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Using *Phragmites australis*(Iraqi plant) to remove the Lead (II) Ions form Aqueous solution.

Khulood A. S. Al-Saade

Dunya Edan AL-Mammar

Huda N. AL-Ani

Department of Chemistry, College of Science, University of Baghdad, Jadiriya, Baghdad, Iraq

E-mail: hudanajim2005@yahoo.com

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Abstract:

Lead remediation was achieved using simple cost, effective and eco-friendly way from industrial wastewater. *Phragmites australis* (P.a) (Iraqi plant), was used as anovel biomaterial to remove lead ions from synthesized waste water. Different parameters which affected on adsorption processes were investigated like adsorbent dose, pH, contact time, and adsorbent particle size, to reach the optimized conditions (maximum adsorption). The adsorption of Pb (II) on (P.a) involved fast and slow process as a mechanism steps according to obey two theoretical adsorption isotherms; Langmuir and Freundlich. The thermos dynamic adsorption parameters were evaluated also. The (ΔH) obtained positive value that meanes adsorption of lead ions was an endothermic processwhile (ΔG)values were negative which means that adsorption of lead ions was a spontaneous process and the decrease in (ΔG) with temperature increasing revealed that lead ions adsorption on (P.a) became favorable with temperature increasing.

Key words: Adsorption, *PhragmitesAustralis*, Lead ions, percentage removal.

Introduction:

Phragmitesaustralis (P.a) was widely used in the last two decades for industrial water treatment to adsorbed metallic ions[1]. The toxic ions and molecules such as heavy metals and other pollutants released into the ground water and surface as results of different industrial activities, agriculture and mining [2]. The possible gender of lead ions to the ecosystem through the soil, water, and air perform to necessity

removing of Pb(II) .Lead ions (Inorganic form) causes a disturbance in central of the nervous system by chang the characteristics of the early organism[3].The pathway for entry of metals in to the environment was particularly industrial waste water in electroplating, metal industrial finishing, tannery process, chemical manufacturing and battery manufacturing industries[4]. In drinking

water there must be the maximum permissible limit (MPL) of lead is about 0.05 ppm [5]. Many methods like chemical precipitations, adsorption and convention [6-11], ion exchange [12], methods of membrane separation [13] and electro-remediation ways [14] available for waste water treatment. Most methods are economically feasible, costly and not eco-friendly and led to secondary effluent impact on the environment. Most of these methods are not efficient to remove low concentrations of the heavy metal ions and mostly very expensive, so a simple effective, eco-friendly and low-cost methods are required to reach fine tuning of polluted waste water. The study for easily available adsorbents with low cost has led to the investigation of agricultural and biological origin materials. Such low cost adsorbents as example are clay [15], cotton by-products [16], wool by-products [17], tea leaves [18] and some other materials [19-21]. Natural materials can potentially be modified using variety of chemical/physical treatment to achieve the desired surface properties for best immobilization performance of specific compounds [22]. When the surfaces are modified using introducing long organic chain compounds like Sodium Dodecyl Sulfate (SDS), high sorption of pollutants can be achieved [23]. The study reported here aimed the ability of seed, *Phragmites australis* (P.a) (Iraqi plant) to uptake lead ions and study the effect of modification of (P.a) by (SDS) on the enhancement of percentage lead removal from aqueous solutions at different pH and temperatures.

Materials and Methods:

Iraqi environment seed, *Phragmites australis* (P.a) were collected, washed, dried then grind to a powder and conserved in desiccators. SDS [$\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$] or

$\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$ with M.wt. = 288.38 $\text{g}\cdot\text{mol}^{-1}$ were supplied from Fluka with purity 99.9% were used to modified Iraqi seed, HCl 36%, NaOH 99.9% also supplied from Fluka were used to adjust pH of the solutions. A stock solution of lead ions (1000 ppm) were prepared from 1g of $[(\text{CH}_3\text{COO})_2\text{Pb}\cdot 3\text{H}_2\text{O}]$ with purity reach 99.9% supplied from Riedel- Dehaenag dissolved in 1L distilled water, different solutions concentration were prepared by dilution. Atomic Absorption Spectrometer method was used to follow lead ion concentration before and after adsorption process. The (AAA) apparatus type GBC 933 plus, Australian origin where used in this study. Two types of adsorbents, P.a. and modified P.a by SDS were used to study the percentage removal of lead from synthesized waste water. The modified P.a/ SDS was prepared by adding 0.2 g SDS to 10g seed with 250 ml distilled water; this mixture left for 24h with stirring then filtered washed then the modified P.a dried in 100°C furnace.

Experiments Part (Experiments of Batch Adsorption)

Batch Adsorption experiments performed by adding the amount of the stock solution 250 ml in a volumetric flask at the designated adsorbent dose, pH, and temperature. The solution was shaken using a mechanical shaker (Griffin and George LTD.), Britain origin a definite period of 250 rpm for adsorbent dose, temperature, contact time, and pH were optimized by variation continuous method (studying one, keeping other data constant). After equilibrium rating, the system allowed settle for 20-30 min, filtered and determined lead. The difference in the lead content before and after adsorption experiments represents the amount of lead absorbed by the P.a or Pa/SDS adsorbent. The P% of Pb^{+2} can calculate using this equation [24]:

$$\text{Percent removal (\%R)} = \frac{(C_0 - C_e)}{C_0} * 100 \dots\dots\dots 1$$

Where, C_0 = initial Pb^{2+} concentration (ppm), C_e =final Pb^{2+} concentration in the solution (ppm).

Results and Discussion:

1.The effect of adsorbent dose

Fig. 1. Shows the variation of %R with adsorbent dose (g) for 40 ppm Pb^{2+} at 298 K at pH 6.

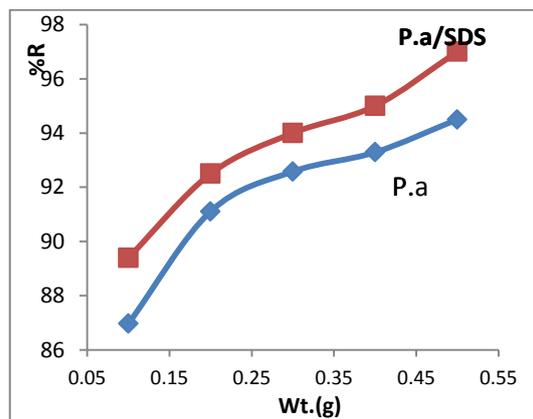


Fig. 1: Variation of %R with different adsorbent dose (a) P.a/ adsorbent;(b) Pa/SDS adsorbent at 298 K, C_0 =40ppm.

2: The effect of pH:

pH plays an important role in adsorption mechanisms. Fig.2 shows the variation of %R of Pb^{2+} with pH by P.a and P.a /SDS adsorbent at 298 K with 20 ppm Pb^{2+} solution.

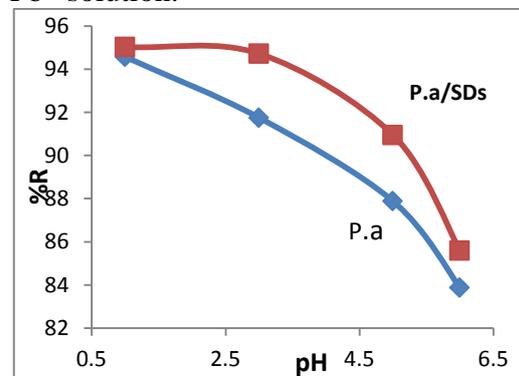


Fig.2: Variation of %R of Pb^{2+} withpH by (a)P.a; (b) P.a/SDS at 298K and C_0 = 20 ppm.

3. The effect of contact time

The adsorption of Pb^{2+} by the two adsorbent was carried out by shaking the aqueous suspensions for a different time to evaluated the equilibrium time, which was (80 min.) for P.a and P.a /SDS as shown in Fig.3.

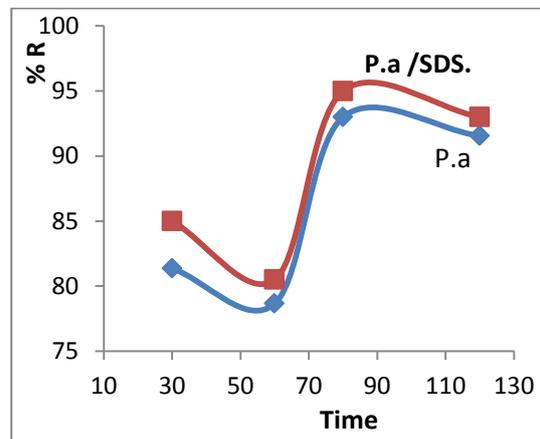


Fig.3: The Variation of %R with time for (a) P.a; (b) P.a /SDS adsorbent at 298 K and C_0 = 20 ppm.

The adsorbed amount of both adsorbent ($mg .g^{-1}$) were calculated as follows[25]:
 $q_e = (C_0 - C_e)V / w \dots\dots\dots 2$
 Where C_0 and C_e the initial concentrations, and final Pb^{2+} concentrations (ppm.),respectively, V is the volume of Pb^{2+} solutions(L) and (w) is the mass of adsorbent (p.a) or P.a /SDS(gm.).

4. Analysis of equilibrium data.

Freundlich and Langmuir adsorption isotherms were applied forthe Pb^{2+} adsorption, and the experimental data was fitted. The best model which was fitted according to statistical criteria (R^2) correlation or regression coefficient. The adsorption isotherm name Langmuir was derived supposing that the Pb^{2+} adsorption was take place on homogenous monolayer with adsorption sites of equal energy,this layer coverage can be described as[26].

$$q_e = q_m[bC_e/1 + bC_e] \dots\dots\dots 3$$

Where $q_e/\text{mg.g}^{-1}$ and $C_e/\text{mg.L}^{-1}$ are equilibrium concentration on adsorbent surface and adsorbate concentration in the solution, respectively b is a constant related to the equilibrium constant, which represents the affinity between Pb^{2+} and the surface, q_m/mg^{-1} is the maximum quantity adsorbed by the surface. The empirical Freundlich isothermic model can represent in following equation [27].

$$q_e = kC_e^{1/n} \dots\dots\dots 4$$

In this model the adsorption amount was increased indefinitely with the concentration of Pb^{2+} in the solution. Freundlich isotherm holds for heterogeneous surface where the adsorption energy sites were not similar. Fig.4: Shows the Langmuir isotherm on (P.a) and (P.a/SDS) at different temperatures.

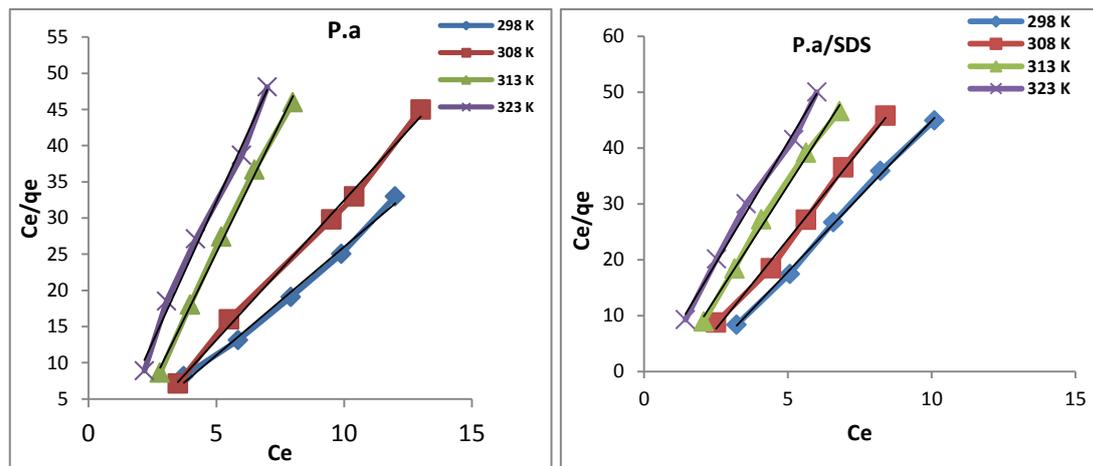


Fig.4: Langmuir isotherm for (a) –(P.a),(b) –(P.a/SDS) at different temperatures.

While Fig.5: Shows the Freundlich isotherm on the two adsorbents.

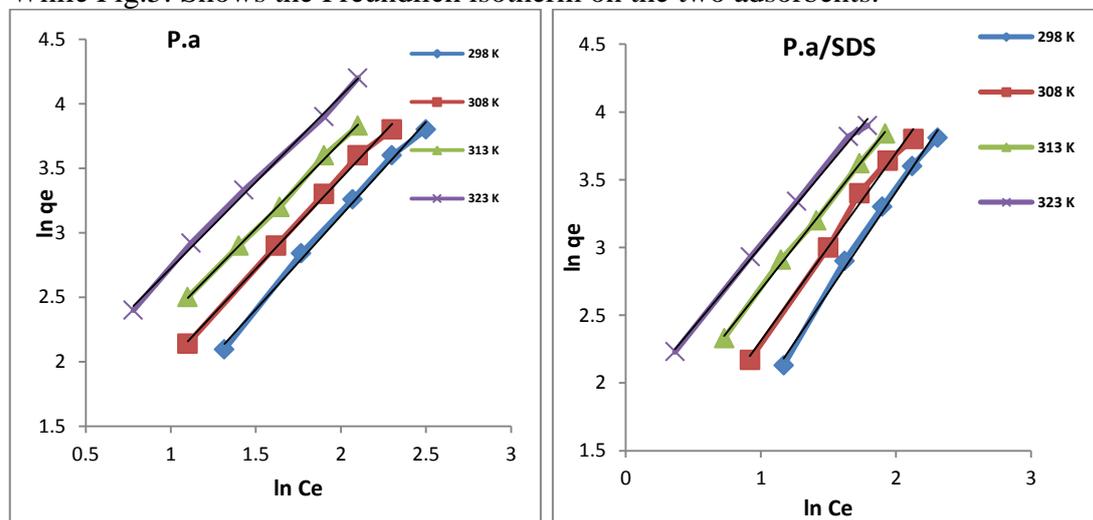


Fig.5: Freundlich isotherm on (a)-(P.a),(b) –(P.a/SDS) at different temperatures.

Parameters were listed in Table 1, where R^2 for Freundlich model are higher in values than for Langmuir R^2 values, that

means the former model is more applicable than the later.

Table (1): Represented the data of the above two model.

Langmuir							Freundlich					
k_L			a		R^2		K_F		n		R^2	
T/K	P.a	P.a/SDS	P.a	P.a/SDS	P.a	P.a/SDS	P.a	P.a/SDS	P.a	P.a/SDS	P.a	P.a/SDS
298	1.981	2.040	0.438	0.059	0.842	0.965	1.256	1.562	0.688	0.675	0.995	0.994
308	2.557	3.077	0.049	0.055	0.879	0.93	1.840	1.154	0.711	0.391	0.997	0.909
318	3.358	5.494	0.054	0.093	0.963	0.868	1.647	3.939	0.613	0.785	0.967	0.981
323	4.549	6.452	0.027	0.035	0.964	0.670	2.792	3.235	0.974	0.550	0.966	0.984

5. The effect of Temperature.

The adsorption extent of Pb^{2+} on (P.a) and (P.a/SDS) at different temperatures are shown in Fig.6. the increasing in temperature cause to enhance the adsorption percentage % R of Pb^{2+} because of increasing the mobility and diffusion of ionic species. Where diffusion process is an endothermic

process, so the increasing in %R was expected. Also, the increasing in temperature led enlargement of pore size according to activated diffusion and micropores be wider and more pores were created than adsorption as enhanced.[28].

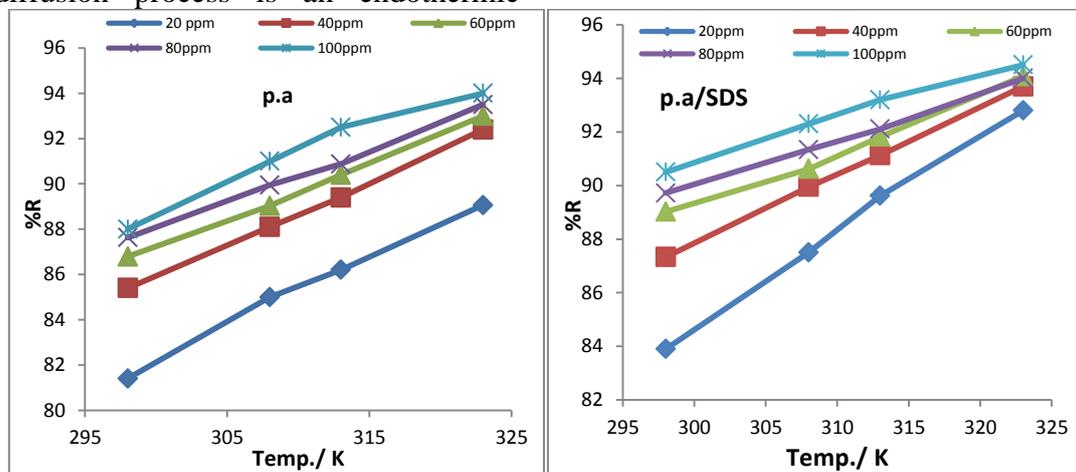


Fig.6:Variation of %R of Pb^{2+} by (a)-(P.a), (b) - (P.a/SDS) surfaces with temperature for different Pb^{2+} concentration.

6. Calculation of Thermodynamic Parameters:

The parameters of Thermodynamic Entropy and Enthalpy (ΔS & ΔH) values for adsorption process were calculated from the slope and intercept of linear Vant Hoff plot, respectively using the following relation [28]:

$$\ln k_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \dots \dots \dots 5$$

Where ΔS is the entropy change for the process, ΔH is the enthalpy change for the adsorption process, R is the gas constant and T is the absolute temperature.

The distribution coefficient (k_d)/mL/gon (P.a) and (P.a/SDS) surfaces

were calculated using the following equation [29]:

$$k_d = (C_o - C_e / C_e) \times (V/m) \dots \dots \dots 6$$

The change in free energy ΔG for the specific adsorption process have also been calculated using the following equation [30]:

$$\Delta G = - RT \ln k_d \dots \dots \dots 7$$

Fig.7 shows the linear relation between link and reciprocal of temperature, ΔH and ΔS values were calculated from the slope and intercept of linear Fig.7 relation respectively, all thermodynamics data were represented in Table 2.

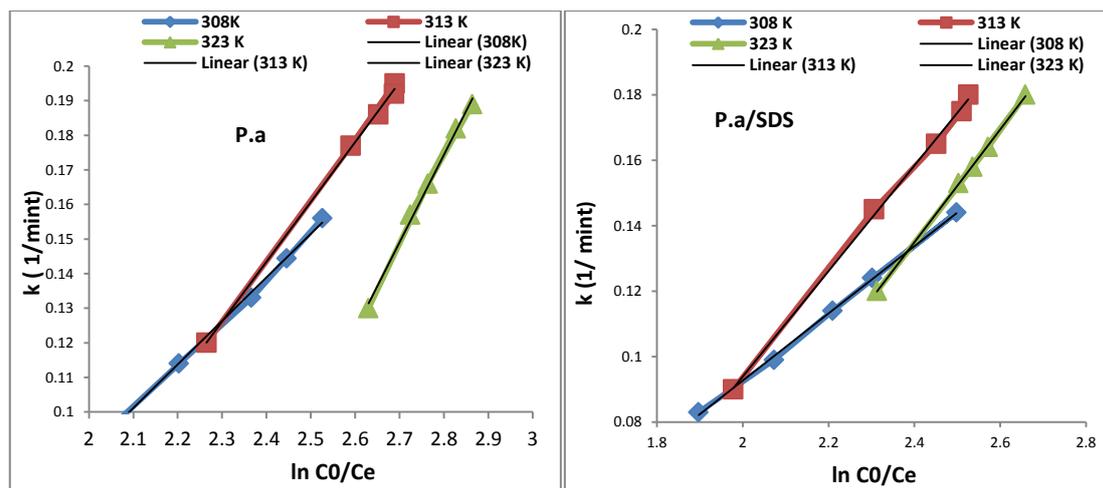


Fig.8:Plot of rate constant k for adsorption process against $\ln C_0 / C_e$ on (a)(P.a),(b) (P.a/SDS) adsorbent.

Table 3.The rate constant values for the adsorption of Pb^{2+} on P.a and P.a/SDS.

P.a				P.a/SDS			
T/K	C_0 /ppm	$\ln C_0/C_e$	k / mint^{-1}	T/K	C_0 /ppm	$\ln C_0/C_e$	k / mint^{-1}
308	20	1.897	0.083	308	20	2.078	0.099
	40	2.073	0.099		40	2.203	0.114
	60	2.210	0.114		60	2.366	0.133
	80	2.498	0.124		80	2.446	0.177
	100	2.302	0.125		100	2.525	0.156
313	20	1.978	0.090	313	20	2.265	0.120
	40	2.306	0.125		40	2.590	0.166
	60	2.451	0.145		60	2.689	0.123
	80	2.510	0.154		80	2.652	0.245
	100	2.526	0.156		100	2.688	0.184
323	20	2.313	0.114	323	20	2.630	0.173
	40	2.572	0.164		40	2.764	0.198
	60	2.659	0.174		60	2.827	0.297
	80	2.503	0.153		80	2.724	0.282
	100	2.536	0.158		100	2.864	0.219

Rate constant values of adsorption on (P.a/SDS) was higher than on (P.a) surface, So SDS enhance the %R and the velocity of the adsorption process.

Conclusion:

The Laboratory batch experiments revealed that modification Phragmitesaustralis (P.a)by SDS lead to increase the rate of adsorption process and increase the Pb^{2+} percentage removal. Adsorption of Pb^{2+} on P.a and P.a / SDS followed first order reaction of Freundlich isotherm type. The obtained thermodynamic calculation indicate an endothermic adsorption process for the adsorption process on P.a and P.a /SDS, and SDS lead to increase

the ΔG values in general which means, adding SDS lead to increase the thermodynamic feasibility of adsorption where SDS molecules act as a center of adsorption sites, these sites make adsorption process more random as ΔS positive values was generally higher in case of adding SDS for (P.a).

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ازالة ايونات الرصاص الثنائية من المحاليل المائية باستعمال نبات القصب العراقي

دنيا عيدان محمد المعمار

خلود عبد صالح السعدي

هدى نجم الدين عبد اللطيف العاني

قسم الكيمياء، كلية العلوم، جامعة بغداد، بغداد، العراق

الخلاصة:

يعد التلوث بـايونات الرصاص من المشاكل الرئيسية في الصناعات النفطية. تم دراسة طريقة فعالة ورخيصة وصديقة للبيئة لتعيين ايونات الرصاص من المحاليل المائية. استخدم نبات القصب العراقي كمادة حيوية جديدة لازالة ايونات الرصاص من المحاليل المائية لغرض الحصول على اعلى سعة امتزاز تم دراسة تأثير عدة عوامل على الامتزاز منها تركيز ايون الرصاص الابتدائي، كمية المادة المازة، زمن التماس، الدالة الحامضية وحجم الدقيقة المازة. سلسلة من تجارب الامتزاز بطريقة الوجبة اشارت الى حدوث عمليات سريعة وبطيئة. كما ان ميكانيكية سرعة الامتزاز تم تحليلها باستخدام متساوي درجة الحرارة للنكماير وفرندلش. وتم تعيين الدوال الترموديناميكية لعملية امتزاز ايونات الرصاص. تشير القيمة الموجبة للانثالبي (ΔH) بان امتزاز ايونات الرصاص الثنائية على السطح الماز هي عملية ماصة للحرارة. ان القيمة السالبة للتغير في الطاقة الحرة (ΔG) هو توقع لعملية تلقائية. ان نقصان التغير في الطاقة الحرة مع زيادة درجة الحرارة هو اشارة الى ان امتزاز ايونات الرصاص على سطح المادة المازة هي مفضلة في درجات الحرارة العالية.

الكلمات المفتاحية: الامتزاز، نبات القصب، ايونات الرصاص، النسبة المئوية للازالة.