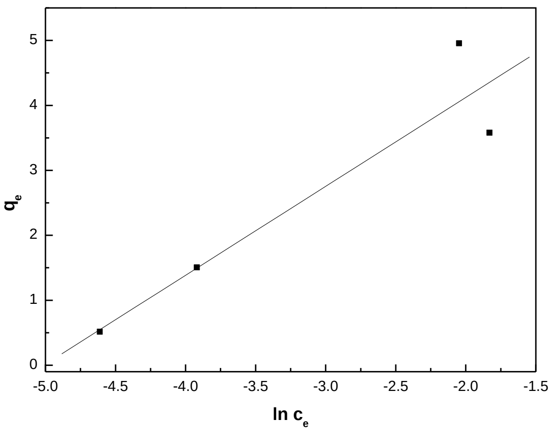
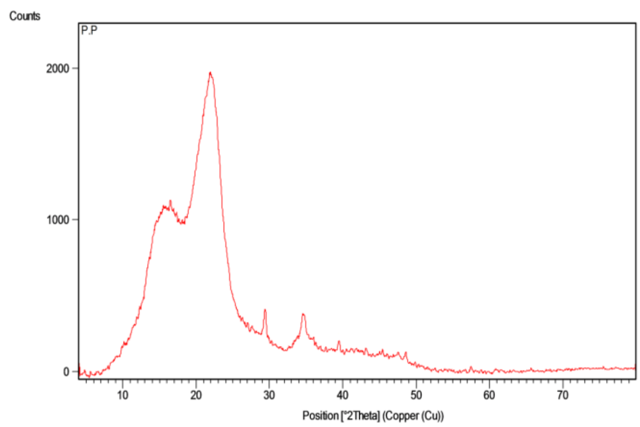


Fig. 6: Plot of q_e vs. ln c_e for the adsorption of Pb^{2+} by 0.1 g SWM at pH 6.



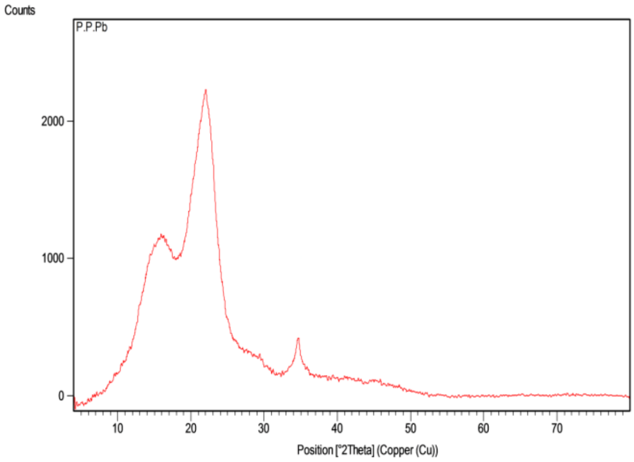
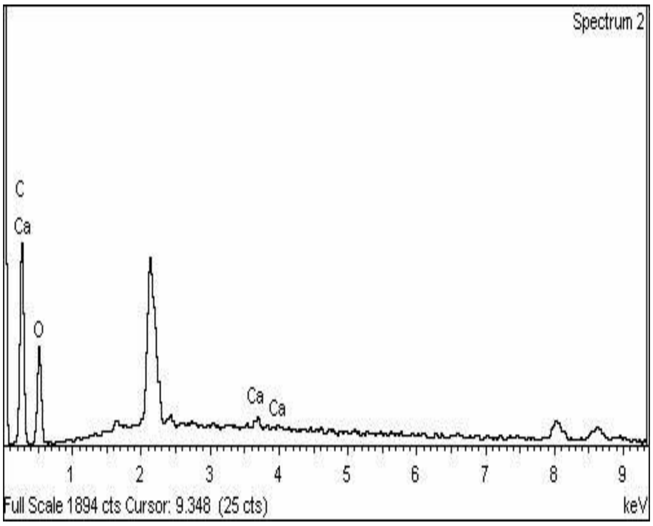


Fig. 9: (a) XRD of SWM before treatment, **(b)**after treatment with Pb^{2+}.



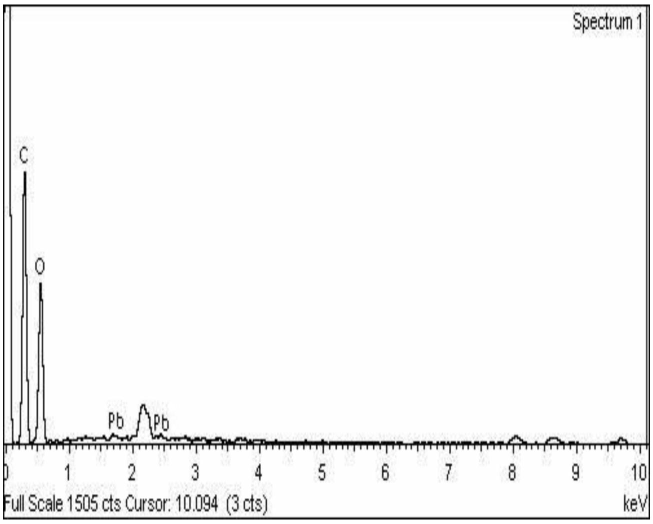
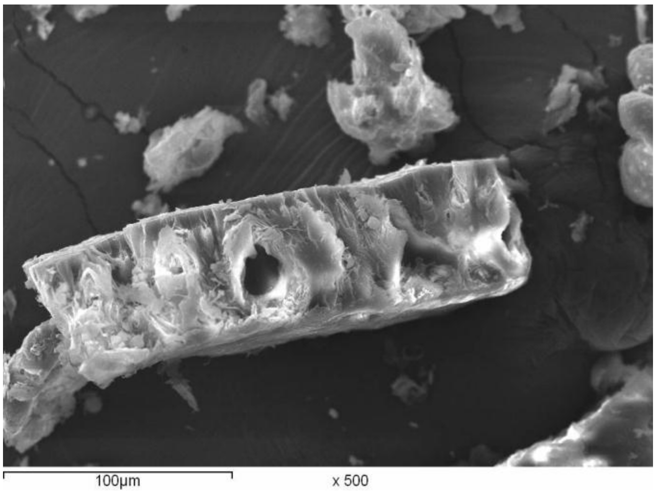


Fig. 10: (a) EDX of SWM before treatment, **(b)** after treatment with Pb^{2+}.



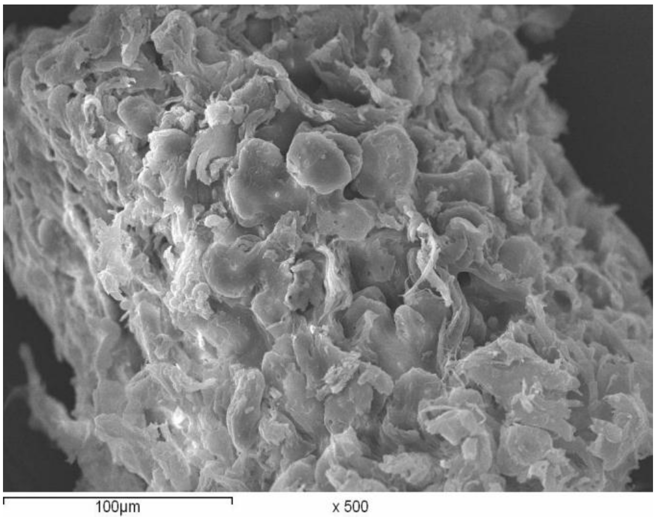


Fig. 11: (a) SEM of SWM before treatment, **(b)** after treatment with Pb^{2+}.