



## Removal of Pb(II) ions from aqueous solution by adsorption using bael leaves (*Aegle marmelos*)

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### ABSTRACT

Biosorption of Pb(II) on bael leaves (*Aegle marmelos*) was investigated for the removal of Pb(II) from aqueous solution using different doses of adsorbent, initial pH, and contact time. The maximum Pb loading capacity of the bael leaves was  $104 \text{ mg g}^{-1}$  at  $50 \text{ mg L}^{-1}$  initial Pb(II) concentration at pH 5.1. SEM and FT-IR studies indicated that the adsorption of Pb(II) occurs inside the wall of the hollow tubes present in the bael leaves and carboxylic acid, thioester and sulphonamide groups are involved in the process. The sorption process was best described by pseudo second order kinetics. Among Freundlich and Langmuir isotherms, the latter had a better fit with the experimental data. The activation energy  $E_a$  confirmed that the nature of adsorption was physisorption. Bael leaves can selectively remove Pb(II) in the presence of other metal ions. This was demonstrated by removing Pb from the effluent of exhausted batteries.

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### 1. Introduction

Industrial effluents are loaded with heavy metals which are hazardous to humans and other forms of life. Their toxic nature has a severe environmental impact. This has resulted in the enforcement of stringent laws for the maximum allowable limits of their discharge into the open landscapes and water bodies. Lead is used as an industrial raw material for storage battery manufacturing, printing, pigments, fuels, photography material and explosive manufacturing [1]. Since Pb(II) is a potent neurotoxic metal, its pollution is of major concern. The presence of lead in drinking water, even in low concentrations, may cause diseases such as anemia, hepatitis, nephrite syndrome, etc [2].

A number of processes exist for the removal of metal pollutants from waste water, viz. precipitation, electroplating, ion exchange and membrane separation. These processes have several disadvantages such as incomplete metal removal, high reagent and energy requirement and generation of toxic sludge/waste products that require disposal and further treatment. This led to the need to develop an effective, low cost and environment friendly process for wastewater treatment. Adsorption is an efficient and economical process used for the removal of heavy metals from industrial wastewater. A number of investigations have been carried out using naturally occurring waste materials for the removal of lead from

aqueous systems. Some of the naturally occurring waste materials used for this purpose are fly ash [3], phosphatic clay [4], clonop-tillolite [5] and sea nodule [6]. Many biological materials such as olive stones, fungus *Aspergillus niger*, seaweeds have also shown potential for the removal of heavy metal [7]. Biosorption of Pb(II) onto a cone biomass of *Pinus sylvestris* was studied which revealed that the maximum adsorption of Pb onto *P. sylvestris* was at pH 4.0 [8]. In another study, ten different seaweed species were compared on the basis of lead uptake at different pH conditions [7]. The study revealed that the brown seaweed, *Turbinaria concoides* exhibited the maximum lead uptake of  $439.4 \text{ mg/g}$  at an optimum pH of 4.5 and temperature of  $30^\circ\text{C}$ . Brown seaweed was extensively used for biosorption and its polysaccharide content was believed to be responsible for its excellent metal binding capacity [9]. It was observed that the biological materials could accumulate heavy metals in their walls, even though the binding sites for chelating were not identified [10].

The objective of the present study is to investigate the utility of various types of locally available biomass to remove Pb(II) from aqueous systems. Dry leaves of bael tree (*Aegle marmelos*) were tested for the removal of Pb(II) ion from aqueous medium as they are very cheap and easily available biomass. Bael tree is a spiny tree belonging to the family Rutaceae and is abundantly found in India, Myanmar, Pakistan and Bangladesh. Literature reports indicate that the leaves of bael tree have medicinal value and are useful for the treatment of ophthalmia, deafness, inflammations, cataract, diabetes, diarrhoea, dysentery, heart palpitation and asthmatic complications [11]. In the present study, leaves of the bael

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tree were successfully utilized for the removal of Pb(II) ions from aqueous solution. The loading capacity of the bael leaves was optimized and the selectivity of the bael leaves towards Pb(II) in the presence of other metal cations was investigated. Attempts have been made to understand the factors responsible for adsorption of Pb(II) to the bael leaves. In an effort to show its practical utility, bael leaves were utilized for the removal of Pb(II) from storage battery effluents at the laboratory scale. This paper aims to examine the use of bael leaves as an adsorbent for the contaminated water bodies.

## 2. Experimental

### 2.1. Biosorbent

In the present study, bael leaves of the Indian bael tree (*Aegle marmelos*) were used as a biosorbent for the removal of Pb from aqueous solution. The bael tree is native to northern India but is found widely throughout the Indian peninsula and in Ceylon, Burma, Thailand, Indo-China [12]. The bael leaves were first washed thoroughly with deionised water. The soluble colored components were then removed by washing repeatedly with hot deionised water (70 °C). The bael leaves were then dried at 70 °C for 24 h. The dried bael leaves were crushed and sieved through 100 mesh and stored in polythene bottles.

### 2.2. Instrumentation

Atomic absorption spectrometer (AAS), GBC, AVANTA equipped with an air acetylene burner was used to determine the concentration of all the metal ions in the aqueous solution. The hollow cathode lamp was operated at an analytical wavelength of 283.3 nm for Pb and the slit was 0.2 nm for all the experiments. FT-IR spectra of bael leaves samples (before and after adsorption) were obtained using FT-IR spectrometer, Thermo Nicolet, Nexus 870. The processed dry bael leaves in powder form (Section 2.1, about 0.1 g) along with KBr were ground into fine particles and pressed to make pellets. FT-IR spectrum of the native bael leaves was then recorded using the pellets. For FT-IR spectrum of Pb loaded bael leaves, the native bael leaves were adsorbed with 1000 mg L<sup>-1</sup> Pb(II) solution for 24 h. After adsorption, Pb(II) loaded bael leaves were filtered, washed with deionised water and air dried. The FT-IR spectrum of Pb loaded bael leaves was then recorded using KBr pellets. A Scanning Electron Microscope, JEOL JSM 840, was used to obtain SEM images of the bael leaves before and after Pb adsorption. Metal mapping of the native bael leaves and Pb loaded bael leaves were performed using the same SEM. All pH measurements were made using a digital pH meter.

### 2.3. Metal solutions

All the chemicals used were AR grade supplied by SRL, Mumbai, India and deionised water was used for preparation of the solution throughout the experiments. The stock solution of Pb(II) was prepared by dissolving Pb(NO<sub>3</sub>)<sub>2</sub> in deionised water. Stock solutions of Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> were prepared by dissolving their corresponding nitrate salts in deionised water. The working solutions were prepared by appropriate dilution of the stock solutions with deionised water.

### 2.4. Batch adsorption studies

Batch adsorption studies were performed in 100 mL conical flasks to optimize the operating conditions for Pb(II) adsorption by bael leaves. In a typical experiment, 0.2 g of processed powder bael leaves (Section 2.1) were added to 50 mL of 98 mg L<sup>-1</sup> synthetic Pb(II) solution. The natural pH of the synthetic Pb(II) solutions was

measured to be 5.1. This pH was maintained throughout for all the experiments except for pH optimization studies. The mixture was shaken for 45 min at 303 K using a mechanical shaker at 120 rpm. The phases were separated by filtration and the Pb(II) concentration in the filtrate was determined by Atomic Absorption Spectrophotometer (AAS). Adsorption parameters, viz. biosorbent dose, initial concentration of Pb(II) and contact time were optimized by continuous variation method. For pH optimization, the initial pH of each Pb(II) solution was adjusted to the required pH by using 0.01 N HNO<sub>3</sub> or 0.01 M NaOH. The concentration of Pb was measured using AAS after the pH adjustment. For desorption studies, Pb(II) was initially adsorbed on the bael leaves at pH 5.1. The equilibrium concentration (C<sub>e</sub>) of Pb in the solution was measured and the pH was then adjusted to the range of 2.0–7.0 using 0.01 M NaOH or 0.01 N HNO<sub>3</sub>. The solution after pH adjustment was shaken for half an hour and the equilibrium concentration after desorption (C'<sub>e</sub>) was measured. The percentage of desorption was calculated as follows:

$$\% \text{desorption} = \left( \frac{C'_e - C_e}{C_o - C_e} \right) \times 100$$

where C<sub>o</sub> is the initial Pb(II) concentration of the solution (mg L<sup>-1</sup>), C<sub>e</sub> is the equilibrium Pb(II) concentration (mg L<sup>-1</sup>) at a particular pH and C'<sub>e</sub> is the equilibrium Pb(II) concentration (mg L<sup>-1</sup>) at a particular pH after desorption. The kinetic studies were carried out at three different Pb(II) concentrations of 48.2, 87.8 and 180.2 mg L<sup>-1</sup> at temperatures of 303, 313 and 323 K.

## 3. Results and discussion

### 3.1. Removal of Pb(II) from synthetic solutions

Dry bael leaves powder was initially used to remove Pb(II) from synthetic aqueous solutions. Different experimental parameters like contact time, adsorbent dose, and pH were optimized to obtain maximum Pb(II) removal using the bael leaves. For optimization of contact time, a solution of 98 mg L<sup>-1</sup> Pb(II) at pH 5.1 with 0.2 g of bael leaves was used. The contact time was varied between 5 and 120 min at three different temperatures of 303, 313, and 323 K (results not shown here). It was observed that during the first 20 min there was a rapid uptake of Pb, up to a maximum of 65%. The time required for attaining equilibrium was 30 min. Therefore, a contact time of 30 min was employed for all other studies. It is to be noted that a contact time of 30 min was sufficient for optimum removal of Pb(II) when the initial Pb(II) concentration was raised to 180.2 g L<sup>-1</sup>.

#### 3.1.1. Effect of adsorbent dose

Three different solutions having an initial Pb(II) concentration of 48.2, 87.8 and 180.2 mg L<sup>-1</sup>, with pH 5.1 were used to study the effect of the adsorbent dose on the removal of lead. The adsorbent dose was varied in the range of 0.01–0.5 g. The result is presented in Fig. 1. It was observed that the removal efficiency increased with increase of adsorbent dose. It reached a maximum (85% approximately) at around 0.2 g and then remained almost constant. Therefore, the optimum bael leaves dose was taken as 0.2 g and this was used for all further studies. The positive correlation between adsorbent dose and metal removal efficiency can be related to the increasing surface area of the available binding sites [13].

#### 3.1.2. Effect of pH

pH is a very important parameter that affects any biosorption process. It affects the activity of the functional groups present in the biosorbent that are responsible for metal adsorption and also affects the competition of metallic ions to get adsorbed to the

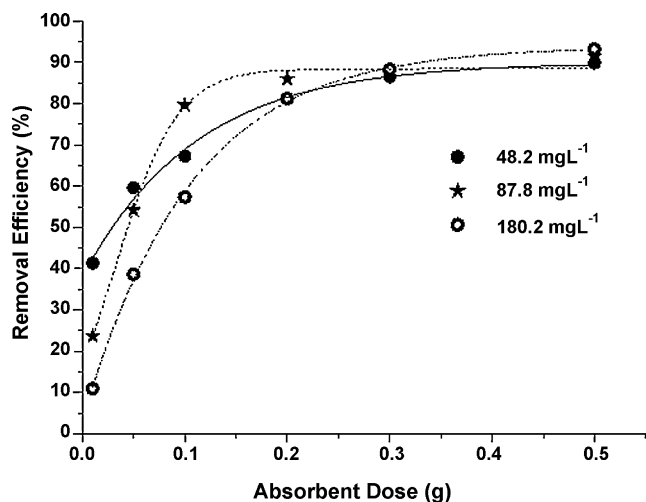


Fig. 1. Effect of adsorbent dose on removal efficiency of Pb at three initial Pb concentrations.

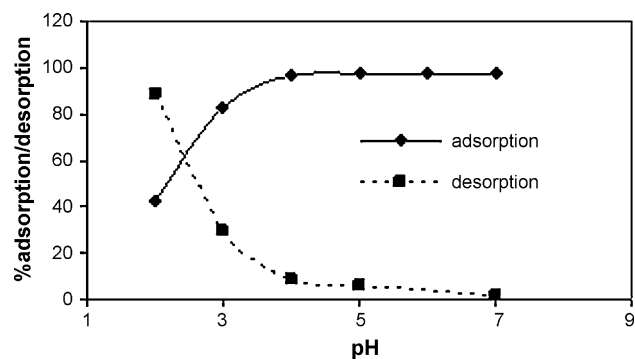


Fig. 2. Effect of pH on adsorption and desorption efficiency of Pb; initial Pb concentration:  $10.8 \text{ mg L}^{-1}$ , contact time: 30 min, adsorbent dose: 0.2 g.

active sites [14]. The pH optimization study was carried out for the removal of Pb(II) using bael leaves in the pH range of 2.0–7.0. A solution of  $10.8 \text{ mg L}^{-1}$  Pb(II) and 0.2 g of bael leaves was used for this study. The result is presented in Fig. 2. The Pb(II) removal is positively correlated with the pH of up to 4.0 and then remains practically constant. Therefore, pH 4.0 was considered as the optimum pH for adsorption by bael leaves and the percentage of adsorption was approximately 97%. Similar values of optimum pH for sorption of Pb are reported in the literature using cone biomass of *P. sylvestris* [8] and pH 5.0 using maple sawdust [15] and activated sawdust [16]. The decrease of adsorption capacity of bael leaves at lower pH can be attributed to the competition faced by Pb(II) ions with  $\text{H}^+$  ions to get adsorbed on the binding sites of the cells which are responsible for metal adsorption [17]. To further investigate the reason for pH dependence of adsorption efficiency of bael leaves, FT-IR studies were performed for the Pb loaded and Pb free bael leaves (native bael leaves). The results of FT-IR studies will be discussed in the following sections.

**Table 1**  
Comparison of Pb sorption capacity of bael leaves with other reported biosorbents under similar conditions.

Biosorbent	Sorption capacity ( $\text{mg g}^{-1}$ )	pH	Temperature (K)	Initial concentration ( $\text{mg L}^{-1}$ )	Ref.
Sago waste	46.6	4.0–5.5	298	100	[29]
Cicer arietinum	50.2	5.0	298	10	[30]
Botrytis cinerea	107.1	4.0	298	350	[31]
Fraxinus tree leaves	172.0	5	298	50	[32]
Ulmus tree leaves	201.0	5	298	50	[32]
Spyrogyra Negiecta	116.1	5.0	298	50	[33]
Bael leaves	104.0	5.1	298	50	Present study

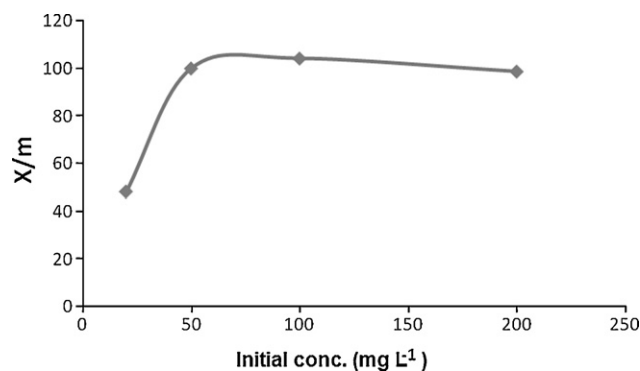


Fig. 3. Plot of Loading capacity of Pb vs. initial Pb(II) concentration.

### 3.2. Regeneration study

Regeneration (by desorption) of the biosorbent is of crucial importance in assessing its potential for commercial application. Desorption study will also help to elucidate the nature of the adsorption process. Desorption experiments were performed by varying the pH in the range of 2.0–7.0. The percentage of desorption of Pb(II) from bael leaves was almost 85% at pH 2.0 (Fig. 2). It was observed that desorption decreased with increase in pH and beyond a pH of 4.0 the percentage of desorption was negligible. In order to examine the reusability of the biosorbent, the adsorption–desorption cycle of Pb(II) was repeated twice. A 5% decrease in the adsorption efficiency was observed after two cycles. The regeneration of bael leaves showed that adsorption of Pb on to the bael leaves was a reversible process.

### 3.3. Loading capacity

Loading capacity of an adsorbent is defined as the amount of adsorbate adsorbed ( $X$ ) per unit weight ( $m$ ) of the adsorbent. Loading capacity ( $X/m$ ) of the bael leaves was determined at different initial Pb concentrations by varying the adsorbent dose in a solution of pH 5.1. Fig. 3 represents the plot of the loading capacity ( $X/m$ ) versus initial Pb(II) concentration,  $C_0$  ( $\text{mg L}^{-1}$ ). The maximum loading capacity was found to be  $104 \text{ mg g}^{-1}$  at  $50 \text{ mg L}^{-1}$  of initial Pb(II) concentration. A comparative study of the loading capacity,  $X/m$  ( $\text{mg g}^{-1}$ ) under similar conditions of pH and temperature was carried out with other reported biosorbents (Table 1). The data revealed that bael leaves were a potential biosorbent with similar or higher loading capacity of Pb compared to some of the other reported biomasses. However, Ulmus tree leaves and Fraxinus tree leaves were better adsorbents with higher loading capacities of Pb.

### 3.4. Mechanism of adsorption

The studies so far indicate that bael leaves can be successfully used for the removal of Pb from aqueous solution. An effort was made to identify the components of the bael leaves that are responsible for Pb adsorption. Hence, the FT-IR spectra for native and Pb

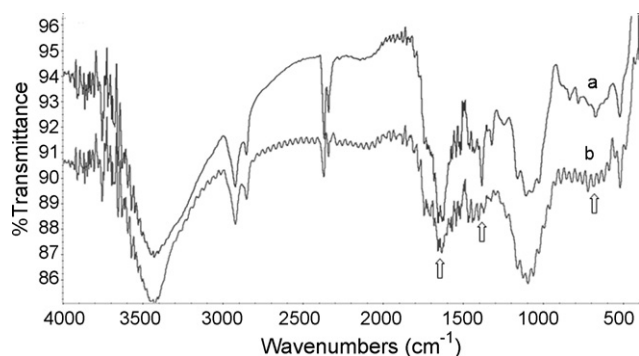


Fig. 4. FT-IR spectra of native bael leaves (a) and Pb(II) loaded bael leaves (b).

loaded bael leaves were recorded (Fig. 4) to identify the different functional groups of bael leaves responsible for lead removal. An analysis of the FT-IR spectra revealed that the functional groups like carboxylic acids, amides, thioesters, and sulphonamides were present in the native bael leaves. In fact, Sudharameshwari and Radhika, in their study involving medicinal activities of bael leaves had identified that bael leaves contain compounds like alkaloids, carboxylic acids, phenols, sterols and xanthoproteins [18]. The complex spectra in Fig. 4 show several strong absorption bands. The bands were assigned on the basis of the structure and chemical composition of the plant cell wall and cuticle and were facilitated by the available data of FT-IR spectra of cell wall components [19] and plant leaf tissues [20]. The broad band positioned around  $3430\text{ cm}^{-1}$  was assigned the stretching vibration of hydroxyl functional groups. The high content of water in the plant leaves and numerous hydroxyl groups in the polysaccharide structure of the

plant cell walls explained the presence of the band. The absorption bands located at  $1631$  and  $1565\text{ cm}^{-1}$  correspond to the aromatic domains of the cuticle and plant leaves [19]. The band frequencies at  $1700$ – $1650\text{ cm}^{-1}$  are the characteristic amide-I frequencies of the protein secondary structures. The absorbance at  $1655\text{ cm}^{-1}$  is due to C=O of carboxylic acids [19]. The absorbance at around  $1550\text{ cm}^{-1}$  is usually associated with the amide-II band that is attributable to N–H bending and C–N stretching in protein amide groups. The thioester group corresponds to the band at  $672\text{ cm}^{-1}$  [20]. The band at  $1382\text{ cm}^{-1}$  is assigned to the sulphonamide group. The changes in peak frequency and intensity of FT-IR spectra of native and Pb loaded bael leaves suggest that carboxylic acid and thioester groups are involved in the adsorption process. The appearance of a band at  $1735\text{ cm}^{-1}$  in the Pb loaded bael leaves can be assigned to the carboxylate ion ( $-\text{COO}^-$ ). At pH greater than 4.0, the carboxylic acid group is converted to the carboxylate ion and Pb(II) ion is adsorbed. The involvement of carboxylic acid groups in the adsorption process explains the effect of pH on the adsorption process (Section 3.1.2). At pH 2.0, majority of the carboxylate ions are converted to carboxylic acid groups ( $-\text{COOH}$ ) and hence the adsorption efficiency decreases. This fact is further strengthened by the regeneration study. As discussed in Section 3.2, the Pb loaded bael leaves can be regenerated by decreasing the pH. The band at  $1382\text{ cm}^{-1}$  disappears in the FT-IR spectra of Pb loaded bael leaves. This suggests a strong involvement of the sulphonamide group in the adsorption process. No marked change in frequency in the region of  $3430\text{ cm}^{-1}$  (hydroxyl functional groups) was observed between the native bael leaf and the lead loaded bael leaf. However, the broadening of the peak decreases indicating that the hydrogen bonding of the hydroxyl groups decreases after Pb loading. All these observations indicate the involvement of functional groups

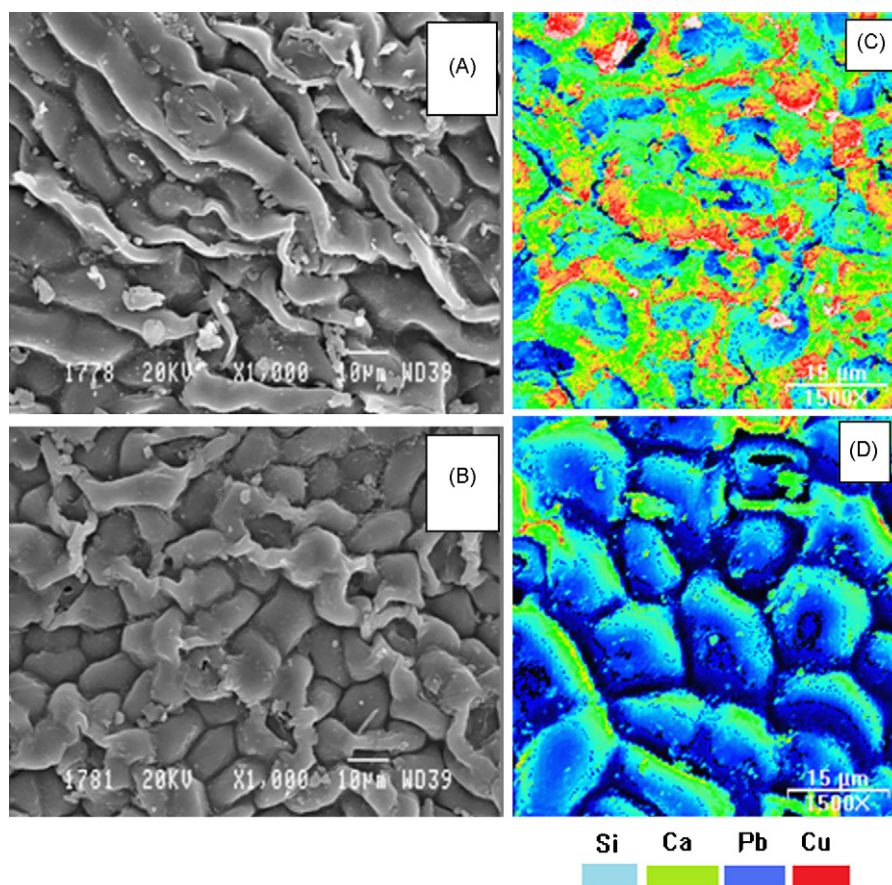


Fig. 5. SEM and metal mapping images of native bael leaves (A and C) and Pb(II) loaded bael leaves (B and D).

like carboxylic acid, thioester and sulphonamide in the biosorption process.

To investigate the adsorption process further, the bael leaves and Pb loaded bael leaves were observed under the scanning electron microscope. The SEM images of the native bael leaves and Pb loaded bael leaves are shown in Fig. 5. SEM image of the powdered bael leaf (Fig. 5A) shows a regular symmetry with hollow tubular structures before adsorption. After Pb adsorption the tubes appear to be prominently swollen as Pb enters the fibers of the bael leaves (Fig. 5B). This observation indicates that Pb is adsorbed to the functional groups present inside the wall of the tubular structures of the bael leaf. To visualize the location of the adsorption sites, a metal mapping was performed using SEM. The metal mapping micrographs of the native and Pb loaded bael leaves are also shown in Fig. 5C and D. The presence of inorganic constituents such as Ca, Cu, Si, and some amount of Pb in the native bael leaves are represented by green, red, sea blue and deep blue color, respectively, in the micrograph (Fig. 5C). Fig. 5D shows that Pb is heavily loaded in the bael leaves and adsorption of Pb(II) occurs inside the wall of the hollow tubes. So, the morphological study of Pb(II) loaded bael leaves confirms that the adsorption takes place inside the hollow tubes of the bael leaves.

### 3.5. Adsorption isotherm

Two models were used to describe the experimental sorption isotherm: Langmuir model and Freundlich model. The linear form of Langmuir equation after rearrangement is

$$\frac{C_e}{q_e} = \frac{1}{bV_m} + \frac{C_e}{V_m} \quad (1)$$

where  $C_e$  is the equilibrium concentration of remaining metal in the solution ( $\text{mg L}^{-1}$ ),  $q_e$  is the amount of metal adsorbed per mass unit of adsorbent at equilibrium ( $\text{mg g}^{-1}$ ),  $V_m$  is the amount of adsorbate at complete monolayer coverage ( $\text{mg g}^{-1}$ ), and  $b$  ( $\text{L mg}^{-1}$ ) is a constant that relates to the heat of adsorption.

Freundlich adsorption isotherm can be represented as

$$q_e = K_f C_e^{1/n} \quad (2)$$

or in the linear form

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (3)$$

where  $K_f$  and  $n$  are Freundlich constants indicating adsorption capacity and intensity, respectively.  $K_f$  and  $n$  was determined from a linear plot of  $\log q_e$  against  $\log C_e$ . The adsorption capacity ( $q_e$ ) was calculated using the equation

$$q_e = \frac{(C_0 - C_e)V}{w} \quad (4)$$

where  $C_0$  is the initial Pb(II) concentration,  $C_e$  is the final equilibrium concentration of Pb(II),  $V$  is the volume of Pb(II) solution (ml),  $w$  is the weight of the bael leaves (g). Adsorption equilibrium studies for Pb(II) adsorption on bael leaves were conducted at the optimum conditions using a contact time of 30 min at pH 5.1 with five different initial Pb(II) concentrations of 8.7, 19.0, 48.2, 87.8 and 180.2  $\text{mg L}^{-1}$  and a fixed adsorbent dose of 0.01 g. The Langmuir and Freundlich isotherm plots are given in Figs. 6 and 7, respectively. It was found that the adsorption of Pb(II) ion onto bael leaves fits better with the Langmuir model ( $R^2 = 0.97$ ) as compared to the Freundlich model ( $R^2 = 0.8$ ) under the concentration range studied. The calculated results of the Freundlich and Langmuir isotherm constants are given in Table 2. The essential feature of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor,  $R_L$  that is used to predict whether an adsorption

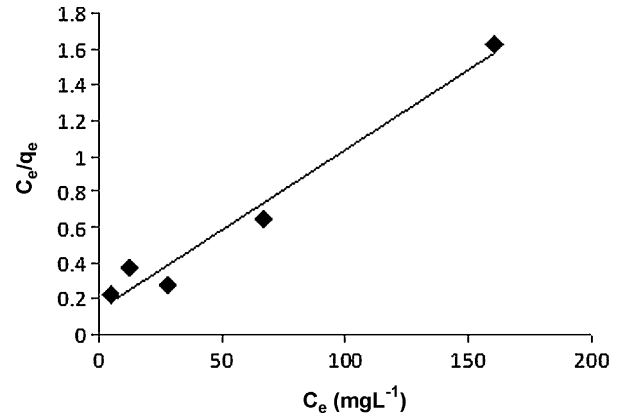


Fig. 6. Langmuir isotherm plot for adsorption of Pb(II) onto bael leaves.

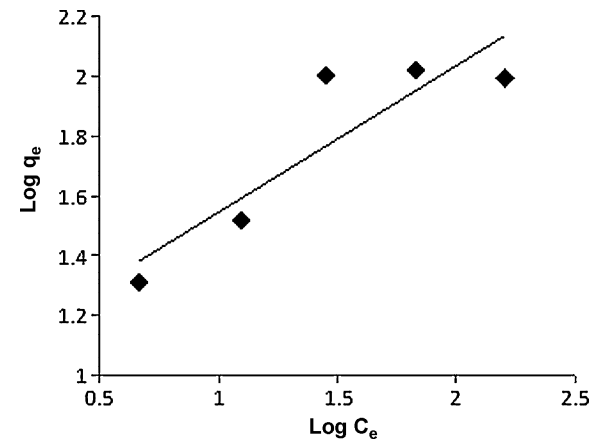


Fig. 7. Freundlich isotherm plot for adsorption of Pb(II) onto bael leaves.

system is “favorable” or “unfavorable” [21]. The separation factor  $R_L$  is defined as

$$R_L = \frac{1}{1 + bC_e} \quad (5)$$

where  $C_e$  ( $\text{mg L}^{-1}$ ) is the equilibrium concentration of Pb(II) and  $b$  ( $\text{L mg}^{-1}$ ) is the Langmuir isotherm constant. The adsorption process as a function of  $R_L$  may be described as  $R_L > 1$ ; unfavorable,  $R_L = 1$ ; Linear,  $0 < R_L < 1$ ; favorable and  $R_L = 0$ ; irreversible. The values of  $R_L$  calculated from different initial Pb(II) concentrations are given in Table 3 which indicates a highly favorable adsorption within the concentration range of 8.7–180.2  $\text{mg L}^{-1}$ .  $R_L$  in the range of 0–1 at all initial Pb(II) concentration confirms the favorable uptake of Pb(II) in the adsorption process [22].

### 3.6. Adsorption kinetics

In order to investigate the kinetics of biosorption, two kinetic models, Lagergren's first order rate equation [23] and pseudo sec-

**Table 2**  
Freundlich and Langmuir model constants for Pb adsorption onto bael leaves.

Langmuir model	
$b$ ( $\text{L mg}^{-1}$ )	0.05
$V_m$ ( $\text{mg g}^{-1}$ )	125
$R^2$	0.97
Freundlich model	
$n$	2.04
$K$ ( $\text{mg g}^{-1}$ )	11.4
$R^2$	0.80

**Table 3** $R_L$  values for adsorption of Pb(II) onto bael leaves based on Langmuir model.

Initial Pb(II) concentration (mg L <sup>-1</sup> )	Equilibrium concentration (mg L <sup>-1</sup> )	$R_L$
8.7	4.66	0.8
19.0	12.42	0.61
48.2	28.3	0.41
87.8	67.09	0.22
180.2	160.5	0.11

and order equation [24] were employed. A solution of 98.3 mg L<sup>-1</sup> Pb(II) (50 mL) and 0.05 g of bael leaves were used for this study. Samples of 5 mL each were drawn from the solution mixture at time intervals of 5, 10, 15, 20, 25 and 30 min and analyzed for kinetics study. Lagergren first order model is

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (6)$$

where  $q_e$  is the amount of adsorbed Pb(II) onto the bael leaves at equilibrium (mg g<sup>-1</sup>),  $q_t$  is the amount of Pb(II) adsorbed at time  $t$  and  $k_1$  is the first order rate constant. Adsorption data of Pb(II) on bael leaves at three different temperatures (303, 313 and 323 K) was fitted to the Lagergren first order rate equation. The results obtained are summarized in Table 4. The pseudo second order rate equation is represented as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (7)$$

where  $k_2$  is the second order rate constant of adsorption (g mg<sup>-1</sup> min<sup>-1</sup>). Integrating Eq. (7) with boundary conditions  $t=0$  to  $t=t$  and  $q_t=0$  to  $q_t=q_t$ , it becomes

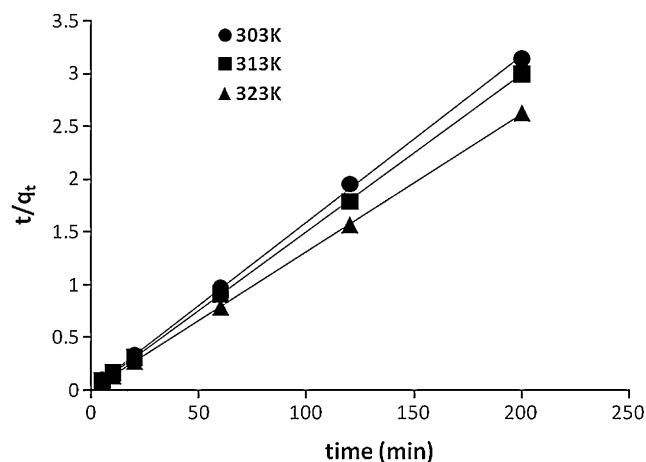
$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + k_2 t \quad (8)$$

Eq. (8) can be rearranged to obtain

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

which is the linear form of Ho second order model. The plot of  $t/q_t$  against  $t$  is shown in Fig. 8. The fitting of kinetic data in second order rate expression shows excellent linearity with high correlation coefficient ( $R^2 = 0.99$ ) over the temperature range of 303–323 K. The data obtained for pseudo second order kinetic model at three different temperatures is tabulated in Table 4. An analysis of the data in Table 4 suggests that the kinetics of adsorption of Pb on bael leaves can be explained more accurately by the pseudo second order kinetics model. The correlation coefficients ( $R^2$ ) obtained for the second order kinetic model are better than that of Lagergren first order kinetic model. The Lagergren first order kinetic model fails to estimate the  $q_e$  values correctly as the estimated values deviate more from the experimental  $q_e$  values. The calculated  $q_e$  values in the second order kinetics were found to be quite close to the experimental  $q_e$  values at all the temperatures (303–323 K). So, it may be inferred that the adsorption of Pb on bael leaves follows the second order kinetics.

Based on the second order kinetic model, the initial adsorption rate and half adsorption time were estimated according to the

**Fig. 8.** Plot of pseudo second order kinetics model for adsorption of Pb(II) onto bael leaves.**Table 5**

Kinetic parameters of second order adsorption model for Pb(II) adsorption onto bael leaves.

Temperature (K)	$U$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$t_{1/2}$ (min)
303	48.79	1.36
313	71.37	1.00
323	112.3	0.68

following equation:

$$U = k_2 q_e^2 \quad (10)$$

$$t_{1/2} = \frac{1}{k_2 q_e} \quad (11)$$

where  $U$  = initial adsorption rate (mg g<sup>-1</sup> min<sup>-1</sup>),  $t_{1/2}$  = half adsorption time (min). The estimated values of  $U$  and  $t_{1/2}$  are presented in Table 5. It can be observed from Table 5 that the initial adsorption rate increases with increase in temperature and the half adsorption time  $t_{1/2}$  decreases with increase in temperature.

The pseudo second order rate equation of Pb(II) adsorption on bael leaves is expressed as a function of temperature by the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT} \quad (12)$$

where  $E_a$  is the Arrhenius activation energy (kJ mol<sup>-1</sup>),  $A$  is the Arrhenius factor,  $R$  is the ideal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),  $k$  is the specific rate constant and  $T$  is the solution temperature (K). The  $k$  value of Arrhenius equation was obtained from the rate constant ( $k_2$ ) of pseudo second order equation. To estimate the Arrhenius activation energy,  $\ln k$  was calculated at three different temperatures of 303, 313 and 323 K and  $\ln k$  versus  $1/T$  was plotted (Fig. 9). The plot gave a straight line with slope  $-E_a/R$  and intercept of  $\ln A$ . The Arrhenius activation energy calculated from the slope was found to be 22.2 kJ mol<sup>-1</sup>. The results of the activation energy confirmed that the nature of the adsorption process is physical adsorption on to the bael leaves. The physisorption process usually

**Table 4**

Kinetic parameters of Lagergren first order and pseudo second order expressions for Pb(II) adsorption onto bael leaves at different temperatures.

Temperature (K)	Lagergren first order kinetic model			Experimental value, $q_e$ $q_e$ (mg g <sup>-1</sup> )	Pseudo second order model		
	$q_e$ (mg g <sup>-1</sup> )	$k_1$ (min <sup>-1</sup> )	$R^2$		$q_e$ (mg g <sup>-1</sup> )	$k_2$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$R^2$
303	5.97	0.011	0.80	61	66.6	0.011	0.99
313	6.53	0.009	0.74	66	71.4	0.014	1.0
323	5.59	0.011	0.62	76.0	76.9	0.019	1.0

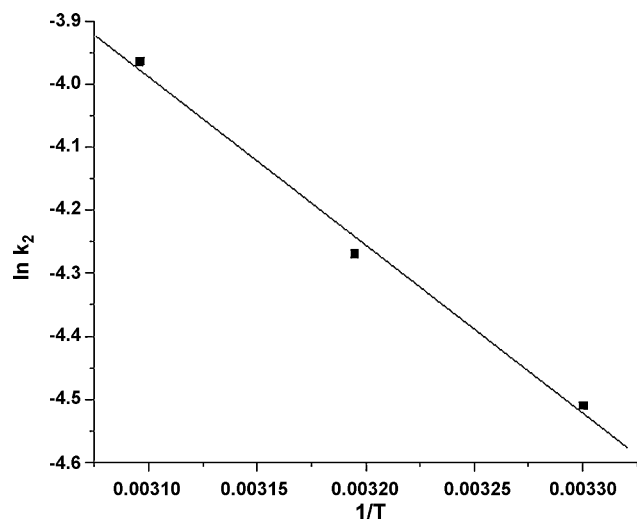


Fig. 9. Arrhenius equation plot for adsorption of Pb(II) onto bael leaves.

has energies in the range of 5–40 kJ mol<sup>-1</sup> while the chemisorptions process has higher activation energy (40–800 kJ mol<sup>-1</sup>) [25,26].

### 3.7. Selective adsorption of Pb(II) over other metal ions

The results obtained from the adsorption studies of synthetic spiked waters (usually distillate water and one or two metals under investigation) can only be applied to real wastewaters to a very limited extent. Waste waters or real samples contain a broad range of different cations as well as other inorganic and organic contaminants that certainly interfere in the sorption mechanisms, including competitive sorption among metals [27]. Therefore, a study was performed to evaluate the effect of the presence of other cationic metal ions on the adsorption process of Pb on bael leaves. Simultaneous biosorption of Pb(II) ions was studied using a medium that contained 10 mg L<sup>-1</sup> of each metal ion Mn<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup> with a common nitrate anion. The pH of the solution was maintained at 3.0 and 0.2 g of dry bael leaves were used for the study. The result of this study is presented in Table 6. It can be observed from the table that about 80% of Pb was removed from the aqueous solution using the bael leaves whereas the removal of other metal ions was negligible. Therefore, Pb(II) adsorption on bael leaves is highly selective. The selective adsorption of Pb(II) on bael leaves can be explained by the higher electro-negativity (2.33 Pauling scale) and lower atomic radius (154 pm) compared to the other metal ions [28]. Sorption of metals having a smaller ionic radius has been reported as superior to those with larger ionic radius [28]. This result is significant in the sense that Pb(II) can be removed specifically in the presence of other cations present in the aqueous system.

Table 6  
Selective removal of Pb(II) by bael leaves in presence of other metal ions.

Metal ion	Initial concentration (mg L <sup>-1</sup> )	Final concentration (mg L <sup>-1</sup> )	Percentage removal
Pb <sup>2+</sup>	9.76	2.11	78.3%
Mn <sup>2+</sup>	9.25	9.19	0.6%
Fe <sup>2+</sup>	8.17	8.06	1.3%
Zn <sup>2+</sup>	9.64	9.16	4.9%
Ni <sup>2+</sup>	10.9	10.78	1.1%
Cu <sup>2+</sup>	10.36	9.8	5.4%
Cd <sup>2+</sup>	9.36	9.23	1.3%
Mg <sup>2+</sup>	9.6	9.54	0.6%

Table 7

Removal of Pb from battery effluent using bael leaves at different pH.

pH	Pb concentration (mg L <sup>-1</sup> ) before adsorption	Pb concentration (mg L <sup>-1</sup> ) after adsorption	% Pb removal
2.2	110	82.4	25%
4.1	78.2	23.2	70%
6.2	55.4	6.6	88%

### 3.8. Application on battery waste effluent

In an effort to examine the practical utility of bael leaves for Pb removal from aqueous solution, an experiment was carried out to remove Pb from the effluent of waste battery. One of the objectives of the present study was also to examine bael leaves as an adsorbent for the purpose of remediation. The effluent of a waste battery was collected by mixing the contents of an exhausted battery in 200 mL of distilled water. The insoluble portions were filtered off and the filtrate was accepted as the effluent. The Pb(II) concentration in the effluent was measured to be 110 mg L<sup>-1</sup> and the pH of the effluent was 0.5. For the treatment of this effluent by bael leaves, its pH was adjusted to pH 2.0, 4.0 and 6.0 using 0.1(M) NaOH and 0.2 g of bael leaves were used for the Pb removal purpose. The results of the study are summarized in Table 7. It can be observed from Table 7 that approximately 70% and 88% of Pb(II) could be removed from the effluent at pH 4.1 and 6.2 using 1 g L<sup>-1</sup> bael leaves. Since the bael leaves are biodegradable, it can be easily disposed after recovering Pb(II) from the biosorbent by desorption.

## 4. Conclusion

The present investigation showed that bael leaves, *Aegle marmelos*, are a potential biosorbent for the removal of Pb(II) from an aqueous medium. It was demonstrated that Pb could be removed from the effluents of waste batteries. The maximum Pb(II) loading capacity of bael leaves was 104 mg g<sup>-1</sup> which was either comparable to or better than the Pb loading capacities of other reported biosorbents. The adsorption process was pH dependent and the optimum pH for Pb(II) removal was 4.0. Pb was adsorbed inside the tubular structures of the bael leaves and carboxylic acid, sulphamide and thioester functional groups were involved in the process. The adsorption process followed pseudo second order kinetic model and the Langmuir model fit better to the adsorption equilibrium data in comparison to the model described by Freundlich. The nature of adsorption of Pb on bael leaves was physical adsorption. The bael leaves could be regenerated using 0.1N HNO<sub>3</sub> but the adsorption efficiency decreased by 5% after repeated adsorption–desorption process. Bael trees grow widely throughout the Indian peninsula, the leaves have no commercial value, and the present study showed that it could be used as a good and inexpensive source of biomaterial for wastewater treatment.

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