Study on Adsorption of Lead Ions from Industrial Wastewater by Dry Cabbage Leaves

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In this study, cabbage leaves waste was used as an adsorbent for removal of Pb(II) ions from aqueous solutions using batch equilibrium process. The initial concentrations of Pb(II) ions were varying between 10 to100 mg/L, temperature was 25 ±2 C °, and agitation speed was 200 rpm for all experiments. The influence of pH, contact time, adsorbent dosage and particles diameter of adsorbed material on adsorption process were investigated. The experiments showed that highest removal rate was 95.67% at solution of pH 6, contact time 120 min, adsorbent dosage 0.5 g per 50 mL of solution, adsorbent particles diameter 1 mm and initial concentration of 50 mg/L. It was found that Langmuir model is better than Freundlich model. Two simplified kinetic models including pseudo-first-order and pseudo-second-order equations were selected to follow the adsorption process. Results showed that the adsorption of Pb(II) ions could obey pseudo-second order equation.

Keywords: Batch adsorption, cabbage leaves, heavy metals, lead ions

Environment have been polluted by several sources such as industrial and agriculture effluent, heavy metals being considered to be one of the most toxic materials in these wastes [1].

Lead is a non-biodegradable material, which can be aggregated inside the living tissues. Therefore, this lead to make this material concentrated within the food-chain, thus in the human body as well [2].

The indiscriminate disposal of lead in many industrial activities like acid batteries, pulp and paper, petro-chemicals. creat a threat worldwide, and refineries, printing, pigments, photo- graphic materials, explosive manufacturing, ceramic, glass, paint, oil, metal, electronic goods, wood production for instance as well as many other activities for example, combustion of fossil fuel, forest fires, mining activity, automobile emissions and sewage wastewater were considered other ways that release to lead ions into the environment [3, 4].

Removing lead from the effluent have been carried out by many techniques such as coagulation- flocculation, ion exchange, filtration, electrochemical treatment, and reverse osmosis and membrane technologies [5, 6].

The choice of these processes depend on many factors including flow rates and metal ion concentration, the industrial application of these processes is restricted by the operating costs leading to limitation of utilizing such removing techniques [7].

Nowadays, the researchers are focusing on using natural products for the purpose of removal heavy metal by adsorption. The use of the natural products was due to their abundance as agriculture waste product which gives an economic benefit [8, 9].

Lignin and cellulose that possess these natural products are the molecules which include the polar functional groups. Alcohols, aldehydes, ketones, carboxylic, phenolic and these groups have the ability to some extent to bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution [10, 11]..

Several previous studies indicate the removal of lead ions using agricultural wastes as low-cost adsorbents e.g. tea waste, rice husk, pinus sylvestris sawdust, green coconut shells, bael tree leaf powder, date tree leaves and etc. [12-18].

The objective of this work is to use dry cabbage leaves, which are agriculture waste, as a low-cost adsorbent material to remove lead ions from aqueous solutions. The effect of various parameters such as *p*H, contact time and adsorbent dose at different initial concentration on adsorption process were studied.

Experimental part

Material and methods

Cabbage leaves were collected from the local market.and washed twice in distilled water to remove the dust, dried for 72 h at temperature 100 °C, ground using laboratory mill, then sieved to 0.5–3 mm and stored in plastic containers ready for use.

A stock solution of Pb(II) ions at a concentration of (100 mg/L) was prepared by dissolving requested amount of $(CH_3COO)_2$ Pb $3H_2O$ (Romania) in distilled water. The concentration range of lead ions were varied between 10 to 100 mg/L, and were kept at room temperature. Before starting *p*H of solutions were adjusted to the required value by adding 0.1 M HCl and 0.1 M NaOH solutions.

The experiments were carried out in 100 mL conical flasks and the total volume of the reaction mixture was kept at 50 mL. Optimum values of parameters affected on adsorption of Pb(II) ions onto dry cabbage leaves were determined. First of all, experiments were carried out by changing the *p*H values between 3 and 8, effect of contact time on adsorption was investigated and experiments

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performed in time periods varying between 10 and 120 min. In order to determine adsorbent dosage, the amount of adsorbent was varied between 0.125 and 1 mg/ 50 mL of solution. Moreover, the effect of particles diameter of adsorbent on adsorption was investigated by performing the experiments between 0.5 and 3 mm. The initial concentrations of Pb(II) ions were varying between 10 and 100 mg/L, temperature was 25 ±2 C ° and agitation speed was 200 rpm for all experiments. After equilibrium, 20 mL as samples were taken from the flask. These samples were filtered through Whatman filter paper No. 40 and the concentration of heavy metal ions in the solutions was analyzed by Atomic Absorption Spectrometer: AAS (GBC 933 plus, Australia). The percent of removal efficiency (R %) was calculated using equation (1).

$$R\% = \frac{C_o - C_e}{C_o} * 100 \quad (1)$$

Results and discussions

Influence of pH

The influence of *p*H on Pb(II) ions removal efficiency by dry cabbage leaves is represented in figure 1 and it can observe that increasing in Pb(II) adsorption with increasing *p*H from 3 to 6 and slightly decreased by increasing *p*H value up to 6. This trend was similar for all initial concentrations. The dropping of removal efficiency at *p*H higher than 6 could be assigned to the complexation of Pb(II) ions by OH^- groups, which would reduce metal adsorption [19]. As shown in figure 1, the optimum *p*H for Pb(II) removal by dry cabbage leaves was 6.

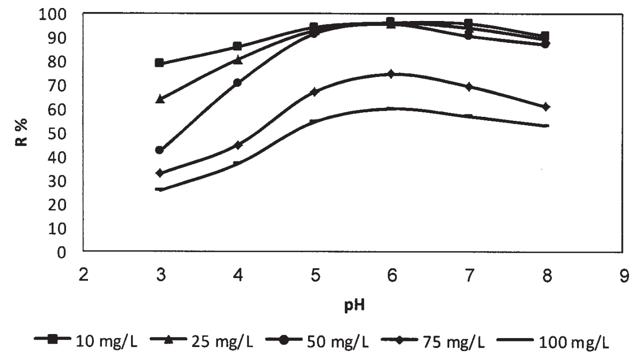

Fig.1. Effect of *p*H on removal efficiency of Pb(II) ions onto dry cabbage leaves for different initial concentrations (contact time = 120 min and adsorbent dosage= 0.5 gm)

Influence of contact time

Adsorption of Pb(II) were measured at given contact times for five different Pb(II) ions initial concentrations of 10, 25, 50, 75 and 100 mg/L. From figure 2, the results reveal that the rate of percent lead removal is higher at the beginning. This is probably due to larger surface area of the leaves being available at beginning for the adsorption of Pb(II) ions. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles [20]. Most of the maximum percent Pb(II) ions removal was attained after about 120 min of contact time at different initial concentrations. The increasing contact time increased the Pb(II) ions adsorption and it remains constant after equilibrium reached in 120 min for different initial concentrations.

Influence of adsorbent dosage

The effect of adsorbent dosage on the adsorption of Pb(II) ions was investigated and the results are shown in figure 3. The experiments were performed with 0.125, 0.25,

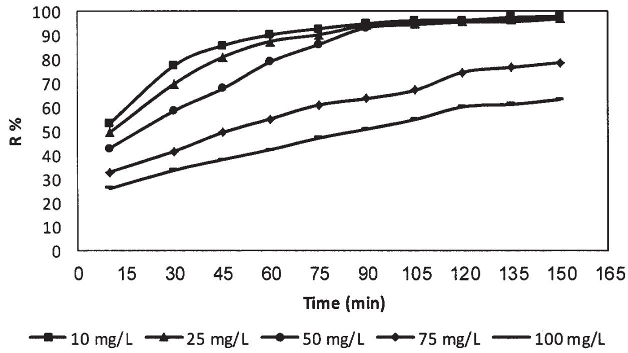

Fig. 2. Effect of contact time on removal efficiency of Pb(II) ions onto dry cabbage leaves for different initial concentrations (pH= 6 · and adsorbent dosage= 0.5 gm)

0.375, 200, 0.5, 0.875 and 1 gm adsorbent dosages in 50 mL sample solution. The experiments were carried out at initial concentration for Pb(II) between 10 and 100 mg/L, 200 rpm agitation speed and 120 min-equilibrium time. It was observed that increasing in adsorbent dosage increases the removal efficiency however a significant change was not determined after 0.5 gm. This may be due to overlapping of adsorption sites as a result of over-crowding of adsorbent particles [21]. Therefore, optimum adsorbent dosage of cabbage leaves in the adsorption for Pb(II) was 0.5 gm.

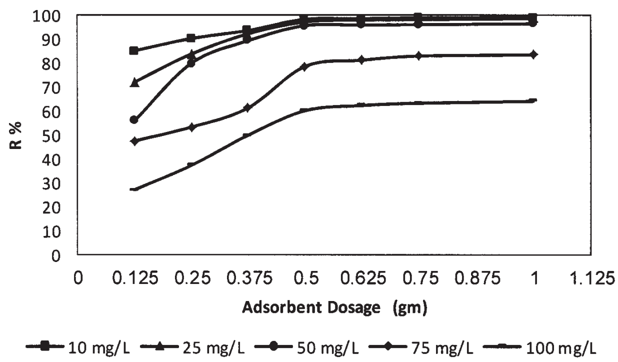

Fig.3. Effect of adsorbent dosage on removal efficiency of Pb(II) ions onto dry cabbage leaves for different initial concentrations (pH=6 and contact time = 120 min).

Influence of adsorbent particles diameter

The particles diameter of adsorbent materials is another important variable during metal adsorption. The effect of particle diameter was investigated for Pb(II) ions solution at four different particles diameter, the *p*H kept at the optimum value and the initial concentration between 10 to 100 mg/L. Figure 4 shows the percentage removal at different particles diameter of cabbage leaves. It is found that the value of cabbage leaves particles diameter has a great effect on the adsorption efficiency. An increase in the particles diameter from 0.5 mm to 3 mm, causes a decrease of adsorption efficiency for all initial concentration of Pb(II) ions in solution, which would be anticipated with the decreasing the surface locations of ion exchange between the metals and particles. The optimum particles diameter of adsorbent materials was 1 mm because there was no significant difference in the adsorption efficiency when using 0.5 mm.

Adsorption isotherm models

Freundlich and Langmuir isotherm models most widely models used discussed adsorption isotherm [22-30]. In

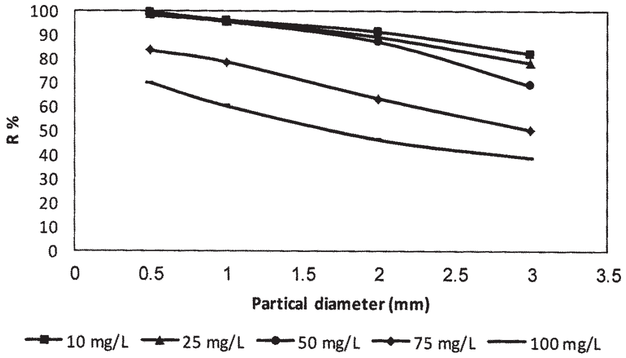

Fig. 4. Effect of particle diameter of adsorbent on removal efficiency of Pb(II) ions onto dry cabbage leaves for different initial concentrations (pH=6 and contact time = 120 min).

equations (2) and (3) were described adsorption by using Freundlich and Langmuir isotherm models respectively.

$$q_e = KC_e^{1/n} \qquad (2)$$

where q_e is the adsorbed metal ions (mg/g), C_e is metal ions concentration in the solution at equilibrium (mg /L), K (mg/g) (L/mg) $^{1/n}$ and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively.

$$q_e = \frac{q_m b C_e}{1 + bC_e} \qquad (3)$$

where: q_e is the adsorbed metal ions (mg/g), q_m is the maximum sorption capacity for monolayer coverage (mg/g), b is the constant related to the affinity of the binding site (L/mg), and C_e is metal ions concentration in the solution at equilibrium (mg /L).

The batch adsorption isotherm for Pb(II) ions using Freundlich and Langmuir isotherm models onto cabbage leaves are shown in figures 5. The parameters for each model were obtained from non-linear statistical fit of the equation to the experimental data (Statistica-version 6). The data in table 1 shows that Langmuir model is better than Freundlich model to study the adsorption for Pb(II) ions onto cabbage leaves depending on the value of correlation coefficients.

Adsorption kinetic models

Kinetic adsorption data for batch adsorption system of Pb(II) onto cabbage leaves was obtained as a function of time, by compared to the pseudo-first and the pseudo-second order kinetic models [24, 25]. Kinetic models of pseudo-first could be described in by eq. (4):

$$\ln(q_{eq} - q_t) = \ln q_{eq} - k_1 t \qquad (4)$$

where: q_{eq} is the amount of pollutant adsorbed at equilibrium (mg/g); q_t is the amount of pollutant adsorbed at time t (mg/g); and k_1 is the equilibrium rate constant of pseudo-first sorption (1/min). A plot of ln$(q_e$-$q_t)$ against t is given a straight line by fitted experimental data in eq. (4). The value of q_{eq} and k_1 can be determined from the slope and intercept, respectively.

The linearized pseudo-second-order kinetic model is representing in eq. (5):

$$\frac{t}{q_t} = \frac{1}{k_s q^2_{eq}} + \frac{t}{q_{eq}} \qquad (5)$$

where k_2 is the rate constant of adsorption, (g/mg.min), q_{eq} is the amount of pollutant adsorbed at equilibrium, (mg/g), q_t is amount of adsorbate on the surface of the adsorbent at any time, t, (mg/g). When applied eq. (5) on experimental data to plot t/q_t vs. t, the values of q_{eq} and k_2 represent slope and intercept of straight line, respectively.

Table 1

PARAMETERS OF ADSORPTION ISOTHERM MODELS FOR PB(II) IONS ONTO CABBAGE LEAVES.

Model	Parameters	value
Freundlich Equation (2)	K, (mg/g) (L/mg) $^{(1/n)}$	2.9226
	n	4.5153
	R^2	0.8949
Langmuir Equation (3)	q_m (mg/g)	6.3070
	b (L/mg)	0.9347
	R^2	0.9804

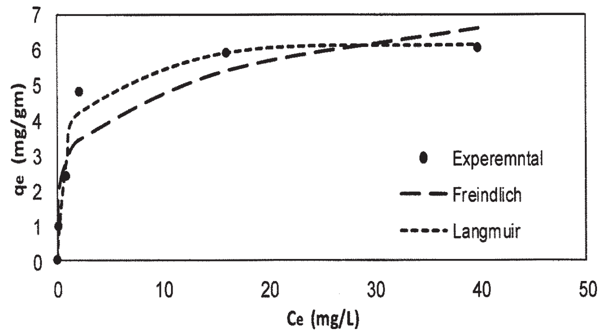

Fig. 5. Freundlich and Langmuir isotherm models of batch adsorption for Pb(II) ions onto dry Cabbage leaves

Table 2 shows that the values of correlation coefficient (R^2) indicate a better fit of pseudo- second- order model with the experimental data compared to pseudo- first- order model. The values of *qe* calculated from the second order kinetic model agreed very well with the experimental values, and the correlation coefficient is 0.99. Therefore, the second-order model can be applied for Pb(II) adsorption process. Figure 6 has shown that the adsorption of Pb(II) ions could be described by the pseudo-second order equation.

Thermodynamic parameters from adsorption

The important thermodynamic parameter including Gibbs free energy change ΔG^o, standard enthalpy change ΔH^o, and standard entropy change ΔS^o were calculated for this system by using the following equations [26, 27]:

Table 2

PARAMETERS OF ADSORPTION KINETIC MODELS FOR Pb(II) IONS CABBAGE LEAVES

Model	Parameters	Value
Pseudo-first-order Equation (4)	q_{eq} (mg/g)	5.3768
	K_1 (L/min)	0.6059
	R^2	0.9484
Pseudo-second-order Equation (5)	q_{eq} (mg/g)	5.3966
	K_2 (g/mg.min)	0.0113
	R^2	0.999

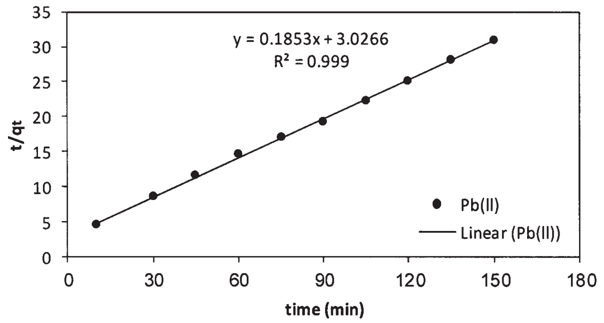

Fig. 6: Pseudo-second order kinetic model for batch adsorption for Pb(II) ions onto dry cabbage leaves

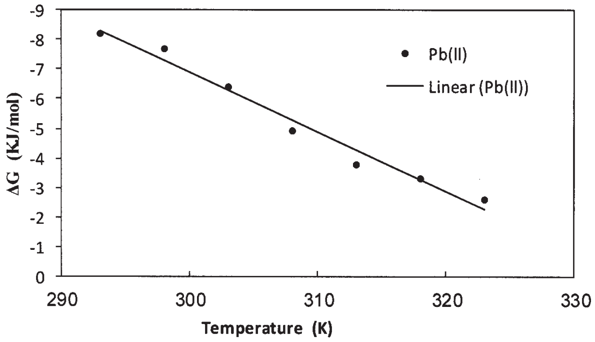

Fig. 7. Free energy change for Pb(II) adsorption

$$K_c = \frac{C_{ad}}{C_e} \quad (6)$$

$$\Delta G^\circ = -RT \ln K_C \quad (7)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (8)$$

where K_c is the equilibrium constant, C_{ad} is the amount of metal adsorbed on the adsorbent per liter of the solution at equilibrium (mg/L), C_e is the equilibrium concentration of the metal in the solution (mg/L), T is absolute temperature (K) and R is the universal gas constant (8.314 J/mol. K).

Thermodynamic parameters were obtained by varying temperature conditions over the range 20 to 50 C° at initial concentration of 50 mg/L and optimum: *p*H, contact time, dosage, and particles diameter. Figure 7 and table 3 show the thermodynamic constants of adsorption obtained for Pb(II) onto dry cabbage leaves. The negative values of ΔG at all studied temperatures indicated that sorption process is spontaneous. The negative value of ΔH, indicating the exothermic nature of the process, which further explain the fact that sorption efficiency decreased with the increase of temperature. The positive value of ΔS indicates an increase in randomness at the solid/solution interface during the adsorption Pb(II). The positive ΔS reflects the affinity of the adsorbent material for metal ions.

FTIR analyses

Fouier transform infrared spectra (FTIR) was used to investigate the changes in vibration frequency in the functional groups of the dry cabbage leaves as adsorbent due to Pb(II) ions adsorption. Figure 8 and 9 show the spectra of samples of dry cabbage leaves before and after loaded to Pb(II) ions when using FTIR, spectrophotometer, TENSOR 27, BRUKER, Germany. Then the adsorbent was scanned in the spectral range of 1000 -3500 cm^{-1}. Peak displacement decreasing define the change in the structure with Pb(II) imply the related functional groups to be responsible for the adsorption process. The bands of hydroxyl and carbonyl groups shifted to higher transmission (peaks of adsorption) and therefore it plays the major role

Table 3

THERMODYNAMIC CONSTANTS OF ADSORPTION OBTAINED FOR Pb(II) IONS ADSORPTION ONTO DRY CABBAGE LEAVES

Temperature (K)	$-\Delta G^\circ$ ($kJ.mol^{-1}$)	ΔH° ($kJ.mol^{-1}$)	ΔS° ($J.mol^{-1}K^{-1}$)	R^2
293	8.23015	-67.387	0.2017	0.9795
298	7.668921			
303	6.380133			
308	4.943345			
313	3.798776			
318	3.321647			
323	2.577713			

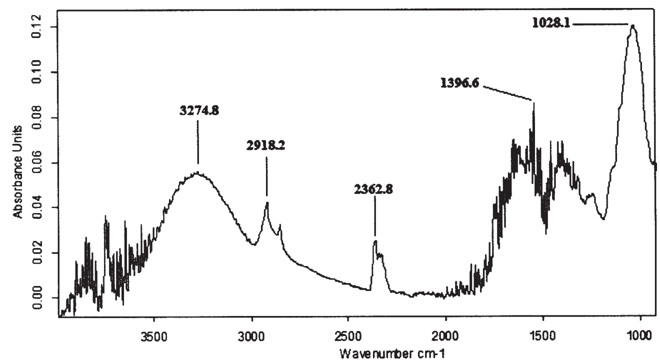

Fig. 8: FTIR analysis of dry cabbage leaves before loaded by Pb(II) ion

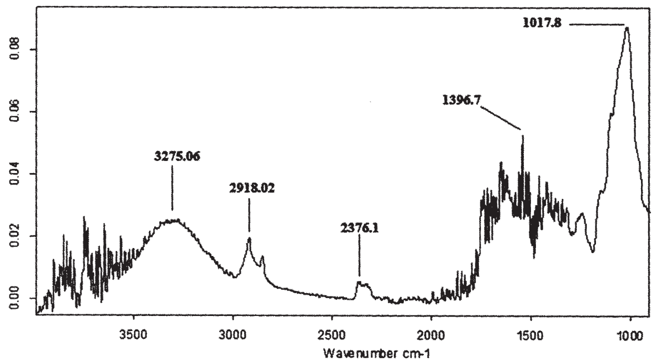

Fig. 9. FTIR analysis of dry cabbage leaves after loaded by Pb(II) ion

in adsorption of these ions and this is apparent in the figures 7 and 8.

Conclusions

A dry cabbage leaves a good efficient adsorbent material to remove the Pb(II) ions from industrial waste water in batch system. Effects of the experimental parameters such as *p*H, contact time, dosage and particles diameter of adsorbent are very important for the adsorption process. The highest removal efficiency of lead ions obtained was 95.67%, at optimum operating conditions of (*p*H 6, contact time 120 min, adsorbent dosage 0.5 gm / 50 mL of solution and adsorbent particles diameter). It was found that Langmuir model is better than Freundlich model when applying the isotherm model on the experimental data. The study of adsorption kinetics has been reasonable agreement with pseudo-second order model.

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