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Removal of Pb(II) from aqueous solutions by citric acid modified *Manilkara zapota* leaves powder: Equilibrium and Kinetic studies

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ABSTRACT

The biosorption of Pb(II) from aqueous solutions onto Manilkara zapota leaves powder modified with citric acid treatment was investigated with respect to initial pH, contact time, initial metal ion concentration and biomass dosage. The adsorbent was characterized by Infrared Spectroscopy, X-ray diffraction, Scanning Electron Microscopy and Elemental analysis. Langmuir, Freundlich and Dubinin-Radushkevich (D-R) isotherm models were applied to describe the biosorption isotherms. Langmuir model provided the best correlation for the adsorption of Pb(II) by CAMMZL and the monolayer adsorption capacity was found to be 53.84 mg/g at pH 5.0 and 60 min equilibrium time. Experimental data was also tested in terms of biosorption kinetics using pseudo-first order, pseudo- second order and intra particle kinetic models. The results showed the pseudo second order model fits the experimental data very well with correlation coefficient greater than 0.999.Desorption experiments were carried out using dilute hydrochloric acid solution and the recovery of metal ions from CAMMZL was found 98 %. Desorption experiments showed the feasibility of regeneration of the adsorbent for further use after treating with dilute HCl.

Keywords: Biosorption; *Manilkara zapota* leaves; Isotherms; Kinetics; Lead

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INTRODUCTION

Removal of heavy metals from aqueous streams is one of the serious environmental problem of worldwide concern in now a days, because heavy metals are highly toxic, may undergo transformations, non-biodegradable and carcinogenic in nature. In addition these heavy metals are harmful to humans, animals, plants, and urban ecosystems [1]. Among these hazardous materials Lead is most commonly found in an industrial wastewater, thus their removal is of utmost importance. Lead is toxic metal contaminants in water, toxic to living organisms and if released into the environment can bio accumulate and enter the food chain. Lead is known to cause mental retardation, reduces hemoglobin production necessary for oxygen transport and it interferes with normal cellular metabolism. Lead poisoning in human causes severe damage to kidney, nervous system, reproductive system, liver and brain [2]. It reduces I.Q level in children. Different industrial processes, such as battery manufacturing, printing and pigment, metal plating and finishing, ammunition, soldering material, ceramic and glass industries, iron and steel manufacturing units are major sources of lead contamination in wastewater. Lead is used as industrial raw material in the manufacture of storage batteries, pigments, leaded glass, fuels, photographic materials, matches and explosives [3].Owing to their adverse effects on living organisms, Global and local agencies have therefore established certain limits on the quantities of toxic metals being discharged into environment. In view of its toxicity, US Environmental Protection Agency (USEPA) has set a safety level of lead in drinking water is 0.05 mg/L [4] and the Bureau of Indian standards as 0.1 mg/L [5]. World Health Organization (WHO) and American water works Association (AWWA) recommended maximum acceptable concentration of lead in drinking water is 0.05 mg/L [6].

Therefore, it is necessary to alleviate these metal ions from industrial effluents, before their discharge into water bodies. Many physicochemical methods have been proposed for their removal from industrial effluents such as electro-chemical precipitation, ion exchange, membrane separation, evaporation, coagulation-flocculation, flotation, reverse osmosis and adsorption [7]. However most of these technologies are suitable where the concentrations of heavy metal ions are relatively high. They are either ineffective are expensive when heavy metals are present in the waste water at low concentrations. The utilization of biosorption technology for the treatment of heavy metal contaminated waste waters has become an alternative method to conventional treatments due to high selectivity, easily handling, lower operating costs, high efficiency in removing very low levels of heavy metals from dilute solutions [8].Hence, there is a growing demand to find low-cost and efficient, locally available adsorbents for the sorption of lead such as the Apple waste [9], Citrus peels [10], rice husk [11], Wheat bran [12], banana peel [13] and *Eupatorium adenophorumspreng*[14] have been examined in the removal of heavy metals from aqueous solutions.

The present paper aims to study the feasibility of using citric acid treated *Manilkara zapota*leaves as on adsorbent for the removal of lead ions from aqueous solutions in batch system. *Manilkara zapota*, commonly known as the sapodilla, is a long-lived, evergreen tree native to southern Mexico, Central America and the Caribbean. It is grown in huge quantities in India, Thailand, Malaysia, Cambodia, Indonesia, Bangladesh and Mexico. Sapodilla can grow to more than 30 m (98 ft) tall with an average trunk diameter of 1.5 m (4.9 ft). The average height of cultivated specimens, however, is usually between 9 and 15 m (30 and 49 ft) with a trunk diameter not exceeding 50 cm. Application of *Manilkara zapota* leaves (CAMMZL) powder as biosorbent for the removal of Pb(II) from aqueous solutions has been systematically investigated. The biosorbent was characterized by Infrared Spectroscopy, X-ray diffraction, SEM and Elemental analysis. The effects of experimental parameters such as pH, adsorbent dose, initial metal ion concentrations and contact time on biosorption efficiency were studied. Experimental data were analyzed by Langmuir, Freundlich and Dubinin-Radushkevich isotherm models. Desorption studies were carried out using the HCl solution.

EXPERIMENTAL SECTION

2.1. Procedure of adsorbent preparation

Manilkara zapota leaves were collected from local fields of Doruvupadu village in the Nelloere district in the state of Andhra Pradesh, India. The preparation and chemical modification of *Manilkara zapota* leaves was performed by the following procedure. The collected leaves were cut into small pieces, washed several times with deionized water, dried under sunlight and grounded in a steel mill to get fine powder which is called as raw *M.zapota* leaves powder. Raw powder was washed with deionized water until water becomes colorless, which indicates the removal of the water soluble color materials and dried at 70 ^{o}C temperature in hot air oven for about 12 hours and stored in desiccator for further use. This product was named as MZL (*Manikarazapota* leaves) powder.

2.1.1. Modification of biomass

Citric acid modification of MZL was carried out adopting the procedure reported elsewhere [15]. The sieved *Manilkara zapota* leaves powder (150 g) was mixed with 2 L of 0.1 N NaOH, and stirred at 200rpm for 1hour at 25^{0}c temperature to remove the excess of base. This procedure was repeated twice to ensure removal of the base from *Manilkara zapota* leaves powder. This biomass was named as BW-MZL, was mixed with Citric acid in the ratio of 1.0 g MZL powder to 7.0mL of CA. BW-MZL completely imbibed the CA solution within a couple of hour. The acid BW-CPH slurry was dried overnight at 50◦C. The CA treated BW-MZL was placed on a whatmann 42 filter paper and washed in a Buchner funnel under vacuum with 150-200mL of double distilled water per gram of the product in order to remove excess Citric acid. Treatment of MZL powder with NaOH and a subsequent Citric acid increases the net negative charge on the surface of biomass due to interactions between the base and pectic substances and thus increases its cation uptake ability. This modified MZL was named as CA modified *Manilkara zapota* leaves (CAMMZL) powder and used in the present study.

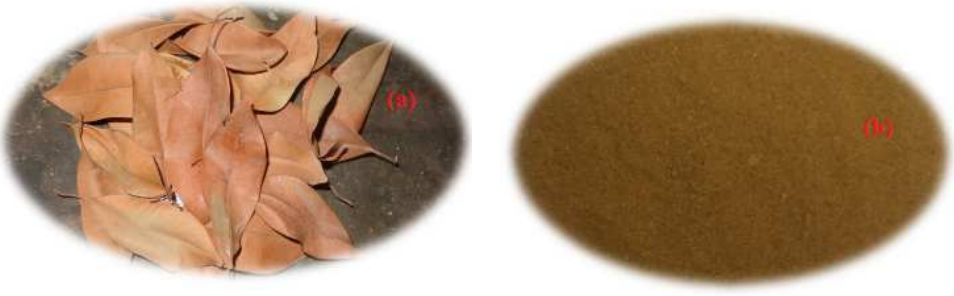

Fig. 1. Picture of (a) *Manilkara zapota* leaves (b*) Manilkara zapota* leaves powder

2.2. Chemicals and equipment

All chemicals used in this study were of analytical reagent grade. Deionized double distilled water (DDW) was used throughout the experimental studies. Stock Lead solution (1mg/mL) was prepared by dissolving Pb $(NO3)_2$ in distilled water.Working standards were prepared by progressive dilution of stock lead solution using DDW water. Analytical reagent grade HCl, NaOH and buffer solutions (E. Merk) were used to adjust the solution pH. An Elico (LI-129) pH meter was used for pH measurements. The pH meter was calibrated using standard buffer solutions of pH 4.0 and 9.2. FT-IR spectrometer (Thermo- Nicolet FT-IR, Nicolet IR-200, USA) was used for the IR spectral studies (4000–400 cm^{-1}) of biosorbent. Vario EL, Elementar, Germany was used for elemental analysis of the WAS. The lead concentration in the samples was determined by atomic absorption spectrophotometer (AAS, Shimadzu AA- 6300) with lead Hallow Cathode Lamp. Samples for X-ray diffraction measurements were prepared by grounding the adsorbent with small amount of methanol in an agate mortar. The mixture was smear-mounted onto the zero-background quartz window specimen holder and allowed to air dry. Wide angle X-ray diffraction (WAXD) patterns of samples were recorded on an X-ray diffractometer (XRD 6000, Shimadzu), using Kα radiation (= 1.5406Å) at 40 kV and 30mA.

2.3. Batch mode biosorption studies

Batch sorption experiments were carried out in 250 mL stoppered flasks using 50 mL metal solution with a fixed amount of CAMMZL. The sealed bottles were shaken by placing in mechanical shaking incubator for 3hours at a speed of 300 rpm and temperature of 25 ^{o}C. After shaking the contents of the flask was separated by filtering through a whattman filter paper and the filtrate was analyzed for metal ion concentration by flame AAS.The amount of metal ion sorbed (Q_e), was computed by the following equation:

$$Q_e = \frac{v}{m}(C_0 - C_e) \tag{1}$$

where C_0 and C_e are the initial and equilibrium Pb(II) concentrations respectively, whereas ‘v’ and ‘m’ are solution volume and mass of biosorbent respectively. Blank test was performed in the same experimental conditions without biosorbent.

2.4. Desorption studies

The desorption studies were carried out with varying concentrations of HCl solution. The sorbent, which was removed from filtration, was transferred into stoppered reagent bottles. To this 100ml of HCl solution was added. The bottles were shaken at room temperature (30±1◦C) using a mechanical shaker. The sorbent was then removed by filtration. The concentrations of lead in the aqueous solutions were determined by AAS method.

RESULTS AND DISCUSSION

3.1. Characterization of the biosorbent (CAMMZL)

The biosorbent (CAMMZL) were characterized through the FT-IR, SEM and X-rd analysis. The physicochemical characteristics like moisture content, bulk density, ash content and the percentage of carbon, hydrogen and nitrogen of the CAMMZL are presented in Table 1.

Table. 1: Physicochemical Characteristics of the CAMMZL

Characteristics	Values
Bulk density (g/cm^3)	0.48 ± 0.02
Moisture content (%)	5.17 ± 1.2
Ash content (%)	8.73 ± 1.41
Carbon (%)	52.58 ± 2.56
Hydrogen (%)	7.214 ± 0.13
Nitrogen (%)	0.24 ± 0.01
Oxygen^a (%)	39.96 ± 1.18
Electrical conductivity (µs/cm)	57.3 ± 1.35

^{a}*Estimated by difference.*

3.1.1. FT-IR Analysis

The infrared spectral analysis was carried out to determine the type of functional groups involved in biosorption of Pb(II) onto CAMMZL. The FTIR spectra of unloaded biosorbent and Pb(II) loaded biosorbent were recorded in the wavenumber range 4000-500 cm^{-1}, and the results are shown in Figs.2(a) and 2(b). The spectra of CAMMZL showed a broad and intense peak at 3333 cm^{-1} which could be assigned to –OH stretching mode from hydroxyl and phenolic groups, involved in hydrogen bonding which was probably attributed to adsorbed water [16, 17]. The band at 2916 cm^{-1} indicates symmetric or asymmetric C–H stretching vibration of aliphatic acids. Peak observed at 1729 cm^{-1} is the stretching vibration of C=O bond due to non-ionic carboxyl groups (–COOH).The peak at 1623 cm-1 is due to C=0 stretching mode of the primary and secondary amides (NH_2 CO). A strong peak at 1027 cm^{-1} was indicated the presence of C-O stretching of alcohols and carboxylic acids [18]. The peaks at these wave numbers were intact, indicating that functional groups were not disturbed after interaction with the metal ions. The intensity of transmittance of peaks were relatively changed in Pb(II) loaded biosorbent, compared with unloaded biomass.

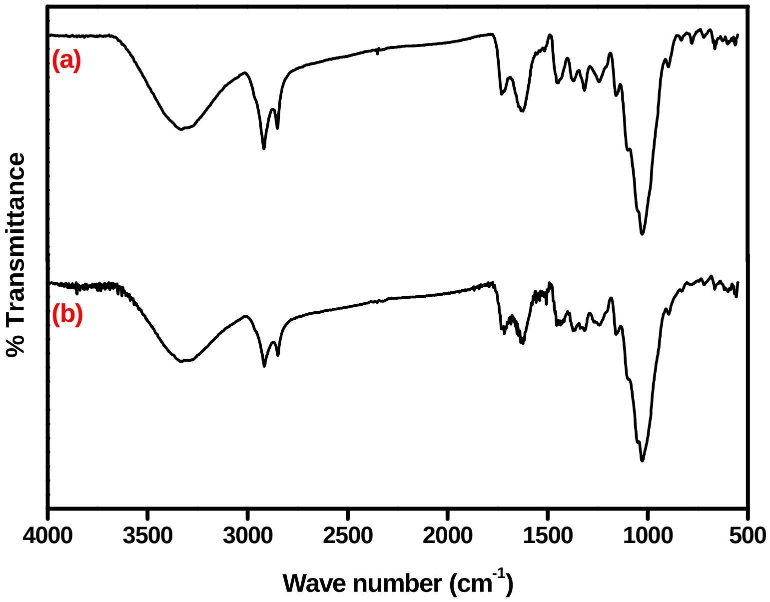

Fig. 2. FT-IR spectra of (a) CAMMZL (b) Pb(II) loaded CAMMZL

3.1.2. SEM Analysis

Scanning electron microscope was widely used to study the morphological features of the adsorbent. An observation of the SEM micrographs of pure CAMMZL (Fig. 3(a)) indicates the presence of many pores, which did not have regular, fixed shape. This porous nature of the adsorbent is favorable for the biosorption of metal ions. The surface morphology of pure CAMMZL changed significantly on loading with Pb(II).

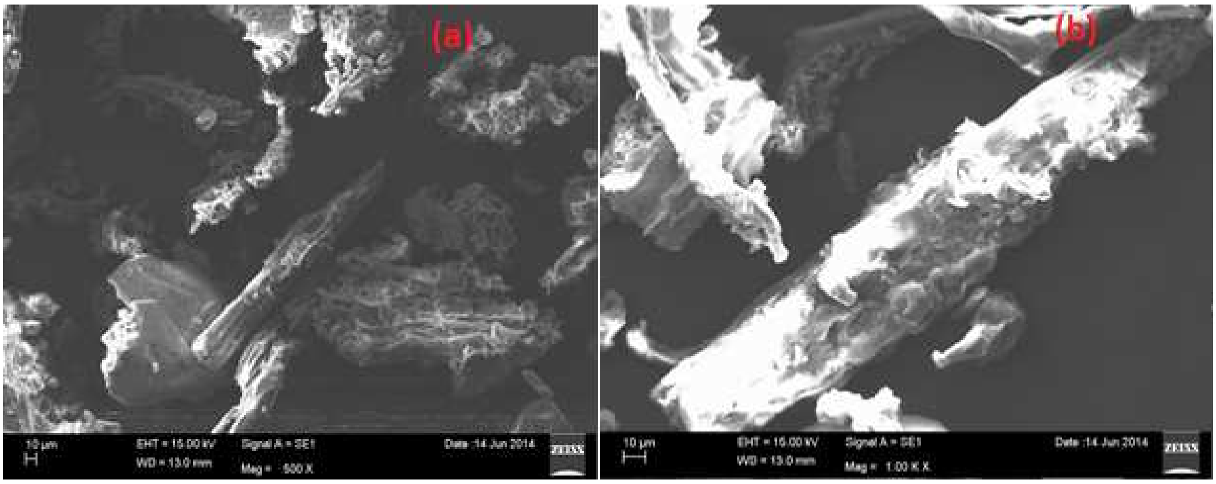

Fig. 3. SEM images of (a) CAMMZL (b) Pb(II) loaded CAMMZL

3.1.3. XRD Analysis

An X-ray diffraction analysis was performed on pure CAMMZL and shown in Fig. 4.

The X-ray diffraction spectrum of CAMMZL biosorbent showed main and secondary peaks at 2θ of 32° and 27°, respectively. The peak heights of the sorbent were short in XRD spectrum indicating that crystallanity is less [19]. The lowering in crystallanity can be attributed to the insertion of the grafted chains onto the CAMMZL backbone, which may lead to breaking of hydrogen bonding in the CAMMZL protein structure, resulting in an amorphous structure [20], which is favorable for biosorption of metal ions onto CAMMZL.

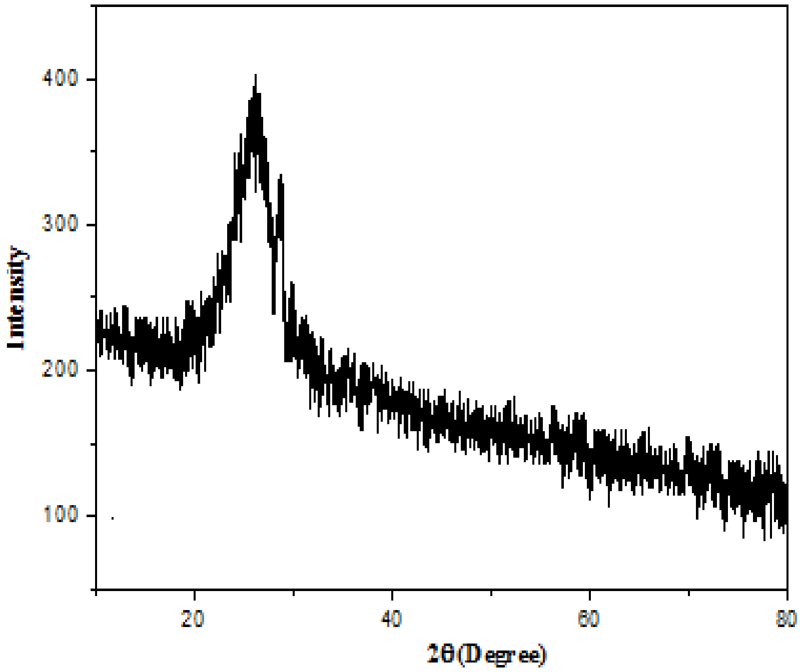

Fig. 4. Powder XRD of CAMMZL

3.2. Effect of pH on removal of Pb(II)

The pH of the adsorbate solution has been identified as the most important controlling parameter in the adsorption process. The binding of metal ions by surface functional groups was strongly pH dependent [21]. The pH level affects the network of negative charge on the surface of the biosorbing cell walls, as well as physicochemsitry and hydrolysis of the metal [22]. Therefore, preliminary experiments have been performed to find out the optimum pH for maximizing the metal removal. The effect of hydrogen ion concentration on the extent of adsorption of Pb(II) was studied by varying pH of the solution from 2.0 to 9.0. The equilibrium concentration of metal ion was determined and the results were graphically presented in Fig. 5. The results indicate that maximum uptake of Pb(II) occurred at pH 5. It has been observed that the percent removal of metal ions is low at highly acidic conditions, due to the presence of higher concentration of H^+ ions in the solution, which leads to compete between the metal cations and protons for binding sites on cell wall. It can be observed that with increasing pH of the solution, the amount of metal ion adsorption also increased to attain a maximum adsorption capacity. The increase in metal ions removal as pH increased can be explained on the basis of a decrease in competition between protons (H^+) and positively charged metal ion at the surface sites, and by decrease in positive charge which resulted in lower repulsion of the adsorbing metal ion [23]. Decrease in biosorption yield at higher pH (pH>5) was due to the formation of soluble hydroxylated complexes of the metal ions and their competition with the active sites, and as a consequence, the retention had been decreased again. Hence pH 5.0 was chosen optimum for further studies.

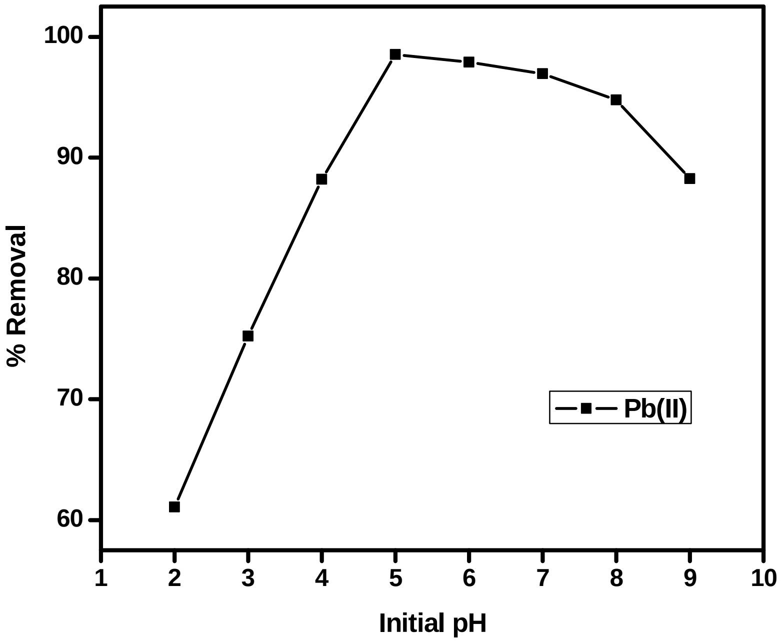

Fig. 5. Effect of initial pH on the removal of Pb(II) on CAMMZL

3.3. Effect of adsorbent dosage on removal of Pb(II)

Adsorbent dose has a great influence in biosorption process and it determines the potential of biosorbent through the number of binding sites available to remove metal ions at a specified initial concentration. The amount of adsorbent is key factor as the adsorption mainly depends upon the surface area of adsorbent available for the contact of pollutant at the interface. For studying the effect of biosorbent dosage on removal of Pb(II),the biosorbent dosage is changed from 50 mg to 500 mg, fixing other parameters like solution pH, initial concentration and temperature. The results were graphically represented in Fig. 6. From the figure it can be observed that increasing the adsorbent dose increased the percent removal of Pb(II) and the maximum removal was attained with the dose of 200 mg. Further increase in the dose did not significantly change the biosorption yield. This suggests that the maximum adsorption is attained after a certain dose of adsorbent. Hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. The increase in removal of Pb(II) percentage with increase in adsorbent dose is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent [24].

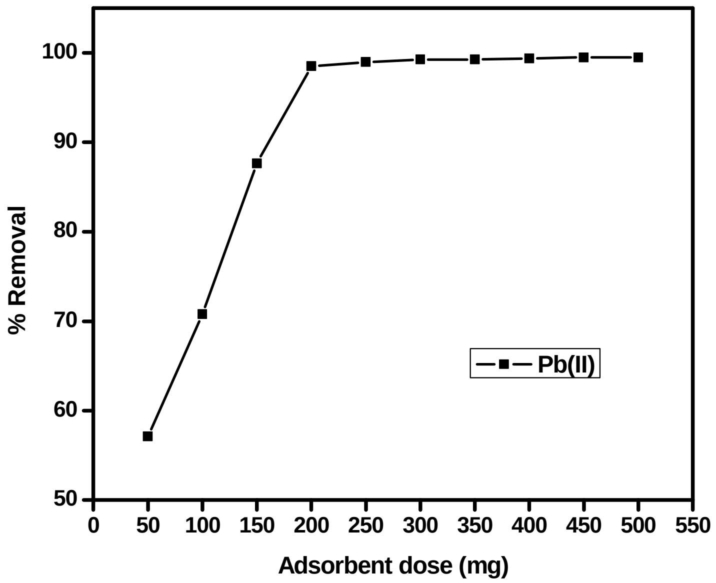

Fig. 6. Effect of adsorbent dose on the removal of Pb(II) on CAMMZL

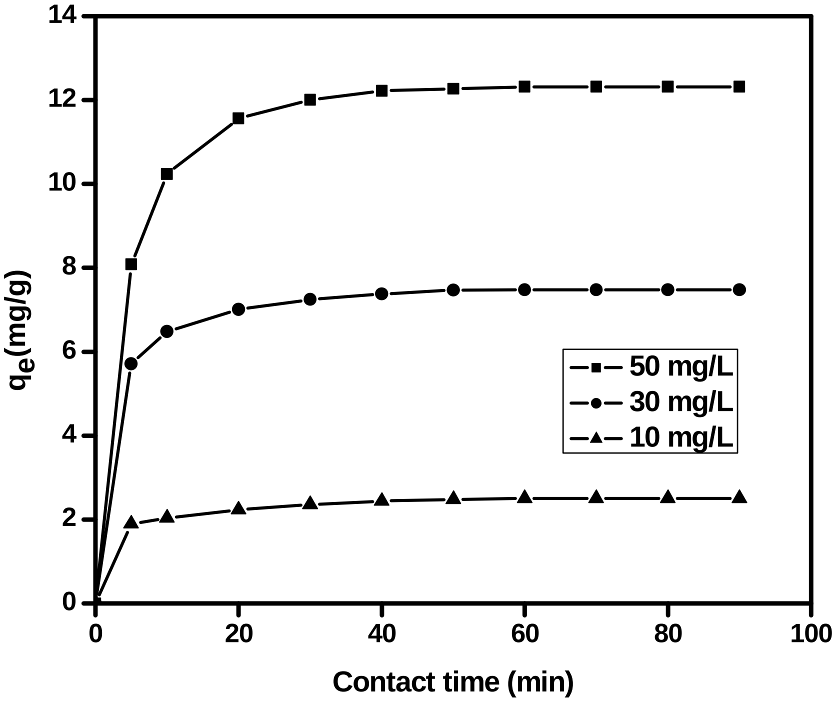

Fig. 7. Effect of contact time on the removal of Pb(II) on CAMMZL

3.4. Effect of Contact time

The effect of contact time on the extent of adsorption of Pb(II) onto CAMMZL were studied in the time range from 5 to 90 min with different initial concentrations (10,30,50 mg/L) by fixing the other parameters such as adsorbent dose and temperature for each experiment. The results were shown in the fig. 7. As contact time increases, metal uptakes increases initially and then become almost stable, denoting attainment of equilibrium for all concentrations. This behavior may be attributed to initially all adsorbent sites were vacant and the solute concentrations were high. Equilibrium adsorption was established within 60 min for three different initial concentrations. When the initial metal ions concentration varied from 10 mg/L to 50 mg/L, the amount of metal ion adsorbed at equilibrium increased. It is very clear from the results that the contact time required for maximum uptake of metal ions by CAMMZL was dependent on the initial metal ion concentration. To make sure true equilibrium is established, all the subsequent sorption experiments were carried out over 1h.

3.5. Analysis of Kinetic studies

Kinetic studies were performed in order to examine the biosorption of Pb(II) onto CAMMZL and potential rate - controlling step. Various kinetic models have been used to analyzing the kinetic data obtained from batch studies. Three kinetic models were tested; Lagergren's pseudo-first order, McKay and Ho's pseudo-second-order and intraparticle diffusion models.

The leniar form of the pseudo – first – order equation of Lagergren[25] is expressed as

$$\log(q_e - q_t) = \log\ q_e\ -\ \frac{k_1}{2.303}t \qquad (2)$$

where, q_e (mg/g) and q_t (mg/g) are the adsorption amount at equilibrium and time t (min), respectively. k_1 (min^{-1}) is the rate constant in the pseudo-first-order adsorption process. The constants were determined experimentally by plotting log (q_e-q_t) versus t and are presented in table 2. The correlation coefficient is less than 0.96, which is indicative of a poor correlation and also $q_{e.cal}$ determined from the model is not in a good agreement with the experimental values of $q_{e.exp}$. Therefore the pseudo-first-order model is not suitable for the modeling the biosorption of Pb(II) onto CAMMZL.

The pseudo-second-order equation [26], based on adsorption capacity at equilibrium, can be expressed by:

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (3)$$

wherek_2 (g/mg min^{-1}) is the rate constant of the second-order equation. K_2 and q_e can be obtained from intercept and slope of the plot of t/q_t versus t is shown in the fig. 8. The pseudo-second - order rate constant k_2 and q_e were determined by the plot and are presented in table 2. The value of correlation coefficients is 0.9999, 0.9999, 0.9997 and the theoretical $q_{e.cal.}$values are closer to the experimental $q_{e.exp}$ values. Therefore, the sorption kinetics of Pb(II) was more favorable by second-order kinetics model rather than pseudo-first-order kinetic model.

The intra-particle diffusion model is based on the theory proposed by Weber and Morris [27]. This equation is expressed as:

$$q_t = K_{id}t^{0.5} + c \qquad (4)$$

wherek_{id} (mg/gmin$^{-1/2}$) is the rate constant of intra-particle diffusion. q_t (mg/g) is the amount of lead sorbed at time t, c (mg/g) is the intercept. Intra-particle diffusion rate constant k_{id} and c can be obtained from the plot of q_t versus the square root of time and presented in table 2. The values of correlation coefficients are not satisfactory and the intercept does not pass through the origin (Fig. 9), which indicates the intraparticle diffusion is not the only rate limiting step in determining the kinetics of the process.

In the view of these results, it can be said that the pseudo-second-order-kinetic model provided a good correlation for the biosorption of Pb(II) onto CAMMZL.

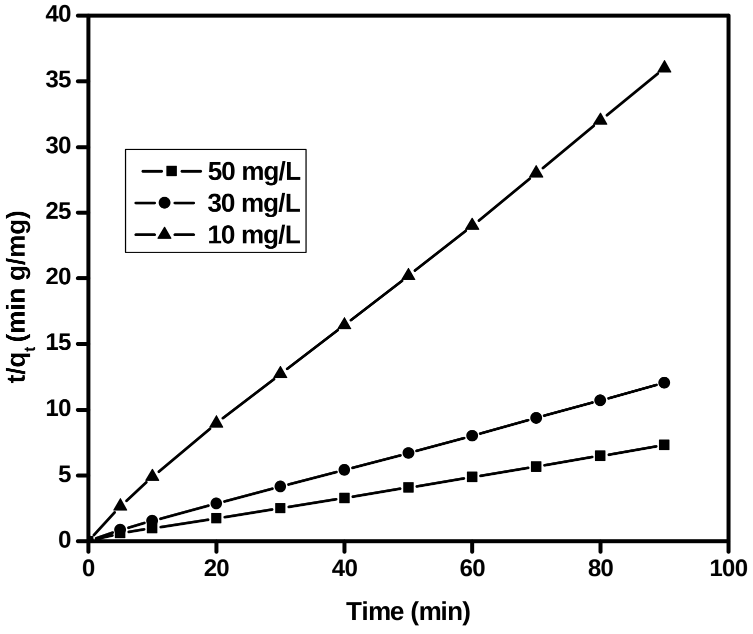

Fig. 8. Pseudo-second-order kinetic model for Pb(II) onto CAMMZL

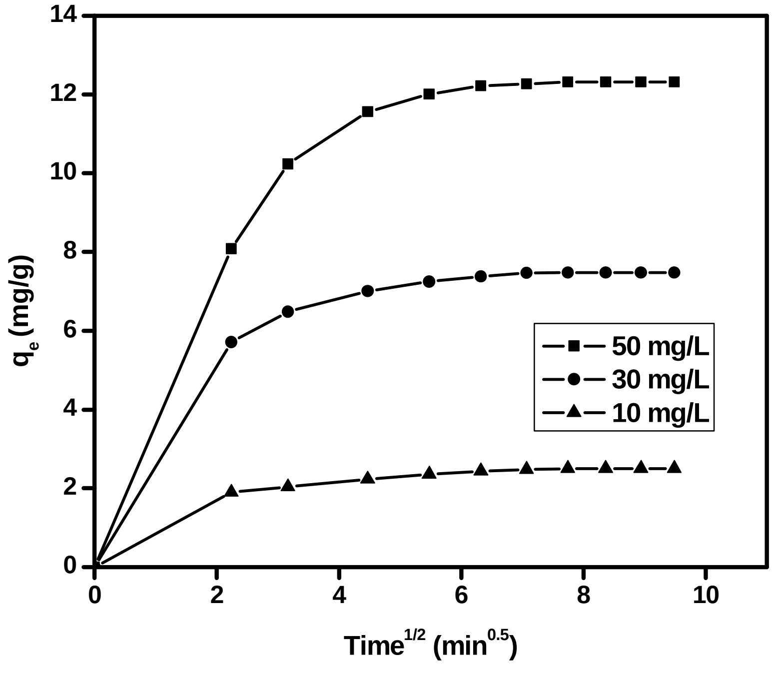

Fig. 9. Intraparticle diffusion kinetics for adsorption of Pb(II) onto CAMMZL

Table 2:Kinetic parameters for the biosorption of Pb(II) onto CAMMZL at different metal ion concentrations

Pb(II) Conc. (mg/L)	Experimental Value $q_{e.\ exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order			Weber and Morris		
		$q_{e.\ cal}$(mg/g)	K_1 (min^{-1}	R^2	$q_{e.\ cal}$ (mg/g)	K_2 (g/mg min^{-1})	R^2	$q_{e.\ cal}$(mg/g)	K_{id} (g/mg min$^{-0.5}$)	R^2
50	12.315	6.139	10.08 X 10^{-2}	0.9982	12.679	3.78 X 10^{-2}	0.9998	8.597	0.4686	0.8325
30	7.472	3.879	9.29 X 10^{-2}	0.9584	7.635	8.20X 10-2	0.9999	5.795	0.2090	0.8764
10	2.5	1.009	7.07 X 10^{-2}	0.9913	2.578	15.96X 10-2	0.9998	1.813	0.0836	0.9366

3.6. Effect of Initial metal ion concentration and Adsorption isotherms

The analysis of isotherm data is very important to optimize the design of sorption system to remove metal ions from effluents. These are also helpful to provide sufficient physico chemical information to understand the mechanism of adsorption. In this study several isotherm models are used to fit the data and examine the relationship between sorption and aqueous concentration at equilibrium.

In order to evaluate the data in this study Langmuir, Freundlich and Dubinin–Radushkevich (D–R) adsorption isotherm models are used.

The Langmuir Isotherm model [28] was assumed to the maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, which is represented by,

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \tag{5}$$

Where q_e is the amount of metal ion adsorbed per unit mass of adsorbent in (mg/g), Ce is the equilibrium solute concentration (mg/L), q_m is the maximum metaluptake, K_L is the Langmuir biosorption constant (L/mg) relating the free energy of biosorption. The essential features of the Langmuir biosorption isotherm can be expressed in terms of a dimensionless constant separation factor (R_L), which is defined in eq (6).

$$R_L = \frac{1}{(1 + K_L C_0)} \tag{6}$$

where K_L is the Langmuir constant (L/mg) and C_0 is the initial adsorbate concentration (mg/L). The values of R_L in the range of 0-1 at all initial Pb(II) concentrations confirm the favorable uptake of Lead onto CAMMZL.

Freundlich adsorption isotherm [29] is an empirical relationship established upon sorption onto a heterogeneous surface on the assumption that different sites with several adsorption energies are involved, which is given by:

$$q_e = K_F C_e^{1/n} \tag{7}$$

Where q_e is the amount of metal ion adsorbed per unit mass of adsorbent (mg/g) at equilibrium, C_e is the equilibrium concentration of metal ion (mg/L); K_f and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively and values are included in Table 3. It is clear that the Freundlich model could not fit all the experimental data well, as R^2 values are not closer to unity compared to Langmuir model.

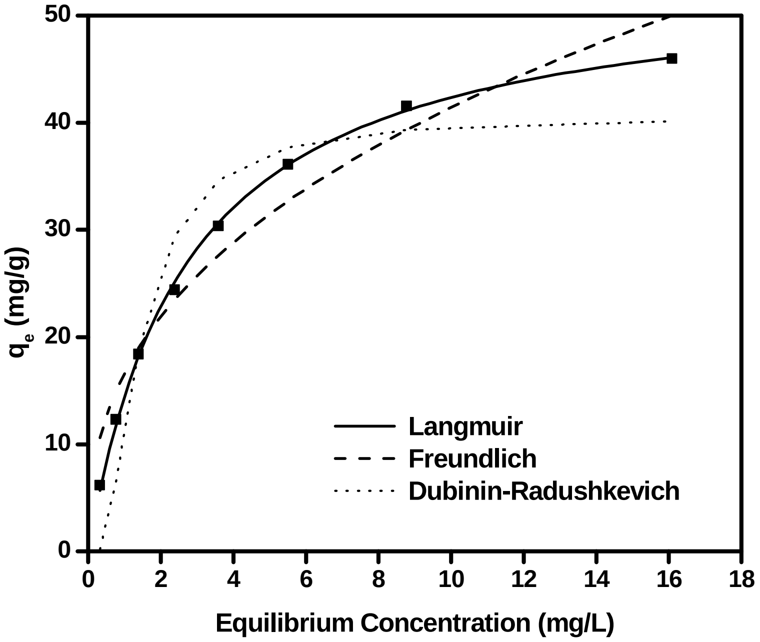

Fig. 10. Biosorption isotherms of Pb(II) onto CAMMZL

The equilibrium data were also examined using the D–R isotherm [30] model in order to determine the nature of biosorption processes as physical or chemical. The nonlinear presentation of the equation is given as

$$q_e = Q_m \exp\left(-K\,[RT\ln(1+\frac{1}{C_e})]^2\right) \tag{8}$$

Where Q_m is the maximum amount of the ion that can be sorbedonto unit weight of sorbent (mg/g), ε is the Polanyi potential which is equal to RT ln(1 + 1/Ce), where R and T are the universal gas constant (kJ mol^{-1} K^{-1}) and the absolute temperature (K), respectively. K is related to the mean free energy of sorption per mole (E) of the sorbate when it is transferred to the surface of the solid from infinity in the solution and E can be computed using the following relationship:

$$E = \frac{1}{\sqrt{2K}} \tag{9}$$

From the equation 9, the mean sorption energy (E) evaluated is presented in the table 3, for the adsorption of Pb(II) onto CAMMZL. According to the available literature, the E value ranges from 1.0 to 8.0 KJ/mol for physical adsorption and from 8.0 to 16.0 KJ/mol for chemical ion exchange [31]. Therefore, these results indicate that the adsorption of metal ions onto CAMMZL might be attributed to chemical ion-exchange mechanism.

Consequently, among the three isotherm models used, the Langmuir model offers the best correlation factors. By comparing the correlation coefficients and other parameters determined by these three isotherms, Langmuir isotherm model is better fit than Freundlich and Dubinin–Radushkevich isotherm models.

Table 3. Isotherm parameters for Pb(II) biosorption by CAMMZL

Model	Values
Langmuir	
Q_m(mg/g)	53.84
b (l/mg)	0.368
R^2	0.9990
Freundlich	
K_f (mg/g)	16.64
n(g/l)	2.525
R^2	0.9511
Dubinin-Radushkevich	
Q_m(mg/g)	40.52
E	15.54
R^2	0.8889

3.7. Comparison of adsorbent with other adsorbents

A comparison of adsorption capacity of Citric acid modified *Manilkara zapota* leaves powder for Pb(II) ions with that of various adsorbents reported in literature [32-41] are shown in Table 4. The adsorption capacity of CAMMZL powder for Lead ions is higher than that of the majority of other adsorbents mentioned, indicating the potential of citric acid modified *Manilkara zapota* leaves powder for the removal of Pb(II) ions from aqueous solution.

Table 4. Comparison of maximum adsorption capacities (Q_{max}) of Pb(II) with various adsorbents

Biosorbent	Q_{max}(mg/g)	Reference
Tobacco dust	39.60	32
barley straws	23.20	33
Olive tree pruning waste	27.40	34
Almond shell	8.08	35
Modified groundnut husk	39.33	36
Chaff	12.50	37
Pinussylvestris	11.38	38
Oryza sativa L. Husk	8.6	39
Palm kernel fibre	49.90	40
Red soil	21.7	41
CAMMZL	**53.84**	**This study**

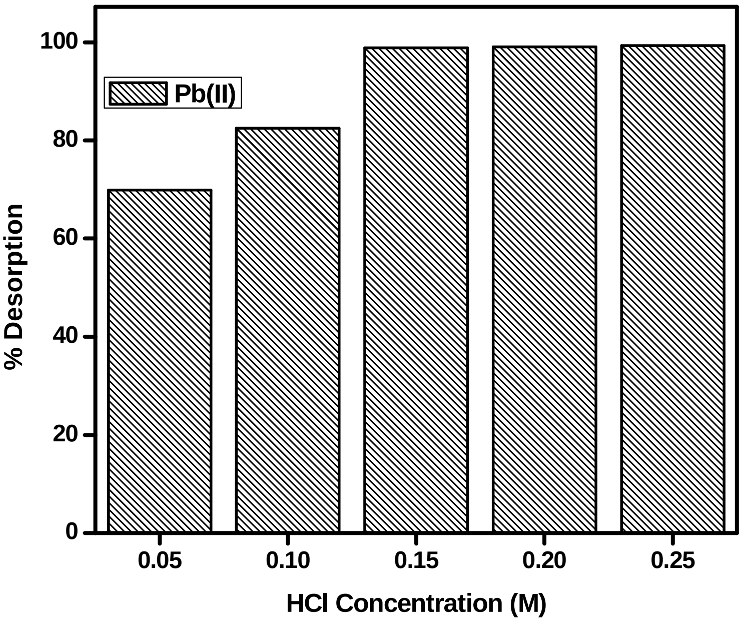

Fig. 11. Desorption of Pb(II) ions from CAMMZL

3.8. Desorption studies

To keep the processing cost down and to open the possibility of recovering the metal ions extracted from the liquid phase, it is desirable to regenerate the biosorbent material. Dilute solutions of mineral acids could be employed for desorption studies. In this study, A strong desorption agent HCl solution was selected as an eluent to desorb Pb(II) from the metal loaded CAMMZL biomass. Desorption experiments were first carried out through various concentrations of HCl (0.05–0.025 M), respectively and the results were shown in Fig. 11. It was found that the desorption efficiency was almost same when HCl concentration was higher than 0.15 M. Hence, 0.15 M HCl solution was chosen as a suitable concentration for the regeneration of Pb(II) from the metal loaded CAMMZL.

CONCLUSION

This study probes the performance of CAMMZL prepared from citric acid modified *Manilkara zapota* leaves, to sequester Pb(II) ions from aqueous solution. Batch sorption experiments were carried to investigate sorption behavior of the lead ions from aqueous solutions onto CAMMZL. The results show that the metal sorption onto modified CAMMZL sorbent is depends on several factors such as: pH, adsorbent dose, contact time and initial metal concentration. FTIR spectra indicated that the functional groups such as hydroxyl, carbonyl and carboxyl groups are involved in the Pb(II) sorption process. SEM analysis showed that CAMMZL has a porous structure. The X-RD spectral analysis showed the amorphous nature of the adsorbent. Kinetic test demonstrated that sorption equilibrium is reached within 60 min. Moreover, a pseudo-second-order model has better fit to heavy metal compared to other kinetic models. The adsorption data are better fitted by the Langmuir model adsorption isotherm as compared to the Freundlich and D-R models. The monolayer capacity (q_{max}) is calculated using the Langmuir isotherm for the sorbent and the maximum sorption capacity is found to be 53.84 mg/g. Calculated R^2 values for Langmuir isotherms are in closure to unity, which showed that the sorption process is favorable. Regeneration studies showed that CAMMZL can be effectively utilized for the removal of Pb(II). From the above results, it may conclude that the CAMMZL is a low cost, easily available and alternative biosorbent for the removal of Pb(II) from aqueous solutions.

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REFERENCES

[1] M Amini; H Younesi; NBahramifar,*Chemosphere*.,**2009**, 75, 1483–1491.
[2]RA Anayurt;A Sari; MTuzen,*Chem. Eng. J.*, **2009**, 151, 255–261.
[3]T Akar; S Tunali; I Kiran,*Biochem. Eng. J.* **2005**, 25, 227-235.
[4]Environmental Protection Agency, Nationa Primary Drinking Water Regulation, Washington, **2002**.
[5] Bureau of Indian Standards, BIS Tolerance Limits for Industrial Effluents Prescribed by Bureau of Indian Standards, IS 2490 (part 1), New Delhi, **1981**.
[6]World Health Organization, WHO Guidelines for Drinking Water Quality, Geneva, Switzerland, Vols, 1 and 2, **1981**.
[7]Q Li; L Chai; Z Yang; Q Wang,*Appl. Surf. Sci*.,**2009**, 255, 4298-4303.
[8]DHK Reddy; K Seshaiah; AVR Reddy; MM Rao; MC Wang, *J. Hazard. Mater*.,**2010**, 174, 831-838.
[9]E Maranon; H Sastre, *React. Polym*.,**1992**, 18, 173–176.
[10]S Schiewer;ABalaria,*Chem. Eng. J*., **2009**, 146, 211-219.
[11]TK Naiya; AK Bhattacharya; M Sailendranath; SK Das,J. *Hazard. Mater*.,**2009**, 163, 1254-1264.
[12]Y Bulut; ZBaysal, *J. Environ. Manage*.,**2006,** 78**,** 107-113.
[13]GAnnadurai; RS Juang; DJ Lee, *Water Sci. Technol*.,**2003**, 47, 185–190.
[14]S Guoa; W Li; L Zhanga; J Penga; H Xiaa; S Zhanga,*Process Saf. Environ. Prot.*, **2009**, 87, 343-351.
[15]WE Marshall; LH Wafrtelle; DEBoler; MM Johns; CA Toles,*Bioresour. Technol*.,**1999**, 69, 263–268
[16] PVinke; MV Eijk; M Verbree; AFVoskamp;H.V. Bekkum, *Carbon*.,**1994**, 32, 675-686.
[17]X Chen; SJeyaseelan; N Graham, *Waste. Manage*.,**2002,** 22, 755-760.
[18]NVFarinella; GD Matos; MAZ Arruda,*Bioresour. Technol*.,**2007**, 98, 1940-1946.
[19]G Renmin; SYingzhi; J Chen; H Liu; C Yang, *Dyes Pigments*.,**2005**, 67, 175-181.
[20]M Moniera; DM Ayad; AA Sarhan, *J. Hazard. Mater*.,**2010**, 176, 348-355.
[21]SM Lee; AP Davis, *Water Res*., **2001**, 35, 534-540.
[22]D Harikishore Kumar Reddy; DKV Ramana; KSeshaiah; AVR Reddy, *Desalination*., **2011**, 268, 150-157.

[23]MMadhava Rao; DKRamana; KSeshaiah; MC Wang; SW Chan, *J. Hazard. Mater*.,**2009**, 166, 1006-1013
[24]YS Ho; DAJ Wase; CF Forster, *Water Res*., **1995**, 29, 1327–1332.
[25]S Lagergren, Zur Theorie der sogenannten Adsorption geloster Stoffe. Kungliga Svenska Vetenskapsakademiens Handlingar., **1898**, 24, 1–39.
[26]YS Ho; G McKay; DAJ Wase; CF Foster,*Adsorpt. Sci. Technol*., **2000**, 18, 639-650.
[27]WJ Weber; JC Morris; J Sanit,*Eng. Div. Proc. Am. Soc. Civil Eng*., **1963**, 89, 31-59.
[28]I Langmuir, *J. Am. Chem. Soc.,* **1918**, 40, 1361-1403.
[29]H Freundlich, *Phys. Chem. Soc.*,**1906**, 40, 1361-1368.
[30]MM Dubinin; LV Radushkevich, Proc. Acad. Sci. USSR, *Phys. Chem. Sect*., **1947**, 55, 331-333**.**
[31] KK Singh; M Talat; SH Hasan,*Bioresour. Technol*., **2006**, 97, 2124-2130.
[32]BC Qi; CAldrich,*Bioresour. Technol*.,**2008**, 99, 5595-5601.
[33]E Pehlivan; T Altuna; SParlayic, *J. Hazard. Mater*.,**2009**, 164,982-986.
[34]G Blazquez; MA Martin-Lara; G Tenorio; MCalero, *Chem. Eng. J.* **2011**, 168, 170-177.
[35]EPehlivan; T Altun; S Cetin; MIBhanger, J. *Hazard. Mater*.,**2009**,167, 1203-1208.
[36]SH Gheraibeh;Y Wail; AE Shar; MM Kofahi, *Water.Res*., **1998**, 32, 498-502.
[37]R Han; J Zhang; W Zou; J Shi; H Liu, *J. Hazard. Mater*.,**2005**, 125, 266–271.
[38]H Ucun; YKBayhan; Y Kaya; ACakici; OF Algur,*Desalination*.,**2003**, 154 233–238
[39]MMD Zulkali;AL Ahmad;NH Norulakmal,*Bioresour. Technol*., **2006**, 97, 21–25.
[40]YS Ho; AE Ofomaja,*Process Biochem*.,**2005**, 40, 3455–3461.
[41]A Sari; M Tuzen,*Desalination*.,**2009**, 249, 260-266.