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Research Article

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# Chemical pretreatments of *Trapa bispinosa's* peel (TBP) biosorbent to enhance adsorption capacity for Pb(II)

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**Abstract:** In this study, *Trapa bispinosa*'s peel (TBP) biomass is exploited as an effective, low cost and new adsorbent to remove Pb(II) from aqueous solution. TBP is pretreated and modified with $HNO_3$, $HClO_4$ and $H_2O_2$ to enhance the Pb(II) removal and it is perceived that chemical modifications enhance the adsorption capacity of TBP. The adsorption behavior of Pb(II) is studied under different conditions, including pH (3-6), TBP dose (0.05-0.8 g), stirring speed (100-200 rpm), initial Pb(II) ion concentration (25-400 mg $L^{-1}$) and contact time (0-1440 min). Kinetic study reveals sorption is fast in first 15 to 30 min achieving equilibrium in 60 min with $q_{max}$ (mg $g^{-1}$) are 77.09, 105.40 and 123.82 for NT-TBP, NA-TBP and HCA-TBP respectively. The Langmuir model successfully defines the sorption data having higher $R^2$ and good agreement between theoretical and experimental uptake capacity of Pb(II). The kinetic study exhibits that the pseudo-second order rate equation is better portrayed sorption process. TBP modified with $HClO_4$ shows the highest metal uptake in comparison to $HNO_3$, $H_2O_2$ modified TBP and native TBP.

**Keywords:** *Trapa bispinosa;* Pb(II); isotherm models; kinetics; chemical pretreatments.

## 1 Introduction

Toxic metals appear in immobilized form and as ores in nature. In the rationalized industrial world, toxic metals have become a serious threat in forthcoming days [1,2] and cause severe degradation in mesosphere, hydrosphere, and atmosphere. These inorganic pollutants largely originate from industrial wastes. Without proper treatment, these metals posses a significant peril to public health as being non-biodegradable and persistent [3]. Pb(II) is a deleterious metal, detected in waste streams from mining, storage batteries of lead acid, allied product, chemicals, glass, ceramic, electronics, tanneries, electroplating and petrochemical industries [4,5]. In human, Pb(II) poisoning causes acute harm to brain, kidney, liver, nervous system and reproductive system. Severe contact with Pb(II) has been coupled with neo-natal deaths, abortion, sterility, and stillbirth [6,7]. World Health Organization (WHO) and Environment Protection Agency (EPA) consider Pb(II) as hazardous and important pollutant and define that Pb(II)'s maximum permissible level is 0.01 and 0.43 mg $L^{-1}$ in drinking water and wastewater respectively [3].

Several remediation techniques for the removal of toxic metal ions such as precipitation, coagulation, membrane process and electrolytic method have been in practice [8]. But they are prohibitive for the removal of toxic metals [9,10]. Toxic metals treatment becomes inevitable and in this endeavor, biosorption seems to be an efficient alternative for the eradication of metal pollutants in streams and have been recommended as cheaper and effective technique [9, 11]. Biosorption of toxic metals involves physiochemical linkage, mainly complex formation or ion exchange among the functional groups present on surface of biomass and metal ions. Different functional groups are involved such as carboxyl, phosphates, amines, amides hydroxyl carbonyl, sulphonates, phosphonates, and sulfhydryl [12]. Biosorbents are prepared from naturally plentiful and

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waste biomass and a variety of cheap and easily available biosorbents reported [5,8,11,13-27].

The attractiveness of using plant wastes for removing pollutants is due to simplicity in technique, less processing, selective adsorption for metals, high uptake capacity, low cost, easy availability and regeneration ability [28]. However many problems are associated when untreated plant wastes were used as adsorbents including high chemical oxygen demand (COD), biochemical oxygen demand (BOD) and low uptake capacity as well as discharge of soluble organic compounds from plant wastes. Therefore, it is important to modify or treat the plant-based adsorbents before their application to remove toxic metals.

An wide survey of the available literature discloses very few articles on the adsorption activity of *Trapa bispinosa*'s towards dyes and metals [29-32] and no reports towards Pb(II) removal. *Trapa bispinosa* (locally known as Singhara) is an aquatic edible plant and member of *Trapaceae* family. The crop yield is approximately 3751 Kg with 6-8 months of growth cycle. The inner edible white part has an average weight of 5 Kg is covered by a thin and hard brown spermoderm. It is a good source of minerals matters, potassium, calcium, phosphate, iron, copper, manganese, magnesium, and sodium and also contains plentiful B vitamins including B1, B2, B5 and B6 and vitamin C [33]. In current research work, this low cost and easily available, *Trapa bispinosa*'s peel (TBP) waste material was selected as a new biosorbent for the removal of Pb(II). The TBP was chemically treated and Pb(II) removal on native and chemically pretreated TBP was investigated and compared. The pretreatments of TBP plant waste were expected to enhance the uptake capacity of adsorbents for Pb(II).

# 2 Material and method

## 2.1 Reagents

All the chemicals $Pb(NO_3)_2$, $HNO_3$, $HClO_4$ and $H_2O_2$ utilized in this research work were of analytical grade and acquired from Fluka chemicals (Buchs, Switzerland). Pb(II) atomic absorption spectrometry standard solutions were also purchased from Fluka Chemicals (Buchs, Switzerland). All sample bottles and glassware was washed by overnight soaking in 10% (w/v) $HNO_3$ and then for several times rinse with distilled water.

## 2.2 Pretreatment of TBP adsorbent

The plant material TBP was collected from different zones of Faisalabad, Pakistan. TBP was washed with deionized distilled water (DDW) to remove soluble and adhering dirt impurities and dried out in the sunlight. The dried TBP biomass was slash, ground by food processor (Moulinex, France), followed by sieving with Octagon siever (OCT–DIGITAL 4527-01, Endecotts Ltd. London, UK) to particles of 0.25 mm size before use. To investigate the influence of different chemical pretreatments on the uptake capacity of TBP, 10 g of TBP was pretreated with 0.1 M of $HNO_3$, $HClO_4$ and $H_2O_2$ for 24 hrs. After each pretreatment, the TBP biomass was washed with DDW until the pH of solutions becomes neutral. The chemical pretreated TBP biomass was then dried at 80°C for 8 hrs in an oven, sieved again and then kept in desiccators until further use for the adsorption studies of Pb(II). The resulting chemically pretreated biomasses were named as $HNO_3$ treated *Trapa bispinosa's* Peel (NA-TBP), $HClO_4$ treated *Trapa bispinosa's* Peel (HCA-TBP), $H_2O_2$ treated *Trapa bispinosa's* Peel (HPO-TBP) and non-treated *Trapa bispinosa's* Peel (NT-TBP).

## 2.3 Batch biosorption studies

The Pb(II) stock solution was made up by dissolving $Pb(NO_3)_2$ salt in DDW. The ion concentration was 1.59 g $L^{-1}$ in stock solution. Solutions of different Pb(II) concentrations were made by suitable dilution of the prepared Pb(II) stock solution with DDW. For all groups of experiments, 100 mL volume of Pb(II) solutions were thoroughly mixed with TBP biosorbent having particle size of 0.25 mm at 30°C and stirred for 4 hrs. To study the influence of chemical pretreatments, pH, TBP dose, stirring speed, initial Pb(II) concentrations and contact time; different conditions of pH (3 to 6), TBP dose (0.05 to 0.8 g), stirring speed (100 to 200 rpm), initial metal concentrations (25 to 400 mg $L^{-1}$) and contact time (0 to 1440 min) were assessed. The pHs of the solutions were adjusted with 0.1 N solutions of NaOH and HCl. The flasks containing Pb(II) solutions were employed on a rotating shaker (PA 250/25. H. Adolf Kühner AG. Birsfelden, Switzerland) with constant stirring. After that the Pb(II) solutions containing TBP biomass were filtered through membrane filter (Millipore) of 0.45 µm size. Preliminary trials were accomplished using 100 mg $L^{-1}$ initial Pb(II) concentrations at pH 4.

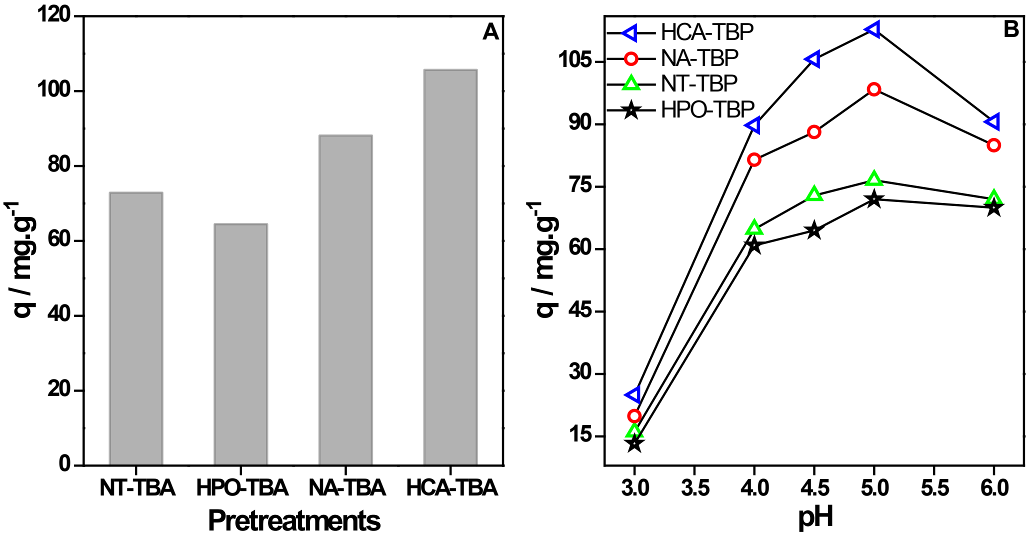

**Figure 1:** Effect of pretreatment (A) and pH (B) on Pb(II) removal by original and chemically pretreated TBP.

### 2.4 Determination of the Pb(II) contents in the solutions

The concentration of Pb(II) in the solutions before and after the equilibrium was determined by Hi-Tach polarized zeeman atomic absorption spectrometer (AAS) equipped with an air-acetylene burner (AAnalyst 300, Perkin-Elmer, Waltham, USA) having 1.3 nm slit width. Deuterium background correction was used and the analytical wavelength was set at 283.3 nm. The instrument response was periodically checked using standard Pb(II) solution.

The % removal and Pb(II) uptake q (mg Pb(II) adsorbed/g TBP adsorbent) were estimated by equation 1 and 2 respectively.

$$\% \text{ removal} = \frac{(C_i - C_e)100}{C_i} \tag{1}$$

$$q = \frac{V(C_i - C_e)}{m} \tag{2}$$

where q is the Pb(II) uptake capacity (mg Pb(II)/g dry TBP), V is solution volume (L), $C_i$ is initial Pb(II) concentration (mg $L^{-1}$), $C_e$ is final PB(II) concentration in solution (mg $L^{-1}$) and m is amount of the TBP (g).

### 2.5 Desorption and reuse of TBP

The Pb(II) loaded adsorbent was regenerated and reused for successive Pb(II) adsorption by means of desorption process. For adsorption/desorption experiments, 0.1 g of HCA-TBP or NA-TBP was treated with 100 mL solution containing 50 mg $L^{-1}$ of Pb(II) and the solution was centrifuged after equilibrium time. The spent HCA-TBP or NA-TBP (0.1 g Pb(II) adsorbed TBP) was added to 40 mL of 0.1 M HCl and incubated for 3 h at 150 rpm agitation rate. After regeneration, the HCA-TBP or NA-TBP was washed and then reused to adsorb 50 mg $L^{-1}$ Pb in 100 mL solution. This procedure was repeated four times using the same approach.

Ethical approval: The conducted research is not related to either human or animal use.

## 3 Result and discussion

### 3.1 Effect of pretreatments and pH on Pb(II) uptake

The chemical and physical pretreatments play a significant role to improve the adsorption/uptake capacity of the biomass [34,35]. The comparison of all chemically pretreated biomasses is shown in Figure 1A. The results in Figure 1A are exposed that the maximum augmentation in uptake capacity of TBP is attained when pretreated with $HClO_4$. The NA-TBP biomass has also displayed certain increase in the uptake capacity of TBP. The possible reason of much enhancement in the uptake capacity of TBP for Pb(II) when treated with $HClO_4$, could be that pretreatment might be responsible to rupture the biomass cells, which results in releasing the polymers such as polysaccharides that have a great affinity towards certain metal cations and also enhance surface area and porosity for adsorption [36,37]. Thus immersion of finely ground biomass in acids may uncover additional binding sites and hence the approachability of the Pb(II) to the sorption sites is enhanced [38]. The assessment between the experimental data demonstrated that the key differences happening are linked to the variation of the total concentration of the active sites: HCA-TBP has more active sites than NA-TBP, HPO-TBP and NT-TBP. This may be because of the oxidation, which increases acid sites concentration. In contrast to this, pretreatment by $H_2O_2$ reduces acid site concentration in comparison with untreated TBP, possibly because of partial degradation of the vegetal matrix. Mainly hydroxyl and carboxyl functional groups on the biosorbent surface are present and the modeling identifies carboxylic and hydroxyl groups in all the biosorbents investigated and assuming that two major kinds of weakly monoprotic acidic sites are present. After the pretreatment, the quantity of oxygen comprising groups such as phenolic, hydroxyl and carboxyl functional groups is increased and exposed considerably more on the surface of the biomass after the $HCLO_4$ pretreatment of the TBP and resulting in higher uptake of Pb(II) [39]. The uptake capacity 'q' (mg $g^{-1}$) of all TBP biomasses is in the following order: HCA-TBP (105.65) > NA-TBP (88.16) > NT-TBP (72.90) > HPO-TBP (64.50). This indicates that the chemical pretreatments are extremely suitable in improving the adsorption capability of biomass.

The pH is a concerned parameter for the sorption phenomenon of metal ions. By the variation of metal ion solution pH, the state of chemically charged active sites on the biomass surface those are accountable for sorption of metal ions is altered rapidly [8,11,15,19]. Figure 1B presents Pb(II) uptake at pH ranging from 3.0-6.0 for native and pretreated TBP biomasses. Results show that equilibrium sorption capacity is minimum at pH 3.0 and maximum at pH 5.0 for all non-treated and pretreated TBP biomasses. At more acidic pH, adsorbent surface is more surrounded by $H^+$, thereby resist Pb(II) ions to bind with active site of the biomass. In fact high concentration of $H^+$ makes more positively charged biomass surface and causes reduction in sorption between metal cations and positively charged biomass. That's why at more acidic environment less uptake of metal ion occurs. Because the surface negative charged density is amplified simultaneously as the pH value increased. As a result, the electrostatic force of interactions between metals ions and adsorbent is improved. Ionic species of metals adsorbs more frequently at less acidic pH value of solution because of less stability in solution. At pH 6.0, decline in the biosorption of Pb(II) ions is also examined. This is due to metal ions may undergo hydrolysis and polymerization in the aqueous solution as shown below:

$$nH_2O + Pb^{2+} \rightarrow Pb(H_2O)_n^{2+}$$
$$Pb(H_2O)_n^{2+} \rightarrow Pb(H_2O)^{n-1}(OH)^+ + H^+$$
$$nPb^{2+} + mH_2O \rightarrow Pb(OH)_m^{(2n-m)} + mH^+$$

Again it is observed that the uptake capacity of all TBP biomasses is in following order: HCA-TBP > NA-TBP > NT-TBP > HPO-TBP and as with $H_2O_2$ pretreatment the uptake capacity of TBP is decreased so in the further study this pretreated adsorbent is not used and further study is carried out using HCA-TBP, NA-TBP and NT-TBP adsorbents.

## 3.2 Effect of TBP dose on Pb(II) uptake

The removal of Pb(II) onto native and pretreated TBP as a function of biosorbent dose is reported by varying the amount from 0.05 to 0.8 g at 5 pH and 100 mg $L^{-1}$ Pb(II) initial concentration for 4 h contact time. The effect of sorbent dose on the removal of Pb(II) is shown in Figure 2A. From the graph, it is clear that the % removal of Pb(II) increases with TBP weight and a maximum % removal is observed at 0.4 g for all native and pretreated TBP. The % removal for Pb(II) by HCA-TBP and NA-TBP is more than 95 and 90% respectively at TBA dose of 0.4 g. As indicated by Shukla et al., particles become aggregated at higher adsorbent amount, which results in decline in the total surface area and increase in diffusional path length. Both of these factors are responsible for decrease in amount of metal adsorbed per unit mass [40].

## 3.3 Effect of agitation speed on Pb(II) uptake

The effect of agitation speed on % removal of Pb(II) (100 mg $L^{-1}$) by 0.4 g each native and pretreated TBP adsorbents at pH 5 is investigated by varying agitation speed from 100 to 200 rpm. The results (Figure 2B) has revealed that the % removal of Pb(II) increases from 45.58 to 95.45%, 38.25 to 88.33% and 27.65 to 70.39% by HCA-TBP, NA-TBP and NT-TBP biomass samples respectively as the agitation speed increases from 100 to 175 rpm. At higher agitation speed a reduction in % removal of is observed. The probable explanation could be that as the agitation speed is increased, the collision between Pb(II) and adsorbent surface is also increased which results in fast

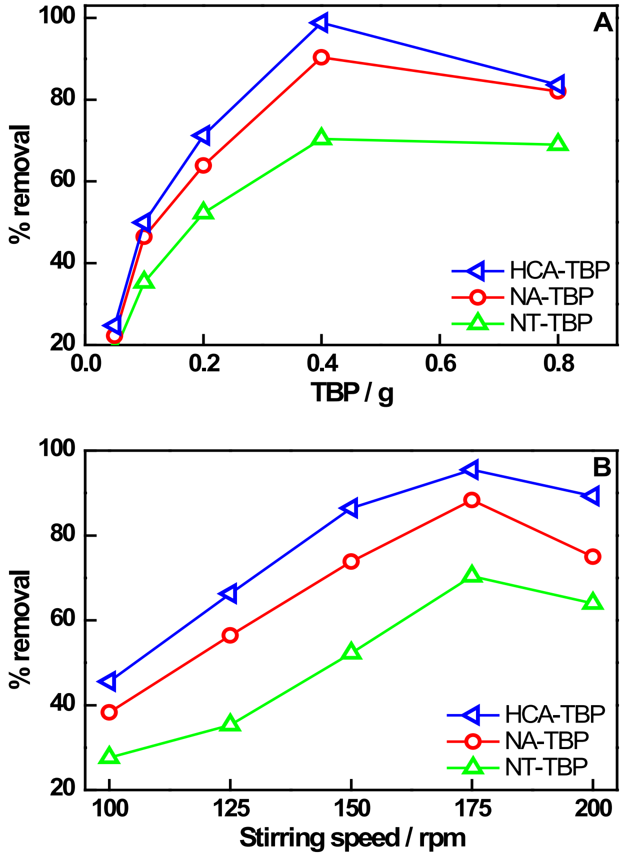

**Figure 2:** Effect of TBP dose (A) and stirring speed (B) on Pb(II) removal by original and chemically pretreated TBP.

reaction between Pb(II) and TBP adsorbents. A decline in % removal at higher agitation speed might be due to desorption of Pb(II) from the surface of TBP adsorbents.

## 3.4 Effect of Pb(II) initial concentration

By the interaction of an adsorbate with an adsorbent surface, sorption occurs over the surface and the dependence of sorption capacity is on adsorbate bulk concentration in the solution [41]. Increasing Pb(II) concentrations effect onto native and pretreated TBP surface is investigated by contacting 0.4 g of TBP with 100 mL of Pb(II) solutions of initial concentrations ranging from 25 to 400 mg $L^{-1}$ agitated at 175 rpm for 4 hours at the pH 5. The results are presented in Figure 3A, which reveal that increase in Pb(II) initial concentration causes rise in Pb(II) uptake capacity. The data shows that the Pb(II) uptake is increased from 24.78 to 158.46 mg $g^{-1}$, 22.25 to 134.30 mg $g^{-1}$, and 18.37 to 105.11 mg $g^{-1}$ onto HCA-TBP, NA-TBP and NT-TBP biomass samples respectively when Pb(II) ion concentrations is increased from 25 to 400 mg $L^{-1}$. However the study shows that there is a decline in the % removal with increase in Pb(II) concentration. The percentage removal of Pb(II) decreases from 99.12 to 45.36%, 90.56 to 26.4% and 78.56 to 21.4% HCA-TBP, NA-TBP and NT-TBP biomasses respectively (results not shown). This phenomenon occurs because the ratio of biomass active sites in the solution to the total Pb(II) ions is high at low concentrations and therefore all Pb(II) ions come in contact with the active sites of biomass and be eradicated from the aqueous solution. However, the driving force is much stronger at high concentration of ions so the quantity of Pb(II) ions adhere per unit weight of biomass is elevated. Further the TBP sorption sites become saturated at the higher concentration of metal ions causes decline in % removal. As a consequence, the TBP is quite efficient for the removal of low concentration of ions in the wastewaters. A similar trend is also observed in various earlier studies for removal of Pb(II) [35,42,43].

## 3.5 Evaluation of isothermal modeling

Adsorption isotherms signify the extent of attraction an adsorbent exhibits for a particular adsorbate and there application on data is important for the design of adsorption mechanism. The adsorption isotherms are explained by constant values, which defines adsorbate affinity and surface properties [44]. Numerous isotherm equations have been used for the adsorption modeling and in the present study, data obtained by isotherm experiments for Pb(II) by native and pretreated TBP are assessed by Langmuir, Freundlich and Temkin model equations. Langmuir model equation as drawn by Langmuir denotes homogeneous distribution of adsorption sites and monolayer adsorption [45]. The model is indicative of adsorbent's active sites saturation with negligible interaction among the adsorbed species. Freundlich model equation proposed by Freundlich focuses on heterogeneity of active sites and multilayer adsorption [46]. Temkin model equation demonstrated by Temkin and Pyzhev describes that adsorption heat of all species in a layer falls linearly by means of interaction between adsorbate and adsorbent [47]. This model also comprises a factor that explicitly considers only the interactions between adsorbent and adsorbate ignoring the very low and high values of concentrations [43]. The linear equations of Langmuir, Freundlich and Temkin are presented in Eqs. 3, 4, 5 respectively.

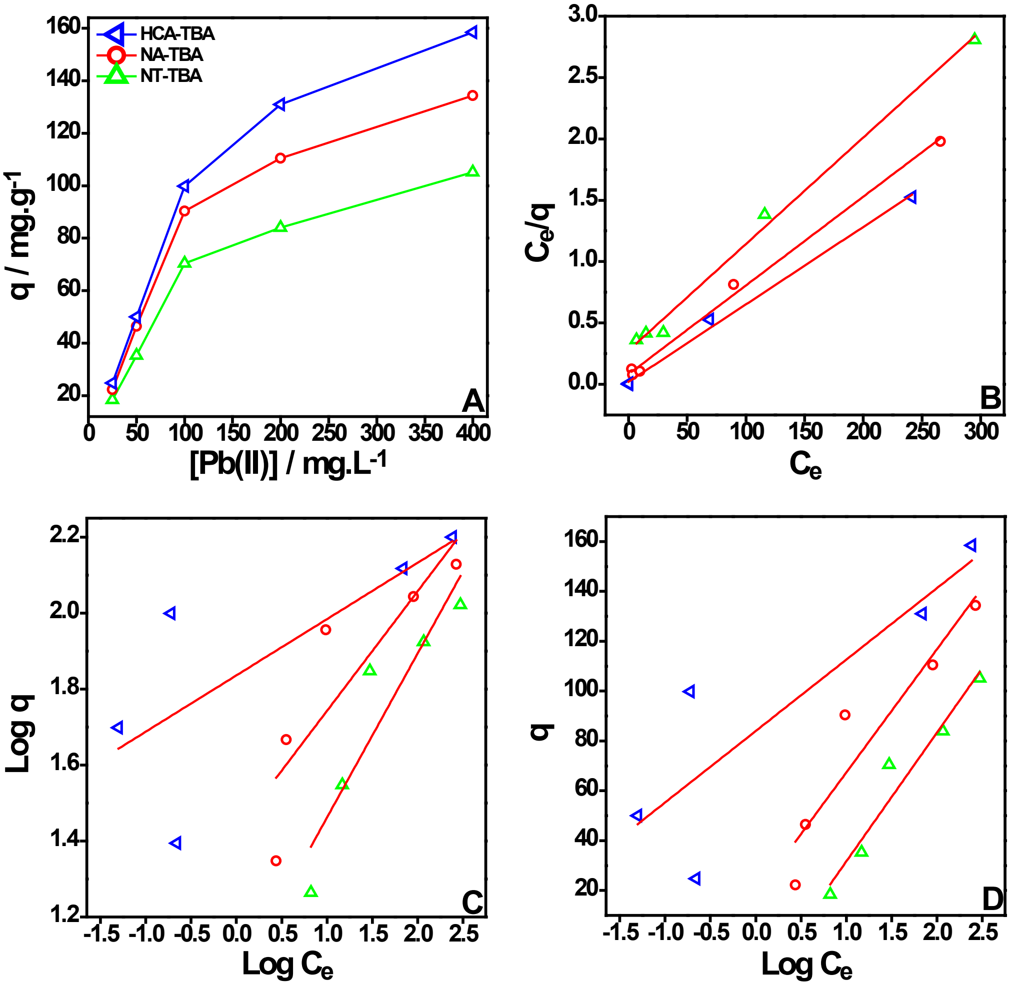

**Figure 3:** Effect of initial Pb(II) ions concentration on Pb(II) uptake by original and chemically pretreated TBP (A), Langmuir isotherm plot (B), Freundlich isotherms plot (C) and Temkin plot (D) for Pb(II) biosorption by original and chemically pretreated TBP.

$$\frac{C_e}{q} = \frac{1}{b_L q_m} + \frac{C_e}{q_m} \tag{3}$$

$$\text{Log } q = \text{Log } K_F + \text{ Log } C_e^{1/n} \tag{4}$$

$$q = B \ln A_T + B \ln C_e \tag{5}$$

where $C_e$ and q are the equilibrium concentration of Pb(II) in solution (mg $L^{-1}$) and on TBP (mg $g^{-1}$). $q_m$ (mg $g^{-1}$) and $b_L$ (L $g^{-1}$) are the Langmuir constants representing Pb(II) monolayer uptake capacity and Pb(II)-TBP equilibrium or apparent energy of adsorption. $K_F$ (mg $g^{-1}$) and 1/n are the Freundlich constants indicating uptake capacity and heterogamous factor. In Eq. 5, B is a constant equal to RT/b, whereas $A_T$ (L $g^{-1}$) and b (J $mol^{-1}$) are the Temkin constants relating to maximum binding energy and heat of adsorption. T is the absolute temperature in kelvin and R is gas constant having constant value of 8.314 J $mol^{-1}$ $K^{-1}$.

Langmuir, Freundlich and Temkin model constants and correlation coefficients ($R^2$) are calculated from the slopes and intercepts of plots $C_e$ vs Ce/q (Figure 3B), Log $C_e$ vs Log q (Figure 3C) and ln $C_e$ vs q (Figure 3D) respectively and presented in Table 1. Examination of isothermal data reveals that Langmuir model appropriately is fitted to the present Pb(II) adsorption process showing higher $R^2$ values of 0.9928, 0.9947 and 0.9951 for NT-TBP, NA-TBP and HCA-TBP respectively and high degree of linearity, confirming monolayer adsorption. The theoretical monolayer uptake capacities ($q_m$) of NT-TBP, NA-TBP and HCA-TBP for Pb(II) are 115.21, 138.31 and 158.48 mg $g^{-1}$ respectively and in close agreement with the experimental uptake capacities (q). Further investigation of isothermal data shows that Freundlich and Temkin models has lower $R^2$ values meaning these models are unsuitable for interpreting uptake of Pb(II) on NT-TBP, NA-TBP and HCA-TBP (Figure 3C and 3D).

**Table 1:** Adsorption isotherms parameters for adsorption of Pb(II) by original and chemically pretreated TBP.

| **Isotherms** | **Parameters** | **Adsorbents** | | |
|---|---|---|---|---|
| | | **NT-TBA** | **NA-TBA** | **HCA-TBA** |
| Langmuir | $R_L$ | 0.2900 | 0.3400 | 0.9500 |
| | $b_L$ (L/g) | 0.0315 | 0.0877 | 0.3166 |
| | $q_m$ (mg/g) | 115.21 | 138.31 | 158.48 |
| | $R^2$ | 0.9928 | 0.9947 | 0.9951 |
| Freundlich | $K_F$ (mg/g) | 10.718 | 26.795 | 68.558 |
| | n | 2.3140 | 3.1752 | 6.7422 |
| | $R^2$ | 0.8153 | 0.6629 | 0.4121 |
| Temkin | $A_T$ (L/mg) | 0.6788 | 1.4367 | 18.665 |
| | b (J/mol) | 48.726 | 50.946 | 87.819 |
| | $R^2$ | 0.9306 | 0.8588 | 0.6698 |
| Experimental adsorption capacity | q (mg/g) | 105.11 | 134.30 | 158.46 |

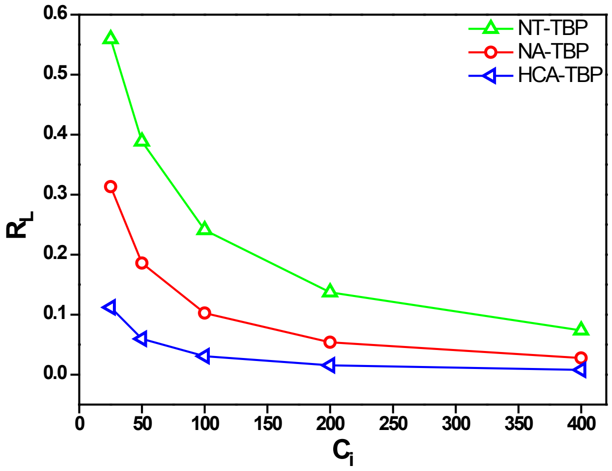

**Figure 4:** A plot between separation factor and initial Pb(II) concentration.

To authenticate whether the present Pb(II) uptake process is favorable or unfavorable, an equilibrium parameter or separation factor ($R_L$) is used which is stated in Eq. 6.

$$R_L = \frac{1}{C_i b_L + 1} \tag{6}$$

where $b_L$ and $C_i$ are the Langmuir constant and the initial metal concentration (mg $L^{-1}$). The $R_L$ values lying within the range of 0–1 indicate favorable adsorption. The $R_L$ values for all TBP adsorbents calculated from Eq. 6 are well within 0–1 range which recognize a favorable feature for adsorption of Pb(II) on NT-TBP, NA-TBP and HCA-TBP. Graphical diagram of separation factor for adsorption of Pb(II) on NT-TBP, NA-TBP and HCA-TBP is presented in Figure 4.

## 3.6 Effect of contact time on Pb(II) uptake

The interaction time of sorbent with adsorbate is meaningful and the adsorption kinetic is valuable for optimization process and beneficial for a successful economical practical application [44]. Figure 5A shows the contact time influence on sorption of Pb(II) ions onto native and pretreated TBP, which is investigated by contacting 0.4 g of TBP with 100 mg $L^{-1}$ of Pb(II) solution having pH 5, agitating at 175 rpm. The data in Figure 5A confirms that the Pb(II) ions uptake capacity is increased rapidly with the contact time up to 30 min, then the biosorption rate becomes slower with gradual increase in uptake capacity and no further considerable biosorption is noted beyond 100 min. This behavior indicates that biosorption of Pb(II) is occurred in two stages. In the 1st stage sorption occurs rapidly because of availability of large surface area of TBP for the accumulation of Pb(II) ions (shorter period). In the 2nd stage the sorption process steady slow down as surface

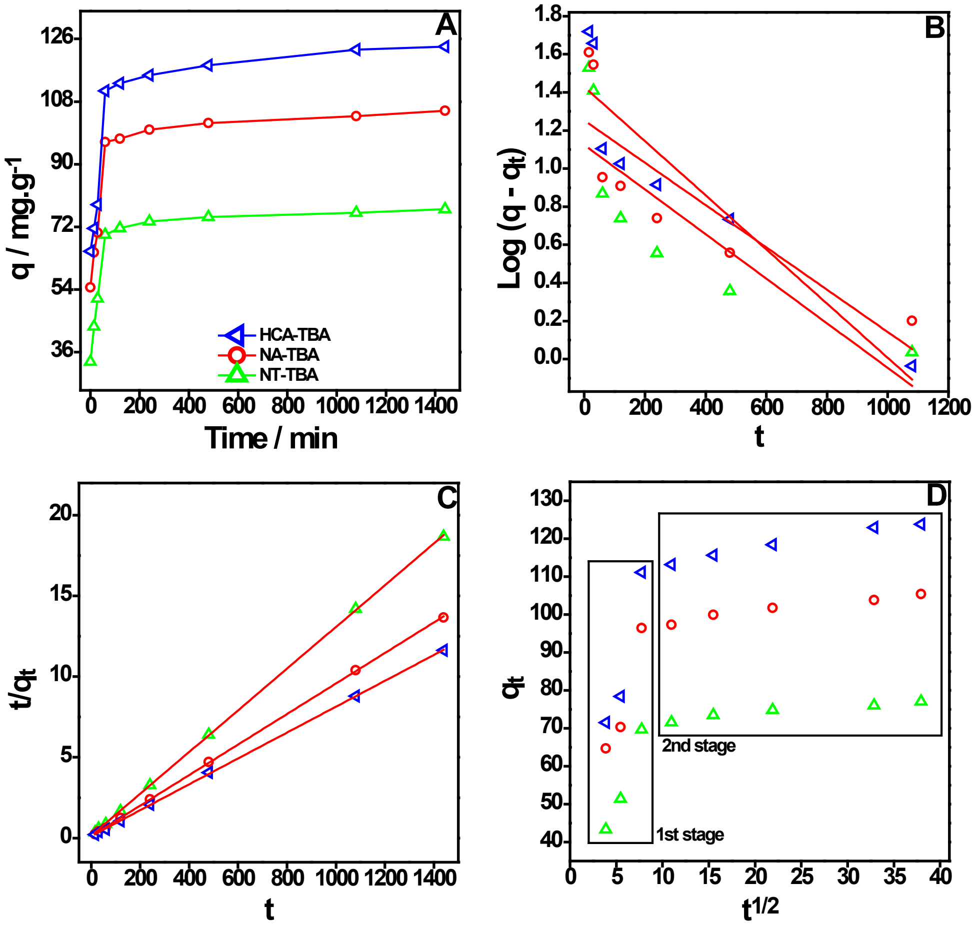

**Figure 5:** Effect contact time on Pb(II) uptake by original and chemically pretreated TBP (A), pseudo first order plot (B), pseudo second order plot (C) and intraparticle diffsuion plot (D) for Pb(II) biosorption by original and chemically pretreated TBP.

active sites of TBP gradually are occupied with Pb(II) ions (longer period) and continued until the equilibrium is established. The slower 2nd stage with low removal is because of metal ions penetration to the inner binding sites of the TBP by slower diffusion and with increasing time the intraparticle diffusion process dominating over adsorption. This trend is in agreement with other similar studies reported previously but shorter equilibrium time in our case compared to these studies [35,43].

## 3.7 Evaluation of kinetic modeling

In the present work the normal pseudo first and second order models, which define the efficiency characteristics, are used to describe adsorption kinetics. The pseudo first and second order equations are represented as [48, 49]:

$$\mathrm{Log}\,(q - q_t) = \mathrm{Log}\,q_e - k_1 t \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{8}$$

where q and $q_e$ are the experimental and theoretical equilibrium concentration (mg g$^{-1}$) of Pb(II) on TBP respectively. The $k_1$ and $k_2$ belongs to pseudo first and second order rate constant for sorption respectively.

The pseudo first and second order rate constant and correlation coefficients ($R^2$) are calculated from the slopes and intercepts of plots Log (q - $q_t$) vs t (Figure 5B) and t/$q_t$ vs t (Figure 5C) respectively. The kinetics of Pb adsorption is elucidated in Figure 5 (B, C) and the kinetic parameters originated from model interpretations are given in Table 2. The adsorption kinetics of Pb onto NT-TBP, NA-TBP and HCA-TBP shows superior fitting by the pseudo second-order model ($R^2$ = 99.9%) than the pseudo first-order model ($R^2$ = 63.5–82.0%). Further the values of q calculated based on pseudo second model are fitted well with corresponding $q_e$ experimental. The adsorption of Pb by

**Table 2:** Adsorption kinetics parameters for adsorption of Pb(II) by original and chemically pretreated TBP.

| **Models** | **Parameters** | **Adsorbents** | | |
|---|---|---|---|---|
| | | **NT-TBA** | **NA-TBA** | **HCA-TBA** |
| Experimental adsorption capacity | q (mg/g) | 77.090 | 105.40 | 123.82 |
| Pseudo first order | $k_1$ (1/min) | 0.0027 | 0.0026 | 0.0033 |
| | $q_e$ (mg/g) | 13.304 | 17.883 | 26.780 |
| | $R^2$ | 0.6354 | 0.6488 | 0.8200 |
| Pseudo second order | $k_2$ (g/mg.min) | 0.0011 | 0.0008 | 0.0005 |
| | $q_e$ (mg/g) | 77.399 | 105.71 | 124.69 |
| | $R^2$ | 0.9999 | 0.9999 | 0.9999 |
| Intraparticle diffusion | $k_i$ (mg/g min$^{1/2}$) | 0.7173 | 0.9094 | 1.1955 |
| | C | 54.955 | 76.951 | 86.504 |
| | $R^2$ | 0.4470 | 0.4669 | 0.4973 |

pretreated TBPs could be divided into two processes. The fast process during initial 30 min reveals rapid adsorption of Pb(II) by NT-TBP, NA-TBP and HCA-TBP and the slower process after 30 min where the amount of Pb adsorption is steadily increased during the next 1200 mins. It is also demonstrated in Table 2 that the adsorption of Pb by both HCA-TBP and NA-TBP is faster than NT-TBP. This behavior could be due to more organic components contained in HCA-TBP and NA-TBP, which may be possible to interact with Pb rapidly. Due to chemical pretreatments, more groups in HCA-TBP and NA-TBP are exposed to the Pb adsorption, triggering to faster the adsorption kinetics. Among the three TBPs, HCA-TBP is proved to be very efficient for the adsorption of Pb with 123.82 mg g$^{-1}$ that is much higher than 105.40 and 77.09 mg g$^{-1}$ for NA-TBP and NT-TBP respectively.

Weber-Morris intraparticle diffusion model is also verified for the assessment of adsorption mechanism that explains the diffusion mechanism and is represented by equation as [50]

$$q = k_i t^{1/2} + C \tag{9}$$

where $k_i$ and C represents intraparticle diffusion rate constant and a constant related to boundary layer thickness respectively. The values of these parameters are estimated from the slop and intercept of q vs $t^{1/2}$ (Figure 5D). The statistics achieved for all TBP adsorbents is given in Table 2. According to this model, straight line passing over the origin means adsorption by intraparticle diffusion only; otherwise, it is managed by a combination of other mechanisms alongside intraparticle diffusion. The curves in Figure 5D reveas that the plots of all TBP adsorbents show multi-linearity meaning Pb(II) adsorption onto TBP adsorbents occurs through a combination of bulk diffusion, film diffusion and intraparticle diffusion mechanisms. The constant C generally provides an indication about boundary layer thickness i.e. the higher C value related to larger the boundary effect. The results of this study are also consistent with the earlier reports for Pb(II) [35,43,44].

## 3.8 Thermodynamic modeling parameter

Thermodynamic consideration for adsorption process is needed to find out whether the process is spontaneous or non-spontaneous. ΔG° (change in Gibbs free energy, KJ mol$^{-1}$) elucidates the spontaneity of a system and Langmuir isotherm equation (Eq. 10) was adopted to estimate the thermodynamic parameters as follows:

$$\Delta G^\circ = -RT \, \mathrm{Ln}\, K_C \tag{10}$$

where $K_C$ , T and R stands for equilibrium constant ($q/C_e$), temperature (K) and gas constant (8.314 J mol$^{-1}$ K$^{-1}$). The

**Table 3:** Gibbs free energy values at different initial Pb(II) concentrations for original and chemically pretreated TBP adsorbents.

| | [Pb(II)] mg $L^{-1}$ | Adsorbents | | |
|---|---|---|---|---|
| | | **NT-TBA** | **NA-TBA** | **HCA-TBA** |
| Gibbs free energy ΔG° (KJ $mol^{-1}$) | 25 | -2.567 | -5.267 | -11.90 |
| | 50 | -2.209 | -6.470 | -17.40 |
| | 100 | -2.181 | -5.629 | -15.78 |
| | 200 | 0.815 | -0.526 | -1.615 |
| | 400 | 2.599 | 1.719 | 1.061 |

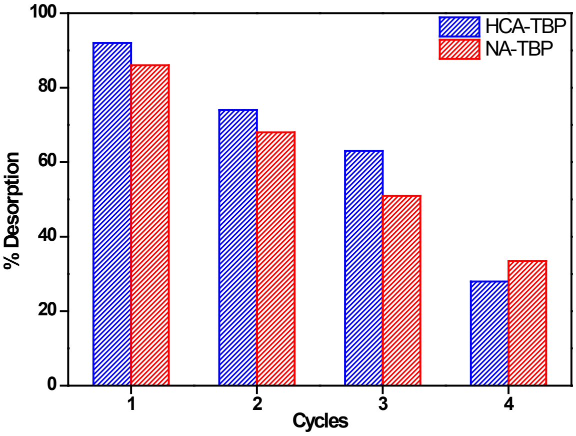

**Figure 6:** Desorption efficiency of HCA-TBP and NA-TBP in four cycles using 0.1 M EDTA.

negative values of ΔG° (Table 3) establish the feasibility and spontaneity of adsorption process for Pb(II) onto TBP biosorbents.

### 3.9 Adsorption/desorption cycles

Desorption analysis of metals are beneficial for the recovery of metal resources and recycling of adsorbents. Desorption is done to regenerate Pb(II) loaded TBP by eluting it with chelating agent (0.1 M EDTA). Figure 6 displays the results of the multiple adsorption/desorption cycles which reveal that 0.1 M EDTA is proved unsurpassed ability desorbing ~92 and 86% of adsorbed Pb(II) from the HCA-TBP and NA-TBP respectively in first cycle. Adsorption-desorption cycles are executed successfully for four times and Pb(II) adsorption capacity of HCA-TBP and NA-TBP is declined by 27.94 and 33.50% respectively after fourth cycle. Thus, it is feasible to recover Pb(II) and regenerate TBP, which would actually decrease the overall cost for the adsorbents. The reason for the small fraction of non recoverable Pb(II) by desorption may be due to Pb(II) binding with HCA-TBP and NA-TBP through strong interaction and that may be the reason of declined desorption efficiency during successive cycles. For the more accurate reason of decrease in desorption efficiency, additional study is needed to understand whether EDTA delivers an ability to change the structure of the adsorbent.

## 4 Conclusions

Water pollution due to rapid industrialization is one of the major problems of Pakistan and all over the world. To cop up this problem, current study is described the removal of Pb(II) by TBP. TBP is pretreated with $HClO_4$, $HNO_3$ and $H_2O_2$ and among all adsorbents, $HClO_4$ pretreated TBP shows the highest adsorption capacity towards Pb(II) which proves that pretreatment could play a vital role in enhancement of adsorption ability of adsorbents. All the TBP adsorbents show maximum sorption at pH 5.0. Kinetic is fast in first 15 to 30 min, having q (mg $g^{-1}$) 123.82, 105.40 and 77.09 for HCA-TBP, NA-TBP and NT-TBP respectively. These findings demonstrate that TBP is cost effective, efficient and novel adsorbent for removing Pb(II) from the aqueous solution.

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