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Phytoremediation of Lead (II) using a Saharan Plant- based boisorbent

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Abstract: The contamination of different water resources with various pollutants such as heavy metals, organic materials, synthetic effluents, and pesticides has become great challenge. Phytoremediation is one of the safer, economical, and environment-friendly techniques in which plants are used to recover polluted soils, particularly those containing toxic organic substances and heavy metals. An eco-friendly and clean phytoremediation technique using different sources of special plants are used in order to decrease the toxicity of these pollutants especially the biodegradable heavy metal. In the present study a novel Sahrawi boisorbent is prepared from Anabasis Articulate plant from naturally growing populations in Wadi Ash-Shaykh, North eastern Desert, Egypt as a novel Sahrawi boisorbent that was successfully used for the removal of lead metal ions from water resources. The Anabasis Articulate biosorbent (ANA) is characterized by Boehm titration, point of zero charge (pH_{PZC}), SEM, FT-IR spectroscopy and TGA analysis. The different experimental parameters affecting the batch mode adsorption of Pb (II) onto ANA biosorbent were assisted such as pH effect, initial concentration of Pb (II) ions, contact time and adsorbent dosage of ANA biosorbent. At optimum conditions, the adsorption capacity of lead metal ions reaches 76.0 mg/gm. The adsorption process is more fitted to pseudo-second order than first-order. Adsorption isotherm studies are fitted to Langmuir. The negative values of $\Delta G°$, and $\Delta S°$ indicated that lead adsorption on Anabasis Articulate biosorbent is spontaneous with random nature on the adsorbent-adsorbate system. .

keywords: Anabasis Articulate, Phytoremediation, Lead, Adsorption

1.Introduction

There are tremendous strains on the environment's natural resources as a result of the world population's rapid rise and the resulting demands for food, water, energy, timber, and other ecosystem services.

Depending on the increase of the world population and development of the industrial applications, environmental pollution became important. There has been a huge growth in the manufacture and uses of synthetic chemicals, metal plating operations and the other industrial applications and productions since the beginning of the 20th century that are seriously polluting the environment with, organic materials, synthetic effluents, pesticides run off from agricultural lands, and heavy metals. There still are many possible sources of chemical contamination including wastes from industrial chemicals production, metal plating operations, and pesticide run off from agricultural lands, and the other industrial applications and productions [1]. these industrial and domestic activities have polluted the surface water as well as ground water up to a greater extent [2]. A significant hazard comes from such industries is posed by heavy metals that affect both human and animal health is, because of their long-term persistence in the environment. Heavy metals not only affect the human health but also affect badly on the aquatic systems. Numerous problems and illnesses are as a result **of** the deposition of heavy metals such as lead, mercury, cadmium and chromium which were pronounced to be on the pinnacle of thetoxicity [3]. Lead is considered as one of the most toxic heavy metals. It is listed as the second most hazardous substance by The Agency for Toxic Substances and Disease Registry (The ATSDR 2011)[4]. Lead contamination in the environment usually results from wastewaters or effluents from lead mining, battery recycling, electronics assembly plants, and military facilities, as well as landfill leachate and urban rainwater runoff [5]. The presence of lead in drinking water is known to cause various types of serious health problems as anaemia, brain damage, mental deficiency, dysfunction of kidneys, liver, and central nervous system in humans, especially in children and behavioural problems in humans leading to death in extreme cases[6]. Hence the cost of removal of organic and inorganic pollutants from water has been increases remarkably in last few years. There are several technologies for treating wastewaters [7]. And this poses a great challenge to chemical engineers to develop low, cost effective and environmentally safe disposal and treatment methods. The most important of these techniques include chemical precipitation, filtration, ion- exchange, reverse osmosis and membrane systems [8-14]. In the last few years، adsorption has been shown to be an alternative method for removing dissolved metal ions and organic pollutants. Due to the highly danger of lead , in this study we touched in phytoremediation green technology using an effective bio Saharan plant, Anabasis Articulata (ANA) that is derived from Egyptian desert as a promising technique for lead ions removal from water resources. The Arabic name of Anabasis Articulata is "Ramet". This plant belongs to the Chenopodiaceae family which is found in Iraq, Algeria, Syria, and Egypt, and widely used by the local population and traditional medicine practitioners to treat several diseases such as diabetes, fever, headache and skin diseases, such as eczema[15, 16]. The present study was carried out to remove lead metal ion by applying batch adsorption technique.

2. Materials and methods

2.1. Reagents and solutions

In this study all chemical and reagents are of analytical grade and were purchased from Sigma-Aldrich.1000ppm lead stock solution prepared from Pb $(NO_3)_2$ was used. The concentration of Pb(II) ions were determined spectrophotometrically using 4-(2-Pyridylazo) Resorcinol monosodium salt (PAR) using borate buffer. The pH effect of the lead solution was studied using (0.1N NaOH and 0.1N HCl) which were purchased from Merck.

2.2. The used apparatus

The lead supernatant solution was analyzed after adsorption using UV-Vis spectrophotometer (Chrom Tech-Co., Ltd., USA). All pH of the used solutions was adjusted using pH meter (Hi 931401, HANNA, Portugal).Water bath shaker apparatus was used for studying kinetics and thermodynamic parameters. Electronic analytical balance was used for preparing all chemicals and solution used in this study.

2.3. Preparation of Anabasis Articulate (ANA) biosorbent

ANA plant was collected from naturally growing populations in Wadi Ash-Shaykh, Northeastern Desert, Egypt (28°40'4.67" N 31° 3'58.47 E). The collected plant samples were cleaned from any impurities with de-ionized water and air-dried at room temperature (25 ± 3°C) in shade conditions for 7 days. The dried plant was ground into a fine powder for analytical use.

2.4. Characterizations.

2.4.1.FourierTransforminfraredspectroscopy (FT-IR)

Functional groups on the surface of present plant is obtained from IR studies[17].Analysis of adsorbents was determined using a Jasco instrument (Model 6100, Japan) where, the obtained data were recorded between 4000 and 400 cm^{-1}.

2.4.2. SEM, Scanning electron microscopy characteristics.

The surface morphology of anabasis articulate is determined using JSE - T20 (JEOL, Japan) microscope having an acceleration voltage of 40 kV. The plant should be dried for 4hrs at 110^oc and then coated with thin layer of gold here, to be ready for imagining.

2.4.3. Boehm titration method.

Using the traditional Boehm titration method , the Surface chemistry and acid/base groups of anabasis articulate were determined [18]. About (0.1) g of the plant was shaken with (0.1N) of the sodium hydroxide, sodium carbonate, sodium bicarbonate, and hydrochloric acid solutions. After that, about 5ml of each supernatant solution was titrated against (HCl and NaOH), depending on the original used titrant. The number of acidic sites was determined under the assumption that NaOH neutralizes carboxylic, lactonic, and phenolic groups; and Na_2CO_3 neutralizes carboxylic and lactonic groups; and $NaHCO_3$ neutralizes only carboxylic groups. The number of basic sites was calculated from the amount of hydrochloric acid that reacted with the plant.

2.4.4. Determination of surface pH and physical prosperities of ANA sample

In order to study the surface pH of the (ANA) sample, about 0.1 g was shaken in 25 ml de-ionized water for about 48hrs the pH of the supernatant was measured. Also, point of zero charge, Moisture content and ash content were determined.

Determination of pH of the point of zero charge (pH_{PZC}) is done by shaking (0.1gm) of the prepared (ANA) sample with (0.01 M NaCl) solutions which was adjusted using (0.05 M HCl or 0.05 M NaOH) between 2 and 12 for 48 h at 120 rpm at 25°C, then that the final pH was measured .The resulting pH was taken as the pH_{pzc}. The final pH was plotted against ΔpH. At $pH_{PZC,}$ there is no change in solution pH occurred during the equilibration period. Ash content is determined by putting about 0.3 g of (ANA) was put in muffle furnace for about 6hrs at 700-800 ^{O}C and then the final weight was recorded.

$$\textbf{Ash content}\,\% = \frac{\textbf{weight (Final)(gm)}}{\textbf{weight(Iintial) (gm)}} \times \textbf{100} \qquad \textbf{(1)}$$ [19]

The moisture content of ANA sample is determined by heating 0.3 g of the sample at 110 ^{O}C for 24 hrs.

$$\textbf{moisture content}\,\% = \frac{\textbf{loss in weight (gm)}}{\textbf{initial weight}} \times \textbf{100} \quad \textbf{(2)}$$ [20]

2.5. Batch adsorption method:

Removal of Pb(II) by (ANA) was applied using batch mode for adsorption. Batch mode was studied by applying different parameters such as pH effect, concentration effect, temperature effect, contact time effect and adsorbent dose effect.

To perform the batch mode experiment, The optimum pH of adsorption process is determined by shaking 0.025 g of ANA sample in 25 ml of fixed 50 mg/l Pb(II) solution at different pH between(2-6) which adjusted using (0.1M NaOH M and 0.1M HCl) at 25 ^{o}C and shaken for about 5 hrs.

The equilibrium isotherm of Pb(II) was studied by varying metal ion concentrations between(10-300) mg/L at constant ANA adsorbent dose of (0.025)g in 25 ml of metal ion solution at constant pH solution and shaken at 160 rpm at room temperature for 5 hr

The maximum uptake (adsorption capacity) and the removal of the Pb(II) ions were determined from the following equations.

$$\boldsymbol{q_e = \frac{(c_o - c_e)V}{W}} \qquad \textbf{(3)}$$

Where, C_o and C_e are the initial and equilibrium lead solution in (mg/g), respectively. V is the volume of lead solution (L) and W is the weight of the adsorbent (g) [21]

$$\%\boldsymbol{R = \frac{(c_o - c_e)}{c_o}} \qquad \textbf{(4)} \qquad \textbf{[22]}$$

Where, %R is the removal percentage of adsorbate (Pb(II)) from aqueous solution.

Contact time is accomplished to study the kinetics of the adsorption process, as 25 ml of (50 mg/l) of Pb(II) solution containing 0.025gm of ANA sample was shaken for 5hrs at room temperature. The solution was filtered and then analyzed at 520 nm at different time intervals (1-300) min.

Thermodynamic parameters ΔG°, ΔH° and ΔS° were determined by using as 100 $mg.L^{-1}$ Pb (II) ion initial concentration at different temperatures between (25-60) °C. In addition, Effect of ionic strength was studied on the removal of Pub(II) using 0.025 g in 25 ml of (20 mg/l) with Pub(II) of (ANA) at different concentration of NaCl (0.001-0.15 M) at room temperature .

3. Results and Discussion.

3.1. Physicochemical characters of the ANA biosorbent

The pH of supernatant of ANA is very important in determination of the functionalities present on the surface. The surface charge of ANA, the pH in aqueous solution, and the amphoteric nature of adsorbent are generally due to the different functionalities present on the ANA sample surface.

The point of zero charge is determined by solid addition method [23]. From Table (1), the pH of supernatant in case of ANA plant was 6.14.

The pH_{PZC} is defined as the pH at which the net surface charge equals to zero or pH at which the total number of positive and negative charges on its surface becomes zero[24] . It allows quantifying the acidic or basic character of the adsorbent surface. The pH_{PZC} and the pH of the solution determine the charge on the surface that will be present; the adsorbent surface is positively charged and surface sites are protonated at pH $<pH_{PZC}$ and, but at pH $>pH_{PZC}$ is negatively charged. This charge on the adsorbent surface is one of the parameters which explain the adsorption characteristics[25].In case ANA, its supernatant pH is slightly higher than pH_{PZC}. The plots to determine the pH of the point of zero charge (pH_{PZC}) are shown in Fig.1 and Table (1).

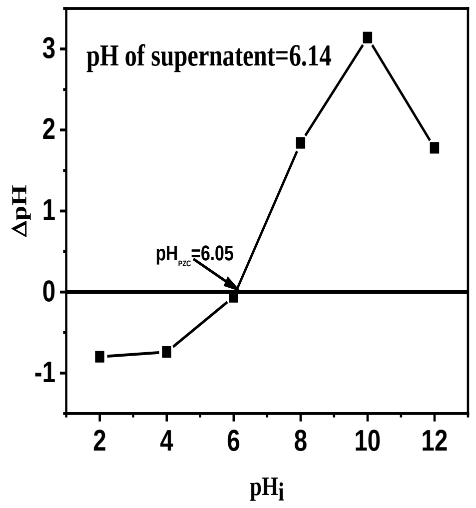

Fig 1: pH_{PZC} of ANA biosorbent

3.2. Surface characterization of the ANA biosorbent

3.2.1. Fourier Transform infrared spectroscopy (FT IR).

The FTIR spectra corresponding to removal of lead before and after adsorption using ANA plant is shown Fig.2. Broad band at (3435 and 3451) cm^{-1} is ascribed to (O-H) hydroxyl groups stretching vibration in alcohol, phenol and adsorbed H_2O in cellulosic materials in both spectra, and the other two weak bands at (2926, 2930) cm^{-1} observed were assigned to aliphatic (C-H) group that may present in such plant[26, 27]. The difference in the FTIR spectra before and after adsorption of lead is very clear as shown in the Fig.2 (a & b).

FTIR spectrum of ANA biosorbent before lead adsorption:

Two absorption bands at (1633 and 1740 cm^{-1})are attributed to (C=O) stretching vibration of carboxylate ion (-COO-) groups in the organic compounds, and the absorption of ester and carboxyl acid groups (-COOH) respectively[28]. The peak at (1512 cm^{-1}) is attributed to(C=C) of aromatic rings of the lignin esters which is stable band in all lignin structure material [29].Another peak can be observed at (1252.11) cm^{-1}that is ascribed to presence of(C-O) stretching vibration of aryl group in lignin[29]. The two observed peak at (1371and 1435) cm^{-1} represent (C-H)methyl groups[27] and phenolic (O-H) of ANA plant respectively[30]. The small band at (1322) cm^{-1}, may be assigned to methylene ($-CH_2-$)and hydroxyls(O-H) groups of aromatic groups[27] of the plant under study. The peak at (1252.11) cm^{-1}may be due to the presence of (C-O) stretching vibration of aryl group in lignin[31]. Very weak peak appears at (1160) cm^{-1} that is assigned to the stretching vibration(C-O)stretching vibration from hemi-cellulose esters[32]. Broad beak at (1048) cm^{-1} is attributed (C-O) stretching vibration from hemi-cellulose esters in case of SCBACP sample (C-O) contribution in glycosidic linkage in case of SCBR sample[33].

FTIR spectra ANA biosorbent after lead adsorption

As shown from Fig.(2, b), there is radical change in the FTIR spectra which confirm the adsorption of lead metal ion by anabasis articulate (ANA) plant with high degree. There are some bands completely disappearing and other changes, where the bands in (ANA) plant at (1740, 1512, 1435, and 1322) cm^{-1} completely disappear, where the beak at (3435) cm^{-1} is shifted to (3451), where (1633) is shifted to be (1640) cm^{-1}, the peak at (1371)$cm^{-1}$is shifted to be (1387) cm^{-1}, and (1253) cm^{-1} become (1263) cm^{-1} .the intensity of the beak at (1048) cm^{-1} decreases and is small shifted to be (1045) cm^{-1}. These changes of the beaks give indication on the adsorption of lead metal ions.

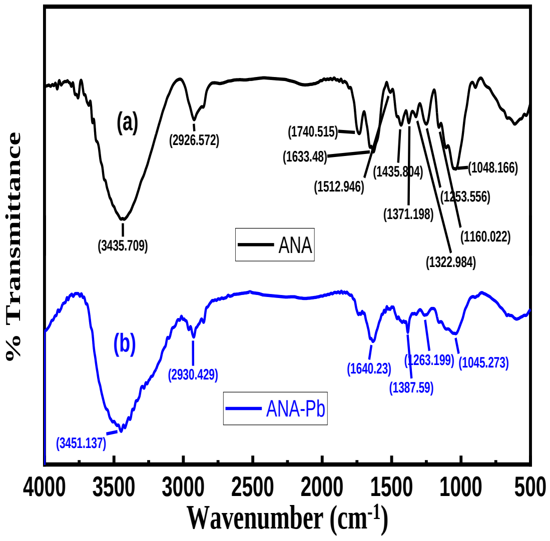

Fig 2: FTIR spectra of (a) ANA), (b) ANA-Pb^{2+}.

3.2.2 Scanning electron microscope (SEM)

The surface morphology of the anabasis articulate plant was done using SEM. The images were taken at two different magnifications (500X and 1000X). From the Fig.3 (a & b) it can be observed the surface texture and the porosity present on the surface of such plant. We can observe the presence of pores on the plant surface that participate on the removal of the lead metal ions.

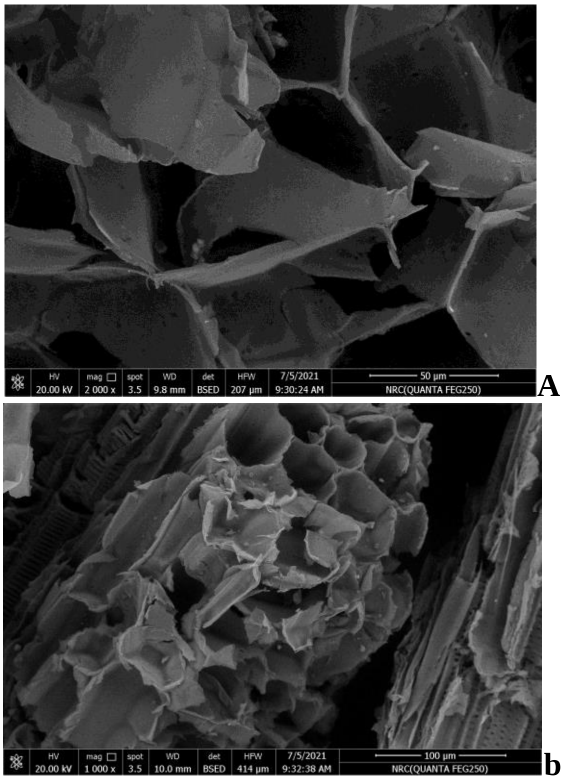

Fig 3: SEM micrograph of (ANA) sample at different magnification a & b

Table (1): Physicochemical characters of the ANA adsorbent

.Anabasis articulate(ANA)		
Moisture content %	7.7	Bohem titration (mmole/g)
Ash content %	1.66	Carboxylic
		1.05
pH of supernatant	6.14	Lactonic
		0.45
Point of zero charge	6.09	Phenolic
		1.45
		Total basic
		3.05

3.3. Uptake of lead using ANA biosorbent

3.3.1. Effect of pH on the adsorption of Pb(II):

The pH of aqueous solution is one of the most important variable influences the adsorption processes, because it controls the adsorbent's surface charge, ionization level, and adsorbate speciation. Removal Pb(II) using ANA sample was tested in the pH ranges between (2, 6.5) to study how the pH solution affects the removal of Pb(II).

Removal of lead ions above pH (6.5) is not favoured since, in these conditions, lead is detected as the precipitated species $Pb(OH)_2$, not in its ionic state[34]

Fig. 4 illustrates how the pH affects the adsorption capacity of Pb (II) ions using ANA plant. It is evident that the adsorption capacity of Pb(II) ions increased with rising pH of aqueous solution and achieved maximum value at pH = (5) . The fact that there is less adsorption at lower pHs can be attributed to hydrogen ions' competition with metal ions for sorption sites. Contrarily, as the pH increases, more negatively charged surfaces become available, permitting increasing in metal uptake. This indicates that with higher H+ concentrations, the adsorbent surface becomes more positively charged.

Lead ions precipitated as their hydroxides at higher pH values (above 6), which reduced the rate of adsorption and, in turn, the percentage of metal ions removed. Consequently, neutral pH of metal ions is the best pH for removing lead.

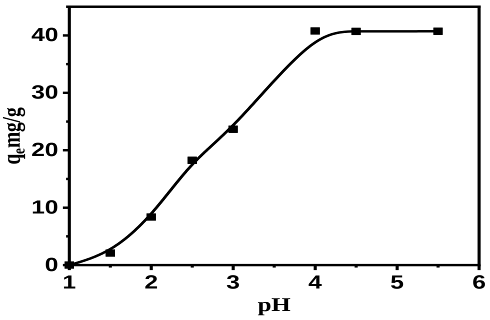

Fig 4: effect of pH on adsorption capacity of Pb^{2+} on ANA

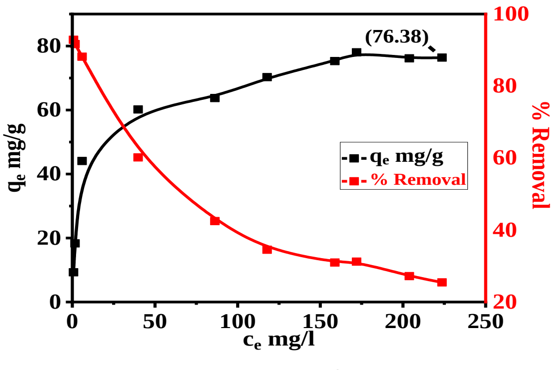

Figure 5: Effect of initial Pb^{2+} concentration on the removal percentage and adsorption capacity on ANA

3.3.2. Effect of initial concentration of Pb (II) solutions:

Initial concentration, is very important parameter in determining how the agriculture bio waste affect the metal ions removal. As observed in Fig. 5 adsorption capacity is gradually increasing as lead initial concentration increases. This is attributed to available adsorption vacant sites at lower initial Pb(II), where at high initial concentrations Pb(II) level, there is decreasing in both adsorption capacity and removal percentage of Pb(II) ions due to the saturation of available active sites of ANA the active sites[35].

As the initial concentrations of Pb(II) ions become more than available active sites of ANA, hence, no more adsorption of Pb(II) ions can be achieved leading to stability of adsorption capacity and decreasing in Pb(II) ions removal percentage.[36]

3.3.3. Effect of contact time:

Agitation time is an important factor in Pb(II) ion adsorption process by ANA sample. This effect was studied to determine the maximum time that is required to attain state of the equilibrium. Adsorption capacity of Pb(II) ion as a function of time was studied between 1 and 300 min using ANA plant is presented in Fig. 6. Pb(II) ions uptakes increased sharply at first 30 min., and then became almost stable after 60 min, giving indication to reach equilibrium state. This may be due the availability of large number of active sites surface of at high Pb(II) solution concentration at first period of time. As time precedes, (approximately reaches 60 min.) low available surface active sites are present leading to a decrease in the adsorption rate of Pb(II) ions and hence low increase in the metal uptake was observed, as a result there was an increased in concentration gradients between adsorbate in solution and adsorbate on adsorbent surface. Therefore, 2hrs of contact time is chosen as the adsorption time for the experimental test to ensure that equilibrium is reached[36].

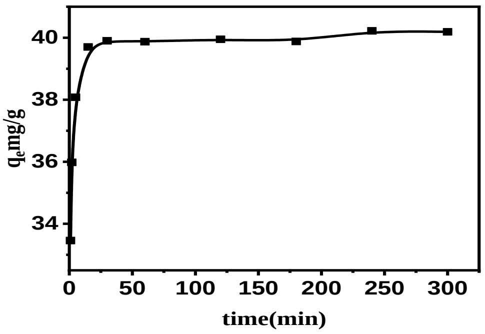

Fig 6: Effect of contact time on adsorption capacity of Pb^{2+} on ANA

3.4. Equilibrium adsorption isotherm studies

Equilibrium study on adsorption provides information on the capacity of the adsorbent. An adsorption isotherm is characterized by certain constant values, which express the surface properties, affinity of the adsorbent, and can also be used to compare the adsorptive capacities of the adsorbent for different pollutants[37, 38]. The several adsorption isotherm models like Langmuir, Frendulich, Temkin, and Redlich-peterson have been used to test the equilibrium kinetics data[39] . In this study, two isotherm models, i.e., Langmuir, and Freundlich were applied to determine the nature of Pb(II) adsorption on the surface of ANA in the solid–liquid equilibrium phase..

For Langmuir isotherm:

Langmuir theory was based on the assumption that adsorption was a type of chemical combination or process and the adsorbed layer was monomolecular.

This model can be expressed in its linear formula as:

$$\frac{c_e}{q_e} = \frac{1}{bq} + \frac{c_e}{q} \quad \textbf{(5)}$$

C_e: the equilibrium Pb(II) concentration (mg/l).

q_e: the amount of the Pb (II) adsorbed per unit weight of the adsorbent for monolayer capacity (mg/g).

b: the Langmuir equilibrium constant (l/mg).

From linear plot of **Ce/qe** versus **Ce** as shown in Fig.(7, a) qe and b is determined. By determination the dimensionless separation factor of equilibrium parameter R_L, the favourable nature of adsorption can be detected, from this formula:

$$R_L = \frac{1}{1+K_L C_O} \quad \textbf{(6)}$$

C_o: is the highest initial solute concentration.

K_L: Langmuir constant.

The values of R_L indicates the type of isotherm to be irreversible where (R_L=0), favourable (0< R_L<1), linear (R_L=1) or unfavourable (R_L>1)[40]. As observed in table (2), the favourability of the adsorption process can be evaluated where, the R_L equal (0.028) which fall in the region of (0< R_L<1) indicating that the adsorption process of Pb(II) using ANA sample here is favourable.

For Freundlich isotherm:

The model described assumes the heterogeneous surface of ANA adsorbent[21]. Its linear formula can be expressed as:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \quad \textbf{(7)}$$

K_F (l/mg): Freundlich constant(distribution coefficient that represents the amount of adsorbed Pb(II) adsorbed onto adsorbent for one unit equilibrium concentration))[22]

n:Freundlich exponent(1/n value is very important in determination of adsorption feasibilities) [41].

(**K_F and $1/n$**) can be obtained from intercept and slope of a linear between **log q_e**against **log C_e** as shown in Fig.(7, b)

1/n values should be <1 for the favorable adsorption process.[42]

From data in Table (2), we can conclude that the adsorption of Pb(II) on ANA is favoured because1/n values<1(0.323).[2]

From data in table (2) and Fig. (4, b), the system is more fitted to Langmuir model than Freundlich one, because R^2 is (0.995) for Langmuir model and equal (0.893) in Freundlich isotherm. So, adsorption equilibrium of Pb(II) onto ANA is better described by the Langmuir isotherm than the Freundlich one.

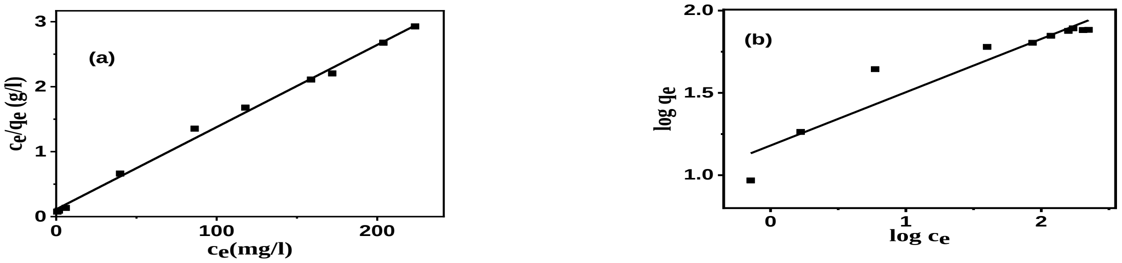

Fig 7: Adsorption isotherm (a) Langmuir and (b) Freundlich models for adsorption of Pb^{2+} at room temperature

Table (2): Langmuir and Freundlich isotherm constants for Pb(II) adsorption**.**

adsorbent	Langmuir model				Freundlich model		
q_{eexp}= 76.38 (mg/g)	q_e (mg/g)	b (L/mg)	R_L	R^2	K_f (1/g)	1/n	R^2
exp=experimentally	79.05	0.112	0.028	0.995	15.13	0.323	0.893

3.5. Adsorption Kinetic Study:

Adsorption kinetic study is important in determining and studying the efficiency and mechanism of adsorption process. Modelling of adsorption kinetics gives information for selecting between different adsorbents under different operational conditions to the optimal design that suite a given operational conditions for pollutants, such as heavy metals, removal from potable water and wastewater systems[43].

Therefore, the rate kinetics of Pb(II) ions sorption onto ANA were analyzed using pseudo-1storder model, and pseudo-2ndorder model.

3.5.1. Pseudo first-order equation

Lagergren proposed a pseudo-first-order kinetic model. This model was successfully applied to describe the kinetics of many adsorption systems[44] . The linearized equation of this model is shown as [45] :

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (7)$$

***q_e* (mg/g):** the amount of Pb (II) adsorbed at equilibrium.

q_t* (mg/g:)** are amount of Pb (II) adsorbed at time t (min). Linear plot of log ***(q_e– q_t) versus ***t*** as shown in Fig.(8, a) determine K1 and ***q_e*** from the slope and intercept.

3.5.2. Pseudo second-order equation:

The adsorption kinetics may also be described by a pseudo-second-order kinetic model [54]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad \textbf{(8)}$$

K_2 (g mg^{-1} min^{-1}): the second order rate constant.

From the linear plot of t/qt against t as shown in figure Fig.(8, b), we can determine both K_2 and q_e .

As shown in table (3) and figure (8), the correlation coefficient (R2) given by the pseudo-second order model **(0.999)** is higher than the first order one (0.643). Also the theoretical values of *q*e agree with the experimental values. We can conclude that, the adsorption conforms to the pseudo-second-order mechanism and can successfully describe the adsorption kinetics of this system.

Table (3): Kinetic parameters for the adsorption of Pb(II) adsorption

Kinetic parametes	**Pseudo 1st kinetic model**		
q_{exp}=98 (mg/g)	q_1 (mg/g)	k_1 (1/min)	R_1^2
	1.717	0.0132	0.643
	Pseudo 2nd order kinetic model		
	q_2 (mg/g)	k_2[g/(mgmin)]	R_2^2
	40.19	0.07	0.999

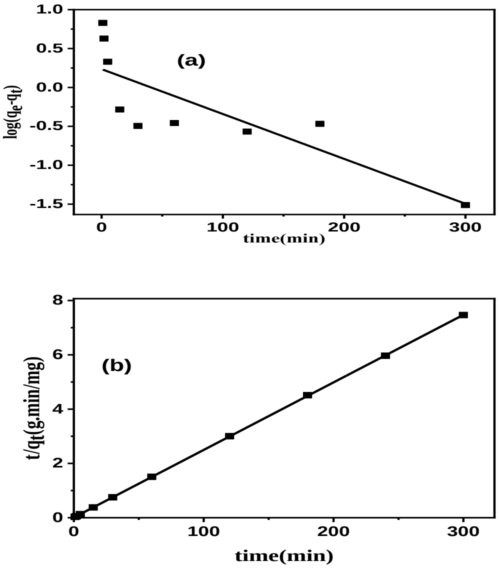

Fig 8: kinetic models for adsorption of Pb^{2+}: (a) Pseudo-first order and (b) Pseudo-second order.

3.6. Adsorption Thermodynamic Study:

Fig. (9, a) Shows the effect of temperature on lead sorption at ANA sample, where the adsorption capacity decreases with increasing temperature. This effect is used to calculate Parameters, such as standard free energy (ΔG^o_{ads}), enthalpy heat (ΔH^o_{ads}) and entropy (ΔS^o_{ads}) of adsorption process.

The values of enthalpy (**ΔH^o**) and entropy change (**ΔS^o**) were assessed from the slope ($\frac{-\Delta H^o}{R}$)and the intercept ($\frac{\Delta S^o}{R}$) of Van't Hoff equation[46] :

$$\ln K_c = \frac{-\Delta H^o}{RT} + \frac{\Delta S^o}{R} \qquad \textbf{(17)}$$

R: universal gas constant (8.314×10^{-3} kJ/mol K).

T: the temperature in (**K**), The spontaneous and feasibility nature of adsorption process is determined by Thermodynamic variables

The data of ΔG^o, ΔH^o and ΔS^o are tabulated in table (4). From table (3) and Fig.(9, b), The negative ΔG^o values indicate thermodynamically feasible and spontaneous nature of the Pb(II) adsorption on ANA. The negative value of ΔH^o indicating an exothermic nature of adsorption process of Pb(II) on ANA plant,

also the negative values of some ΔS^o indicate a decrease in the randomness at solid/solution interface

during the adsorption of Pb(II) on ANA [47] and the system's lower randomness and higher alignment[11]

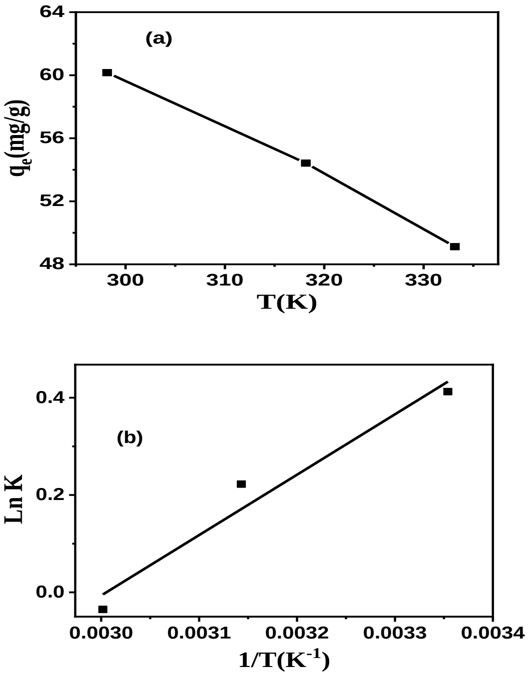

Fig 9: (a) effect of temperature on the adsorption capacity of Pb^{2+} on ANA, (b) Van't Hoff isotherm for adsorption of Pb^{2+}.

Table (4): Thermodynamic parameters for adsorption of Pb(II) ion on ANA .

sample	**Kc**			**ΔG^0 (kJ/mole)**			**ΔH^0(kJ/mole)**	**ΔS^0(J/mole K)**
	298.15 K	318.15 K	333.15 K	298.15 K	318.15 K	33315 K		
ANA	1.51	1.29	0.965	1.02-	-0.67	-0.098	-10.31	-30.92

3.7. Comparison of the proposed adsorbents with other cited adsorbents.

The adsorption capacity of novel biosorbent ANA plant in this study is compared to other published adsorbents to evaluate its efficiency in the removal of Pb(II) ions from water. As shown in table (5), we can deduce that this plant as a novel biosorbent has high efficiency in the removal of Pb(II) ions compared to other published ones[48-50].

Table (5): Comparison of maximum sorption capacity of Pb(II) by proposed derived bio-sorbent with previously published adsorbents.

Adsorbent	q_e mg/g	temperature	Ref.
H2SO4-treated CNS	8.73	30	[48]
Plum kernel	1.3	22	[49]
Peanut shell	7.13	30	[50]
Anabasis Articulata(ANA)	76.38	room	Present study

4. Conclusion

Anabasis Articulate as a Saharan plant collected from North Eastern Desert in Egypt

exhibit high adsorption efficiency of Pb(II) ions from water samples as deduced in this study.

In comparison with other adsorbents mentioned in the literature, we can observe the high efficiency in the metal ions removal per each gram of this plant that reaches up to 76.38 mg/g. it is found that, the adsorption process is more fitted to Langmuir model than Ferundlish one. The removal of lead from water by this plant reaches equilibrium at 60 min from kinetic data which is subjected to pseudo 1st order than 2nd model. Thermodynamic studies show the exothermic nature of the adsorption process of Pb(II) on ANA plant with spontaneous nature at low temperature. Summarization of this study that the adsorption of Pb(II) using ANA plant is favoured with high adsorption capacity by using an eco-friendly biosorbent and phytoremediation method.

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