BIOSORPTION OF DISSOLVED Pb(II) IN DILUTE AQUEOUS SOLUTIONS BY USING AGRO-WASTE PRODUCTS

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ABSTRACT

The potential to remove Pb(II) from aqueous solutions through biosorption using four raw dead plant biomasses (karab, bardie, rice hulls and corn-cobs) was investigated in batch tests and compared with that for the PAC. From tests, it was found that the four types of dead-plant biomasses had shown high removal efficiency with the descending order (karab, bardie, rice hulls and corn cobs). Their percent removal (% R) of Pb(II) were (98.76, 96.10, 95.16 and 94.70) respectively at pH 4 with 0.2 g of sorbent/100 ml of 10 ppm lead solution , while it was (99.8 %) for PAC. Generally through batch system at a laboratory scale, karab has proved to be an efficient biosorbent for the removal of Pb(II) from aqueous solutions with low initial ion concentration (1–10 mg Pb(II)/ℓ) at pH (4 - 4.5). The EPA discharge limit (0.1 ppm) for lead was achieved. The biosorption rate is quite rapid and within 5 min of mixing more than 90 % of Pb(II) ions were removed by the karab biomass. Varying agitation speed has no influence on the rate of uptake and the Pb(II) uptake was not affected by karab particle size. The Freundlich and Langmuir isotherms described the data well. According to the evaluation using Langmuir equation, the maximum capacity q max obtined from equilibrium biosorption isotherm test was 13.2 mg/l for pb (II) . The ultimate sorption capacity K_F in the Frendlich model was 3.1 .

الخلاصة

إزالة أيونات المعادنِ الثقيلةِ مِنْ المياه الملوثة بها وخاصة المياه الصناعية منها, تعتبرمشكلة بيئية رئيسية مما دفع العلماء والباحثين بإقامة دراسات كثيرة حول هذا الموضوع منذ الثمانينات وكان من أحد الحلول للمشكلة هو إستعمال كتل عضوية ميتة حيوانية أو نباتية المصدر كوسائل لإنتِزاع أيوناتِ المعادنِ الثقيلة من الماء الملوث بها, ولتكون المعالجةِ البيئيةِ أقتصادية يتطلب أنّ يكون مصدرالكتل العضويةَ مِنْ الطبيعةِ أَوَ فضلات عضوية ناتجة من المصانع أو من النشاطات الزراعية وأن تكون متوفرة بكثرة و متجددة. إن المعالجة بطريقة فصل الأيونات من المياه بالكتل العضوية الميتة أخذت تجذب الكثير من العلماء والجهات المسؤولة عن حماية البيئة لأنها طريقة أقتصادية وكفوءة و يَمكن لهذه التقنيةً أَنْ تُساهمَ في تَحسين البيئةِ.

الغرض من هذا البحث هو دراسة إمكانية استخدام أجزاء نباتية ميتة ككتل عضوية لمعالجة المياه الحاوية على أيونات الرصاص الذائبه وتخليصها منها ومدى كفاءة هذه المعالجة وخواصها و دراسة الشروط البيئية والتشغيلية لإزالة أفضل ولتحقيق الغرض الأقتصادي المطلوب في معالجة مشكلة تلوث البيئة.

أولاً، في هذا البحثِ تم اختيارأربع كتل عضويةَ ميتةَ ذات أصل نباتي وهي كرب النخيل و البردي وقشور الرز (السبوس) وعرانيص الذرة حيث تعتبر مخلفات زراعية ما عدا البردي وتم أختبار قابليتها لإزالة أيون الرصاص ومقارنتها بالكاربون المنشّطِ المطحونِ(PAC) حيث تبين من التجارب بأن كفاءة الأنواع الأربعة من الكتل العضوية النباتية الميتة كانت عالية جدا وإن نسب الإزالة المئوية لها كانت كما يلي (98.76 %للكرب, 96.10 % للبردي, 95.16 % لقشور الرز وأخيرا 94.70 % لعرانيص الذره) بينما كانت 99.80 % للكاربون المنشط المطحون (PAC). إن كفاءة الكرب في إزالة أيون الرصاص أعلى من الثلاث الأخرياتً و مقاربة لكفاءة ال PAC, لذلك تم التركيز على دراسة كرب النخيل في التجارب الأخرى.

نفذت التجارب مختبريا بأستخدام الدوارق الزجاجية و الخلاط المغناطيسي. الماء الملوث بأيونات الرصاص المذابة و المستخدم في المعالجة تم تحضيره مختبريا بتراكيز مخففة ومختلفة ضمن المدى (1- 100 ملغ رصاص\لتر). عموماً حصلنا بعد المعالجة على قيم تراكيزمتبقية من أيون

الرصاص صغيرة جدا مساوية و حتى أقل بكثير من الحد الموصى به والمسموح به لأيون الرصاص في الماء الذي يتم تصريفه للأنهر حسب المواصفة العراقية و كذلك منظمة حماية البيئة العالمية (0.1ppm).

KEYWORDS

Heavy metal removal, wastewater treatment, sorption, isotherms, biosorption, agro-wastes, dead- plant biomass, agricultural by products.

INTRODUCTION:

The world suffers from chemical contamination of water supplies, largely due to uncontrolled industrial activity and so a water treatment technique which is able to deal with such pollutants in an effective way is very valuable.

The presence of heavy metal ions in surface and ground water supplies have been prioritized as major inorganic contaminants in the environment. It has been established that dissolved metals (particularly heavy metals) escaping into the environment pose a serious health hazard. They accumulate in living tissues throughout the food chain, which has humans at its top, multiplying the danger (Volesky, 1999). Besides, metal resources are non-renewable and natural reserves are becoming depleted. It is therefore imperative that those metals considered environmentally hazardous, or which are of technological importance, strategic significance or economic value, be removed/recovered at their source using appropriate treatment (Atkinson et al., 1998).

The biosorption appears to be a promising technology that could contribute to improving the environment. Biosorption technology, utilizing any natural form of biomass to passively sorb and immobilize solubilized heavy metals (Atkinson et al., 1998). Therefore, biosorption can be defined as the ability of certain types of inactive, dead biomass to binde and concentrate heavy metals from aqueous solutions (even very dilute ones) (Cordero et al., 2004; Ahalya et al., 2004). The use of non-living biomaterials as metal-binding compounds has been gaining advantage because high levels of contamination do not affect them. Moreover, they require minimum care and can be obtained more cheaply (Horsfall et al., 2003). Hence, the advantages of biosorption are the low cost, high efficiency of heavy metal removal from diluted aqueous solutions and environmentally friendly.

The economics of environmental remediation dictate that the biomass must come from nature, or even be a waste material (Vieiral and Voleskey, 2000). Therefore, suitable biomass comes as a waste material or by-product from large-scale industrial operations (eg. Use of olive mill residues as heavy metal sorbent material) or certain waste from agricultural operations or biological materials that are available in large quantities (Nomanbhay and Palanisamy, 2005).

Several studies have shown that non-living plant biomass materials are effective for the removal of trace metals from contaminated waters (Horsfall et al., 2003). The unique ability of these plants (lignocellulosic biosorbents) to bind metals has been attributed to the presence of various chemical functional groups such as carboxyl, hydroxyl, amino, or phenolics, which can attract and sequester metal ions from their solutions (ABIA et al., 2002; Shin et al., 2003).

Research on biosorption is revealing that it is sometimes a complex phenomenon where the metallic species could be deposited in the solid biosorbent through various sorption processes, such as ion exchange, complexation, chelation, microprecipitation, etc. Due to the complexity of the biomaterials used, it is possible that at least some of these mechanisms are acting simultaneously to varying degrees, depending on the biosorbent and the solution environment (Jeffers et al. 1991). The most probable mechanism may be ion exchange (Han et al., 2000).

Biosorption not only offers an innovative alternative to other remediation approaches, it also allows metals recovery. The metal ions can be readily desorbed from the biomass by use of a suitable eluting agent. It has been shown in certain cases, at least, that the biomass can be subjected to a number of loading and elution cycles without the biomass losing its sorption capacity (Schneider et al., 2001). Biosortpion can be carried out as a batch process and/or a continuous process.

The goal for this research is to develop inexpensive, highly available, effective metal ion sorbent from agricultural by-products or agro-wastes as alternative to existing commercial adsorbents.

The work on this project include carrying out different equilibrium sorption tests for finding the optimum environmental and operating conditions and sorption isotherm experiments also performed using a synthetic single-solute aqueous solutions polluted with Pb(II).

MATERIALS AND METHODS:

Sorbate:

In the experimental works, the dissolved Pb(II) in aqueous solutions has been selected as the sorbate. The selection to this sorbate is based on the following reasons:
Lead is one of the oldest metals known to human and the most widely use of the toxic heavy metals (CWA, 1972). The hazard from lead is aggravated by its widespread distribution as the metal, inorganic and organometallic compounds (Manahan, 1999). In addition lead is non-biodegradable, persists in the environment and has a tendency for bioaccumulation (Reimann and De Caritat, 1998).

Lead is widely distributed in the environment of Iraq as a result of the use of tetraethyl lead in gasoline to control premature ignition (knocking), battery industrial factories, petrochemical industry, electroplating, metallurgy, paints, radiation protection equipment, pigments, stabilizer in plastic industries, ammunition, cable sheathing and in printing processes. Moreover, the absence of the direct control from environmental protection agencies on above industries has increased the size of this problem. Thus, it is existed in rain, runoff, soils, dust and industrial and municipal discharges.

The health hazards due to the presence of lead in water are of extreme concern to the public, government and industry. Lead is known to have a toxic effect on the neuronal system and on the function of brain cells (Baig et. al., 1999). The health hazards due to the toxicity of lead in waters have been reported in many journals and emphasize the need to identify effective lead sorption systems.

According to the U.S. EPA standards, the maximum concentration limit for Pb(II) for discharge into surface water is 0.1 mg/ℓ and in drinking water is 0.05 mg/ℓ (Nomanbhay and Palanisamy, 2005). This limit has been recommended for Iraqi water standards according to the Law No. 25, (1967) (Standard Iraqi Pollution Control Regulation for the Preservation of Water Resources from Contamination). While for lead in drinking water the maximum acceptable concentration (MAC) recommended by (WHO) is 0.01 mg/ℓ (10 μg/ℓ) (Reimann and De Caritat, 1998).

Biosorbents used:

- The old bases of leaves for date palm tree (karab),
- Phragmites australis (bardie) a large grass native to wetland sites.
- Rice hulls (or rice husks) and
- Maize cobs (corn cobs)

PREPARATION OF THE BIOMASS:

The palm Karab was collected from Baghdad, Khastawi type, sun dried and washed with tap water then rinsed with distilled deionized water several times and thereafter dried at a temperature of 105^o C in an oven for 24 hours. Following cutting into small pieces then it was ground using a food processor (Blender) and screened through a sieve No.40 (ASTM E 11- 81). This was done to remove any large particles and to obtain particles of size less than (0.425 mm). This fine biomass was used in the batch experiments described below. For preservation, it was kept in plastic bags to minimize its contact with humidity. Same procedure was followed for preparing bardie, rice husk and corncobs.

PREPARATION OF SYNTHETIC POLLUTED WATER:

Firstly an aqueous stock solution (1000 mg/l) of Pb(II) ions was prepared using $PbNO_3$ salt according to (Standard Methods for the Examination of Water and Wastewater, 1971). Synthetic polluted water samples containing definite concentrations of Pb(II) were prepared by diluting stock (1000 ppm) solution with distilled water. Fresh dilutions were used for each study. The adjustment of lead solution pH at a desired value was done by adding drops of 0.1N HCl or NaOH.

ANALYTICAL MEASUREMENTS:

The polluted water sample and the samples resulted from each treatment were analyzed for Pb(II) using atomic absorption spectrometer (AAS).

BATCH TESTS:

A batch technique was used to perform biosorption experiments and to find the optimum environmental and operation parameters for biosorption of Pb(II) .
All experiments were carried out in 250 ml Erlenmyer flasks. In each experiment a solution of (100 ml) with known initial lead concentration adjusted to a desired pH value was mixed with a definite amount of biosorbent. After that the sample was mixed (stirred) for certain time by using a magnetic stirrer until reaching equilibrium condition. The suspension was then filtered with Whatman filter paper and the concentration of metal ion in the filtrate was measured by AAS. Then the final metal concentration can be recorded as a function of the initial metal concentration and the biomass loading.

Effects of various parameters such as pH, contact time, stirring speed, amount of biosorbent, initial metal concentration and effective biosorbent particle size were studied and details shown in Table 1. All experiments were carried out at room temperature (25 ± 2^oC).

THE BIOREMOVAL EFFICIENCY:

The results were expressed also as the removal efficiency of the biosorbent on Pb(II), which was defined as follows (Aslam, M. M., et. al., 2004):

$$\text{Removal efficiency (\%)} = [(C_i - C_f)/C_i\,] \times 100$$

where C_i and C_f are the metal ion concentration in the sample solution before and after treatment, respectively.

CALCULATION OF METAL UPTAKE BY BIOMASS:

The amount of metal ion uptake by the biomass during the series of batch experiments, were determined using a mass balance equation which expressed as follows (Hussein et al., 2004):

$$q_e = \frac{(C_i - C_f)\,V}{S}$$

where q_e is the metal ion uptake capacity (mg of metal ion sorbed/g dry biomass) at equilibrium, C_f is the final metal ion concentration in solution (mg of metal ion/ℓ) at equilibrium, C_i is the initial metal ion concentration in solution (mg of metal ion/ℓ), V is the volume of initial metal ion solution used (ℓ) and S is the mass (dry weight) of biomass used (g).

Table 1: Examined conditions of batch tests.

Test type	Test No.	Type of biosorbent	S (g of biomass/100ml)	Initial pH	C_o (mg/ℓ)	Time of stirring (t)	Particle siz, d_p (mm)	Speed of stirring (rpm)
Effect of pH	1	PAC, Karab, Bardie, Rice hulls, Corncobs	0.2	**(2, 3, 4, 5, 6, 7, 8.5) for each sorbent**	10	1 h	< 0.425	120
	2			**4**				
Effect of biosorbent amount	1	Karab	**(0.05 – 1.0)**	4.5	10	1 h	< 0.425	120
	2		**(0.05 - 1.5)**		106.5			
Effect of contact time	1	Karab	0.2	4.5	10	**(5 min- 4 h)**	< 0.425	120
	2		1		106.5	**(5 min- 4 h)**		

Effect of initial Pb(II) concentration & biosorption isotherm (by changing Ci)	1	Karab	1	4.5	**(1-100)**	1h	< 0.425	120
Effect of stirring speed	1	Karab	1	4.5	37	1 h	< 0.425	**(0-600)**
Effect of particle size	1	Karab	0.2	4.5	10	(5 min- 60 min)	(< 0.426, 0.425 - 1.4, 2.0 - 2.36)	**120**

EQUILIBRIUM MODELING:

Biosorption has been studied as simplified sorption systems, usually containing one heavy metal. This is an appropriate simplification for effective experimentation. Langmuir and Freundlich are some of the simple sorption isotherm models that are most frequently applied. There is no critical reason to use a more-complex model if a two-parameter model (such as the Langmuir and Freundlich isotherm models) can fit the data reasonably well (Volesky, 2003).

The Langmuir equation has been extensively used for the evaluation and comparison of metal uptake capacities of biosorbents. The Langmuir isotherm is based on these assumptions (Muraleedharan et al., 1995):

1. Metal ions are chemically adsorbed at a fixed number of well defined sites;
2. Each site can hold only one ion;
3. All sites are energetically equivalent and;
4. There is no interaction between the ions.

The general form of the Langmuir relationship as follows (Ahalya et al., 2005):

$$q_e = \frac{q_{max}\, b\, C_f}{1 + b\, C_f}$$

where q_e is milligrams of metal bound per gram of biosorbent at equilibrium, C_f is the metal residual concentration in solution at equilibrium (mg/l); q_{max} is the maximum metal uptake corresponding to the site saturation (mg/g) and b is constant and is the ratio of adsorption and desorption rates .

The linearised Langmuir isotherm allows the calculation of adsorption capacities and the Langmuir costants and is equated by the following equation.

$$C_f/q_e = 1/q_{max}.\, b + C_f/q_{max}$$

The Freundlich isotherm is represented by the equation (Watts, 1998):

$$q = K_F C_f^{1/n}$$

where C_f is the equilibrium concentration (mg/l), q is the amount adsorbed (mg/g) and K_F and n are constants incorporating all parameters affecting the adsorption capacity and intensity respectively.

The linearised forms of Freundlich adsorption isotherm was used to evaluate the sorption data and is represented as:

$$\ln q = \ln K_F + 1/n \ln C_f$$

Results and Discussions

Effect of pH:

Four types of dead plant biomass (karab, bardie, rice hulls and corncobs) were chosen to examine their ability to remove Pb(II) from aqueous solutions under different pH values. Also the PAC was used only in this test as a commercial sorbent for comparison. The comparison of the sorption performance of the different biosorbents was achieved under the same environmental and operating conditions.

The pH profile studies showed that the biosorption of Pb(II) is pH dependent. This effect in pH suggests that the binding mechanism for the metal investigated may be an ion-excahange type process. The protons of the acid functional groups in the biomass were exchanged with cationic Pb (II) at slightly acidic pH. Also, the Pb(II) uptake for the four types of agro-biomass is very low at a pH of 2.0, then increasing the pH of the solution from 2 to 4, leads to a rapid increase in the Pb(II) uptake. The optimum Pb(II) uptakes occur at pH value 4, with a further increase in pH to about 5 and more, the Pb(II) uptake by all of the four agro-biomass decreases due to the hydrolysis and precipitation of lead ions, as shown in Fig. 1. It is also notised from the figure that the Pb(II) uptake of PAC is very high at a pH of 2.0 .The increasing of the pH of the solution leads to a decrease in Pb(II) uptake . Steel and McGhee(1980) stated that the forces holding a molecule against the carbon curface may result from chemical bonding or Van der Waals attraction .

Adsorption is greatest at low pH since at low Ph activated carbon is positively charged due to adsorption of hydrogen ion , while most colloids and all ionized polar grups on organic molecules are negativly charged .

The pH represents the negative logarithm of protom (H^+) concentration in aqueous solution , different levels of pH reflecting the hydrogen ion concentration , which affect the uptake of metal ions . Researchers rported that the decrease in metal uptake capacity for the biosorbents at lower pH values (≤ 2) can be attributed to the presence of H^+ ions in high concentration and compete with cations for the binding sites. While others stated that at the lower the pH value the highel the proton concentration in the solution and the surface of the sorbent would bclosely associated with hydronium ions (H_3O^+) which hinder the access of heavymetel ions (i.e.cations) , by repulsive forces , to the surface functional groups of biomass , consequently decreasing the percentage of metl big removal conversely , the increase in biosorption as pH increases can be explained on the basis of a decrease in competition between protons and dissolved metal ions for the surface sites and by the decrease in positive surface charges which results in a lower coulobic repultion of the cations (Tilaki and Ali , 2003 cossich et al 2002).

From Figure 2, it can be seen that the high percent removal values were obtained at pH 4 by the four agro-biomasses used with the order as shown in bar chart. The karab has the higher ability followed by bardie, rice hulls and corncobs consequently. The removal efficiency with karab was (98.76 %) which gave the lower remaining concentration for Pb (II) in solution sample and it is comparable to that for the commercial sorbent PAC. Therefore, the karab biomass was selected as our objective biosorbent to study in more detailes. Besides, no further researches have been done on the use of Karab as agro-biomass sorbent for heavy metal ions removal.

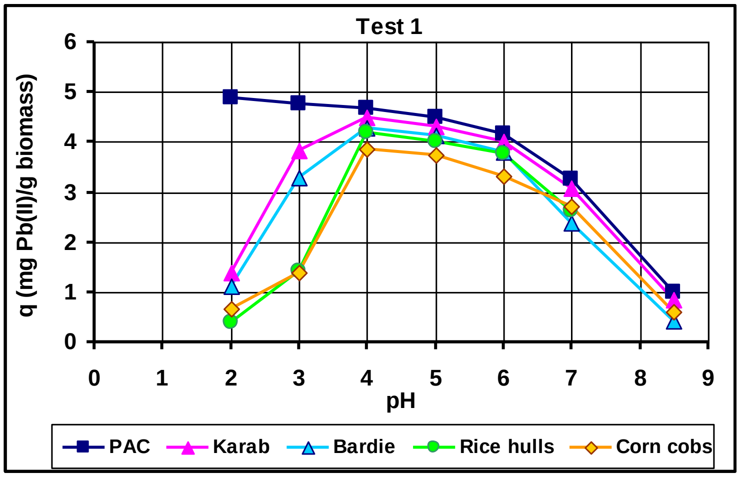


Fig 1 The pH profile for Pb(II) uptake for $C_i = 10$ ppm, by 2 g/1 at 120 rpm with equilibrium time of 1 h.

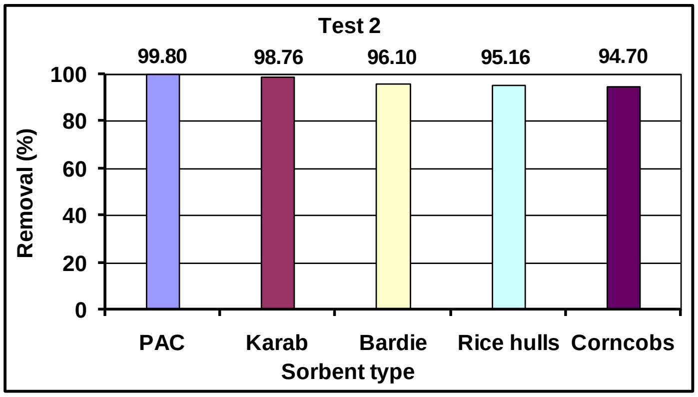


Fig 2 Effect of sorbent type on percent removal of lead ion.

Effect of biomass quantity on Pb(II) uptake by karab:

Effect of karab dosage on biosorption process was carefully studied through doing two tests with varied karab dosages, started with 0.05 to 1.5 g of karab/100 ml lead solution of two varied initial concentrations 10 and 106.5 ppm and keeping pH, agitation speed and contact time constant. The results have been plotted on arithmetic papers as shown in Figure 3 and 4 respectively.

It can be seen in Fig. 3 that the increase in the biomass concentration leads to decrease the metal ion uptake, this attributed to the responsibility of metal ion concentration shortage in solution.

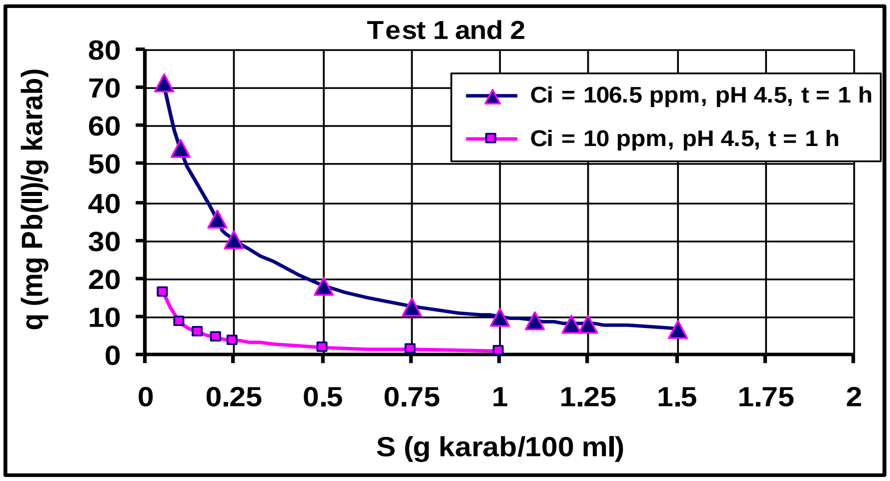


Fig3 Effect of karab dosage on Pb(II) uptake at various initial concentrations.

While, Figure 4 demonstrates that the metal bioremoval efficiency increases with increasing biosorbent dosage up to a certain value. Hence, the optimum sorbent amount required for cost-effective treatment can be well noticed from Fig. 4, where at 10 ppm the maximum percent removal for Pb(II) was about 96.63 % at the karab dosage of 0.2 g/100 ml. While at 106.5 ppm the maximum percent removal for Pb(II) was about 93.15 % at 1g/100 ml karab dosage.

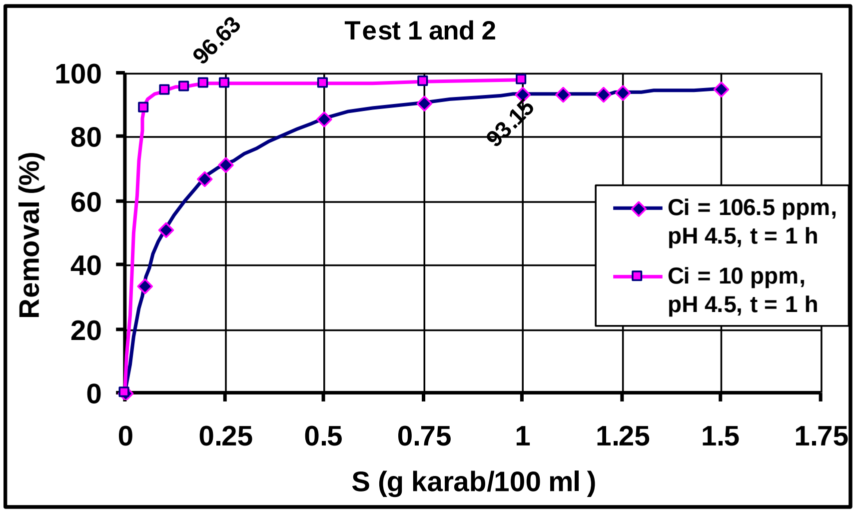


Fig4 Effect of karab dosage on lead percent removal from aqueous solutions of two different initial concentrations of Pb(II).

Biosorption kinetics:

The rate of Pb(II) uptake by karab biomass was investigated, in order to assess the required contact time between the biosorbent and the polluted water to reach an equilibrium state between the dissolved and solid-bound sorbate (lead ions).

From Figure 5 and 6, one can notice how rapidly the biosorption process happens; more than 90% of the equilibrium sorption has occurred within 5 minutes of exposure and remains relatively constant thereafter. This is explained by that, the initial rapid sorption of Pb(II) is due to ion exchange with surface cations on the biomass, while the later slow sorption of lead(II) represents a gradual uptake of cation exchange at the inner surface.

Generally, the equilibrium is attained at less than 30 min. After one hour Pb(II) concentration was found to be time invariant in all tests. Thus, one hour contact time was more sufficient to approach equilibrium. This result is important, as equilibrium time is one of the important parameters for an economical wastewater treatment system.

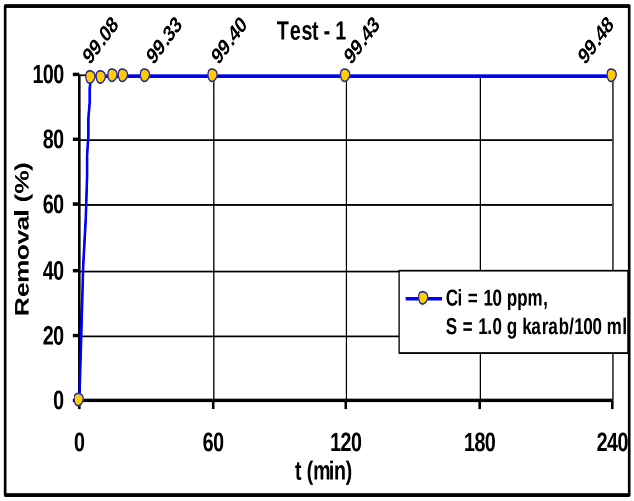


Fig 5 Rate of percent removal of Pb(II) by karab biomass for [C_i = 10 ppm].

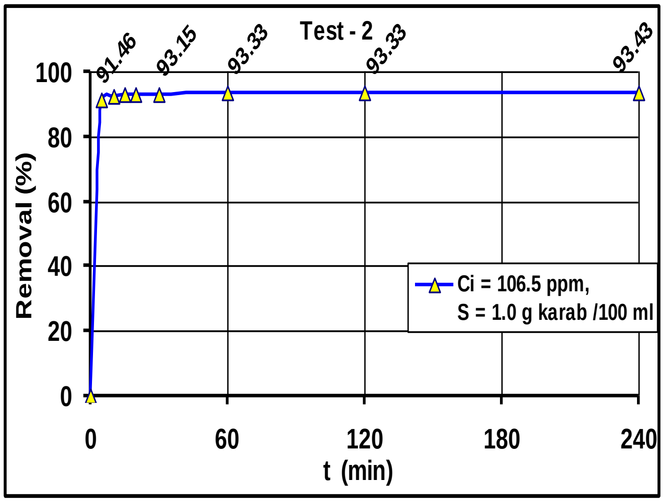


Figure 6 Rate of percent removal of Pb(II) by karab biomass for [C_i = 106.5 ppm].

Effect of initial concentration of Pb(II):

The initial concentration of the metal ion is a significant factor to be considered for effective biosorption.

The Pb(II) percent removal from solutions within the low concentration range (1-100 ppm) is shown in Fig. 7, the Pb(II) uptake percentage for 1 g karab biomass/100 ml is considered high and approximately in the range of (95 – 99 %).

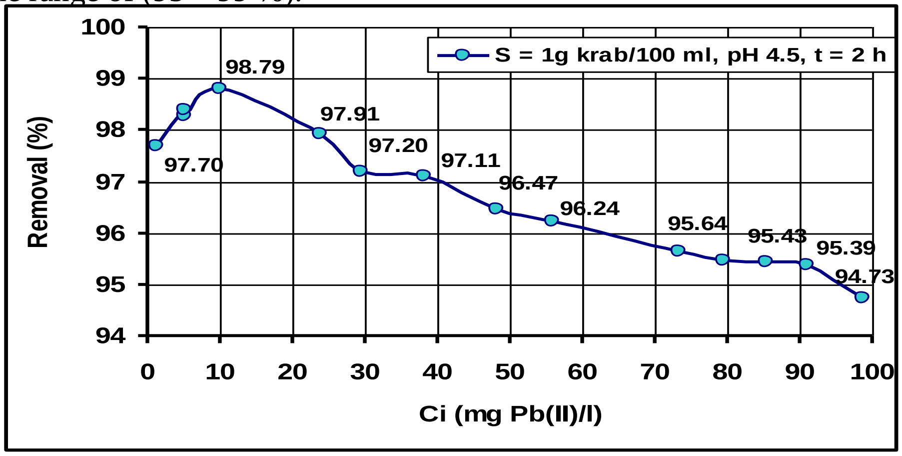


Fig 7 Percent removal of Pb(II) by karab biomass from solutions of various initial concentrations.

Also, it can be seen in Fig. 8, the final lead concentrations (C_f) for lower concentrations range (1-10 ppm) are within the allowable limit of wastewater discharge (0.1 ppm) for Pb(II). Moreover, some results are within the limit of drinking water (0.05 ppm) for Pb(II). Thus, results have encouraged us to continue the tests with column system.

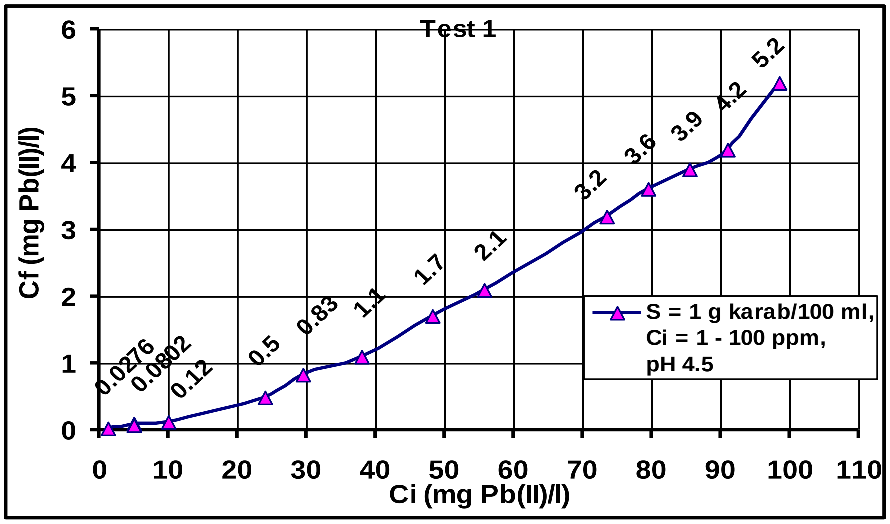


Fig 8 The final concentrations of Pb(II) at equilibrium.

- Effect of stirring (mixing) speed:

The effect of stirring (mixing) the biosorbent/sorbate system on Pb(II) removal efficiency by karab was studied by varying the speed of mixing from 0 (with no-mixing as a control for comparison) to 600 rpm, while keeping the dose of biosorbent, the contact time and optimum pH as constants.

It can be seen in Fig. 9, the Pb(II) bioremoval efficiency has increased with samples mixed at different speeds over the non-mixed samples of the karab/lead solution system. The Pb(II) removal efficiency increased from (21.62 %) for the sample without mixing to (96.5 %) for the sample mixed with 100 rpm. Then increasing the mixing speed from 100 rpm to 600 rpm there is no effect observed on Pb(II) removal efficiency and the biosorption capacity for karab remained constant with speed increase as shown in Fig. 10. Thus, results indicate that the contact between the karab biomass and lead solution is effective even at low mixing speed (100-120 rpm).

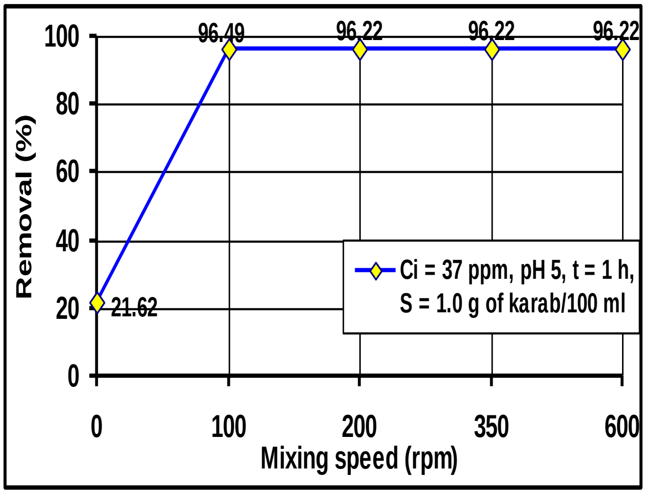


Fig 9 Effect of mixing speed on Pb(II) percent removal by karab.

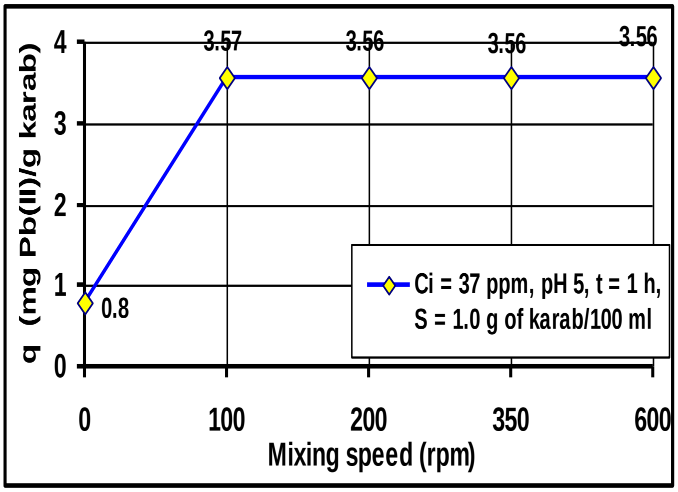
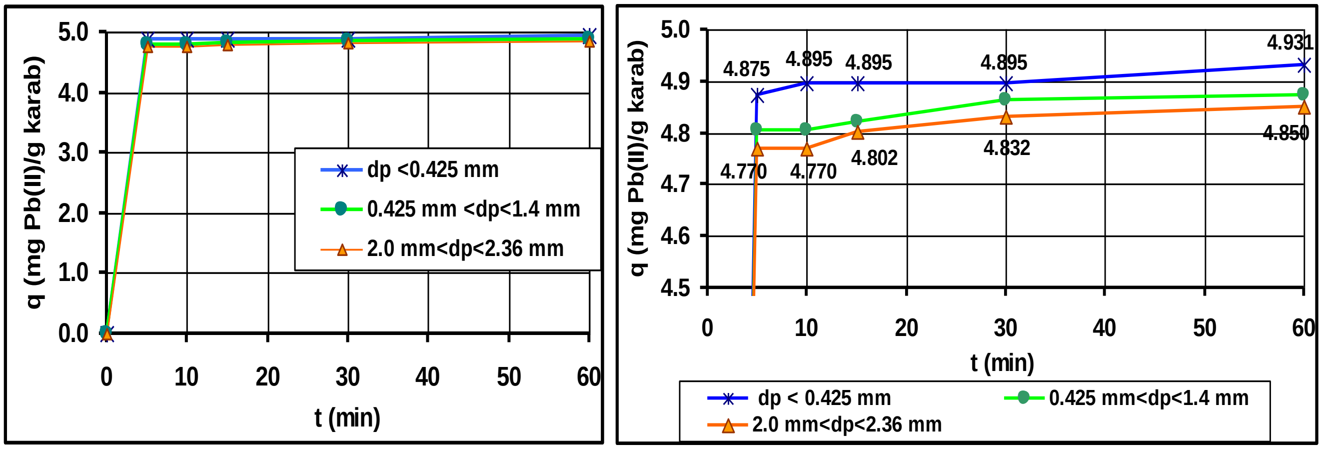


Fig 10 Effect of mixing speed on Pb(II) uptake for karab.

Influence of biosorbent particle size on lead biosorption:

From Figure 11(a), one can notice that the effect of karab particle size on Pb(II) uptake is negligible and can not be recognized easily. This small effect has been shown better in Fig. 11(b), after changing the scale of y-axis of Fig. 11(a). From this figure, it can be seen that the karab particle size has little influence on the capacity and rate of Pb(II) biosorption.



(a) (b)

Fig 11 Pb(II) uptake related to time for various karab particle sizes.

Sorption equilibria studies:

The experimental results were analyzed in terms of two adsorption isotherm equations, the Langmuir and Freundlich isotherms. These two models were used to adjust (fit) the experimental data obtained for biosorption of Pb(II) from the synthetic lead solution by karab biomass. The parameters of the two models, the ultimate sorption capacity (K_F) and the sorption intensity (n) in the Freundlich model as well as the maximum uptake capacity (q_{max}) and the equilibrium constant (b) in the Langmuir model were calculated using the linear regression analysis of the experimental data. Also, the correlation coefficient (R^2) for each model and experiments was calculated.The Langmuir capacity (q_{max}) is the maximum specific uptake corresponding to the site saturation . q_{max} is used to compare the effeciency of the adsorbent (karap biomass) with other materials ,which have been tested as biosorbent for Pb(II) .the magnitude of K_F and n is used to compare easy seperation of heavy metal ion from wastewater and high adsorption capacity of karab biomass with other materials.

K_F is the Freundlich capacity factor for various compounds is extremely wide .Because of the wide variatoin the Freundlich capacity factor must be detrmined for each compound (Metcalf and eddy ,2003) .

Table 2 Summary of Freundlich and Langmuir equilibrium biosorption isotherms results.

Exp. No.	pH	S (g of karab/100 ml lead solution)	t (h)	C_o (mg/ℓ)	Linear Freundlich isotherm constants				Linear Langmuir isotherm parameters		
					K_F	1/n	n	R^2	q_{max} (mg/g)	b (ℓ/mg)	R^2
1	4	1.0	1	1 - 100	3.1	0.759	1.32	0.9732	13.2	0.4	0.9331

The correlation coefficient (R2) of both models, were mostly greater than 0.9 (close to one). The values of correlation coefficients (R2) indicated a strong positive relationship between the data and the linear equations of Langmuir and Freundlich as shown in Fig. 12 and 13 respectively. Also, that both models adequately describe the experimental data of the biosorption of these metals but Freundlich model fits experimental data better than Langmuir one as shown in Fig. 14.

According to Ahalya et al., (2005), n values between 1 and 10 represent beneficial adsorption. Hence, the value of n, which is related to the distribution of bonded ions on the sorbent surface, is found to be greater than unity for karab, indicating that adsorption of Pb(II) is favourable for karab biomass.

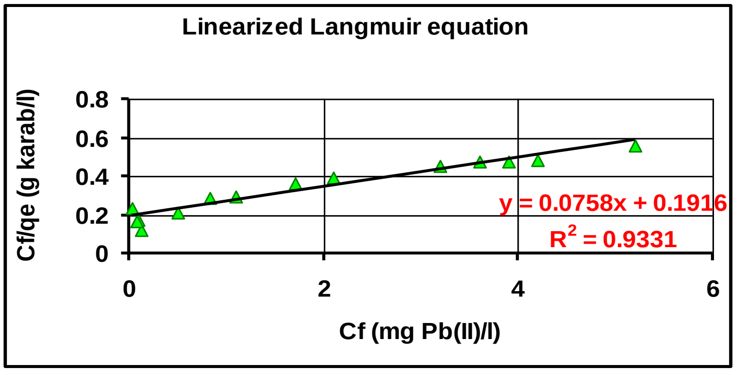


Fig 12 Langmuir adsorption isotherm for Pb(II) biosorption by karab, for [C_i = 1-100ppm] and at optimum conditions.

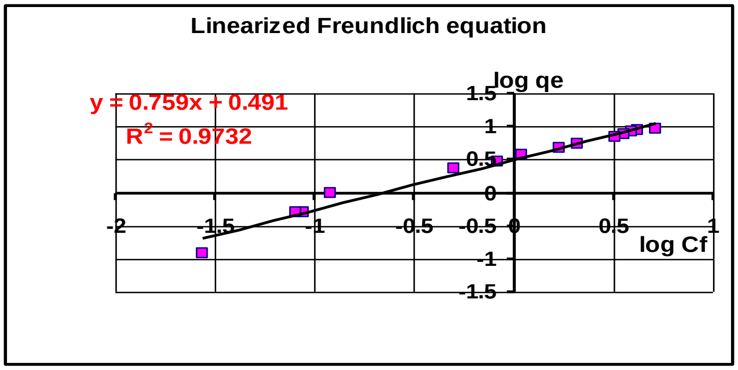


Fig 13 Freundlich adsorption isotherm for Pb(II) biosorption by karab, for [C_i = 1- 100 ppm] and at optimum conditions.

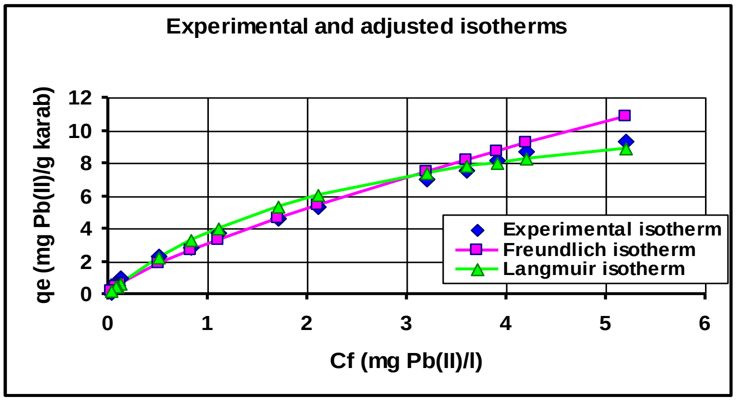


Fig14 Equilibrium biosorption isotherms for Ci = 1-100 ppm.

Conclusion

Human populations need methods and technologies to clean waters and diminish the environmental dangers related to technological progress. Biosorption can be one such solution to clean up heavy metal contamination. The ability of the karab biomass to remove Pb(II) from synthetic aqueous solution with a single solute has been found higher than the ability for the other three biomasses “bardie, rice hulls and corncobs”, and as good as that for PAC. The karab biomass was used as an inactivated natural dead plant biomass. It is a lignocellulosic material. It is an agro-waste or agricultural by-product has negligible cost (cheap material) and has also proved to be an efficient biosorbent for the removal of Pb(II) ions from a synthetic aqueous solutions with low concentrations (1-100 mg of Pb(II)/L) in a laboratory scale. So its utilizing in industrial wastewater treatment plants would be convenient to provide economic metal decontamination of large amounts of wastewaters of low concentrations waste streams.

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