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# Sorptive activity of potential native biosorbent for the elimination of lead and cadmium in one and two-component system: characterization, kinetic activity, and mechanism exploration

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## ABSTRACT

It is infrequent to have a single metal in the wastewater. For this reason, the elimination of $Pb^{2+}$ and $Cd^{2+}$ in one and two-component system was examined by xanthate-modified *Phaseolus vulgaris* in a batch mode. Through grafting, sulphur-bearing groupings with the help of magnesium xanthate were added onto *P. vulgaris* and xanthate-modified innovative *P. vulgaris* biosorbent has been produced for the removal of metal ions, that is, lead and cadmium. These innovative sulphur sites were attained successfully and confirmed with the help of Fourier-transform infrared spectroscopy, elemental analysis, and change in surface morphology by scanning electron microscopy. The point of zero charges $pH_{pzc}$ of xanthate-modified *P. vulgaris* was observed to be 7.20 which makes it appropriate for the sorption of cations. The batch sorption implementation of xanthate-modified *P. vulgaris* includes sorbent amount, pH, linear and non-linear regression analysis, and kinetic curves. The xanthate-modified *P. vulgaris* adsorbed 95.65% cadmium (at pH 4.0) and 90.36% of lead (at pH 5.0) from a single aqueous system. The sorption of $Pb^{2+}$ and $Cd^{2+}$ by xanthate-modified *P. vulgaris* follow the linear regression of Langmuir isotherm with $q_{max}$ of 160.97 and 150.50 mg/L, respectively which is substantially greater than that of many other reported ones. The xanthate-modified *P. vulgaris* demonstrated rapid uptake capacity of $Pb^{2+}$ and $Cd^{2+}$ following the high value of correlation coefficient with pseudo-second-order kinetics. This sorption process for $Pb^{2+}$ and $Cd^{2+}$ was found to be endothermic and spontaneous. The binding capacities however reduced in the binary system. This, therefore revealed that the xanthate-modified *P. vulgaris* can be an encouraging biosorbent for the remediation of $Pb^{2+}$ and $Cd^{2+}$ from contaminated water.

*Keywords:* Xanthate; Binary system; Non-linear; Equilibrium; Thermodynamics; Kinetics

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## 1. Introduction

In this age of industrialization, clean and uncontaminated water availability to humans is at a crucial stage. Uncontaminated and pure water has become a highly requested commodity in the 21st century. Our earth's surface contains 71% water but according to global standards, the suitable water for drinking is less than 1% [1]. The persistent expansion of the world population causes important shifts in the environment. Rapid social and economic

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developments around the globe have triggered destructive impacts like water pollution, which is a major threat to aquatic ecosystems, resources, and as well as to human health. This one is the ramifications of the addition of a wide range of contaminants into water resources. Effluents from different industries, agricultural activities, mining activities, and environmental changes are the main sources of these contaminants. These contaminants include heavy metals, dyes, organic compounds, fertilizers, sewage wastes, pesticides, and radioactive wastes [2]. Due to their non-biodegradability and environmentally persistent nature, heavy metals have become a global level concern. These heavy metals deposits in an aquatic environment and bioaccumulate in the food chain [3] till their concentration becomes toxic to humans and aquatic animals [4]. They amass to a maximum toxic concentration in different aquatic ecosystems, therefore, causing significant ecological destruction. Such an aquatic ecology disorder results in degraded water quality that in turn leads to a decline in biodiversity [5]. Among these heavy metals, toxic ones are arsenic, cadmium, lead, copper, nickel, mercury, and zinc [6].

In present days lead and cadmium are leading the row of heavy metals that are present in wastewater. Cadmium is viewed as perhaps of the most harmful heavy metal mainly generated by the discharge of effluents from industrial activities like petroleum refining, fossil fuels combustion, alloying industry, pigment industry, manufacturing of batteries, and especially from the electroplating industry where it is used to galvanize other metals [7]. When cadmium enters into the environment, it remains there for a long period because of its non-biodegradable nature and can supplement in major internal organs of living beings [8]. Acute cadmium poisoning occurs when people are exposed directly to it while chronic poisoning may be because of eating cadmium-contaminated Cadmium chronic exposure can produce substantial risk factor associated with Angio cardiopathy, nephropathy, bone lesions and central nervous system [9,10].

Similarly, lead-a heavy metal with lot of beneficial properties has been tapped for ages but now in the 21st century, Pb(II) is labelled as a major health problem causing substance. It is used in various industrial activities as in recycling of batteries, mining of lead and assembling of electronic devices [11], pigments, printing press, storage batteries, leaded gasoline, photographic materials, in explosives and in cosmetics [12,13]. It is discovered to be a neurolysin specifically in infants in addition to causes psychological impediments [14], hepatic and renal diseases [11,15]. Lead toxicity leads to health problems like learning difficulties, behavioral issues and convulsions [1,16]. Lead is considered as topmost toxic material to environment because of its non-decomposability [17]. According to WHO legitimate amount of lead in drinking water should only be 0.01 ppm [18].

Consequently, to safeguard people's wellbeing, remediation of heavy metals contaminated water is essential effectively before its discharge to prevent their biomagnification and bioaccumulation. For that reason, environmental regulation require techniques to remove contaminants from wastewater and recover heavy metals [19]. Various methods have been proposed, demonstrated and utilized for the heavy metals removal for instance membrane filtration [20], chemical precipitation [21], ion-exchange [22], electro-floatation [23], reverse osmosis [24], electrodialysis [25], and adsorption [26].

From all the above-mentioned treatment methods, adsorption leads the way for the removal of heavy metals. It has several advantages like, easy to operate, inexpensive compared to other techniques, no sludge formation and widespread applications [27]. At present, biosorption appeared as cost-effective and most efficient technique. Amongst adsorbents, agriculture waste based biosorbents have been gaining popularity because of the easy access to and remarkably inexpensive materials. Modern narrative displayed significance of minimal expense agro-based material for the fruitful removal of these heavy metals [28]. Many explored biomasses like hazelnut and almond shells [29], rice husk [30], wheat straw [31], sawdust [32], chitosan [33], mung bean husk [34], sugarcane bagasse [35], cocoa shell [36], sorghum (Jawar) [6], and *Gardenia jasminoides* biomass [37] have been discovered as compelling sorbents for heavy metal remediation. Past narratives uncover that at some point utilization of crude sorbent causes auxiliary contamination and thus showed low metal uptake. Even though these agro-residues might be possibly helpful for the removal of heavy metals, but their uptakes capacities should be upgraded [38]. Variety of methods like treatment with mineral or organic acids, redox agents, bases and chemicals like KOH, $H_2O_2$, NaCl, $ZnCl_2$, $Na_2CO_3$, epichlorohydrin, and glycerol and also hydrothermal methods have been reported in literature for the enhancement of biosorbent [39,40].

Current study was designed to explore the sorption capacity of xanthate treated *Phaseolus vulgaris* for the removal of heavy metals like lead and cadmium from wastewater in one and two-component system. It was used by enhancing its surface functionalizing to improve its adsorption performance. Among the various present functional groups like carboxyl and amino, we selected xanthate functionalization due to its excellent simple synthesis, its ability to form highly stable metal complexes formation [41] and also its effectiveness to prevent eutrophication during process [42].

## 2. Materials and methods

### 2.1. Preparation of xanthate-modified biomass P. vulgaris

*P. vulgaris* (Common or French beans) branches were obtained from the Botanical Garden of University of the Punjab (Lahore 31°29′56.9″N, 74°18′02.1″E). Branches were converted into small sections for easy grinding then dust particles were washed away with distill water and dried in open air for 48 h. The branches were oven dried at 90°C until all the moisture were removed to obtained constant mass. Then these minor pieces were converted into fine powder with the help of electrical grinder (Kenwood, Hampshire, UK). The grinded form of *P. vulgaris* was washed thoroughly with double distilled water up until all the color seeped out from it. In the end this washed sorbent was oven dried at 70°C till it became moisture less.

### 2.2. Modification of P. vulgaris

The washed and dried *P. vulgaris*-biomass obtained was modified with xanthate by following the method of Qu et al.

[43]. Firstly, *P. vulgaris*-biomass steeped in sulfuric acid (98%) at room temperature in the ratio of 1:3 (g/mL) and stir up constantly for the complete dehydration. The obtained charred material (RH-C) was then washed with water followed by filtration and oven drying at 70°C. Secondly, charred stuff was imperiled to alkalization dipping material into 4 M NaOH solution and stirring for 1.5 h at room temperature.

After alkalization, the substance was blended with carbon disulfide (1:1) and it was agitated for 1 h at room temperature for xanthation of material. At the end, in last 15 min 1% $MgSO_4$ solution (1:1) was added to the material for substitution reaction. After the completion, material was then washed with double distilled water till the pH of leeched water becomes 7.0. After washing it was dried at 70°C and labelled as xanthate-modified *P. vulgaris* for further use. As shown in Fig. 1, how xanthation of *P. vulgaris* is carried out by the functionalization of cellulose group with xanthate group.

### *2.3. Characterization of xanthate-modified P. vulgaris*

For the determination of neutral charge point, $pH_{pzc}$ were performed utilizing pH-meter (Model: inoLab WTW Series, Germany). The main functional groups responsible for the binding of metals were identified using Fourier-transform infrared spectrophotometer (Agilent Cary 630 Technologies, California) in a range of 4,000–600 $cm^{-1}$. Scanning electron microscopy (SEM) analysis was used for the analysis of surface morphology of *P. vulgaris* and xanthate-modified *P. vulgaris*. The elemental composition of xanthate-modified *P. vulgaris* was defined by using energy-dispersive X-ray spectrophotometer, which was attached to scanning electron microscopy (FEI Nova NanoSEM 450). The composition of each element was given in the form of percentage of solid weight. Additionally, Boehm's titration and percent weight gain (pwg) was determined for the acidic and basic group concentration and weight gain by biomass after xanthate modification.

### *2.4. Preparation of lead and cadmium solutions*

All the chemicals and regents used in this study was of analytical grade and all the solutions were prepared in double distilled water. Chemicals used, that is, cadmium nitrate, lead nitrate, sulfuric acid, sodium hydroxide, and sodium chloride were obtained from Merck (USA). A standard solution of lead ions (1,000 mg/L) and cadmium ions (1,000 mg/L) were prepared from lead nitrate and cadmium nitrate salts, respectively.

### *2.5. Batch adsorption experiments*

#### *2.5.1. One-component biosorption system*

Batch experiment in one-component system was carried out using 50 mg/L of lead and cadmium ions solution. The amount of xanthate-modified *P. vulgaris* was applied in the range of 0.1–0.9 g/50 mL and agitated in orbital shaker (VORTEX model: OSM-747) for both lead and cadmium, respectively. Another series of batch steps are carried out by using 0.1 g of xanthate-modified *P. vulgaris* with varying pH (1.0–10.0) at room temperature. Other influencing parameters on adsorption performance was also studied for both metals separately. After experimentation, mixture of metal solution and xanthate-modified *P. vulgaris* was separated and put to analysis under atomic absorption spectroscopy (Perkin Elmer AAnalyst 100, USA).

The adsorbed capacity ($q_c$) was computed by:

$$q_c = \frac{\left(C_i - C_e\right)V}{m} \tag{1}$$

And similarly, removal percentage (%) was attained as:

$$R\% = \frac{\left(C_i - C_e\right)}{C_i} \times 100 \tag{2}$$

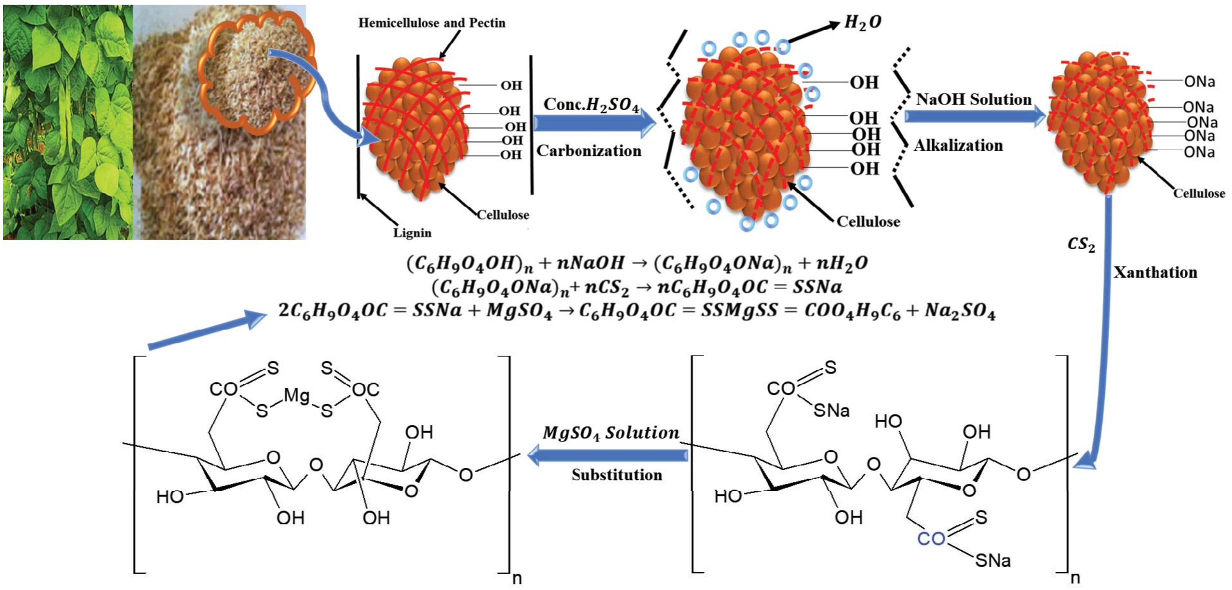


Fig. 1. Xanthation process of *Phaseolus vulgaris*.

where $C_i$ and $C_e$ are initial and equilibrium concentrations (mg/L). Volume used of these concentrations are represented as $V$ (L) and amount of biomass utilized in procedure as $m$ (g).

### 2.5.2. Two-component biosorption system

For two metal components, that is, $Pb^{2+}$ and $Cd^{2+}$ experiments were performed with the help of mixture of both metals. Both were taken as 50 mg/L and mixed with xanthate-modified *P. vulgaris* and by varying influencing factors. The future experiments and analyzing procedure were as same as of single component systems.

## 3. Results and discussion

### 3.1. Characterization of xanthate-modified P. vulgaris

All the dried samples of *P. vulgaris* and xanthate-modified *P. vulgaris* were dried for 1 h before subjecting to any characterization.

The percentage weight gain (pwg %) by xanthate-modified *P. vulgaris* after xanthate modification was evaluated as:

$$\text{pwg}\% = \frac{w_{\text{XPV}} - w_{\text{PV}}}{w_{\text{PV}}} \times 100 \tag{3}$$

where $w_{\text{XPV}}$ refers the mass of xanthate-modified *P. vulgaris* and, $w_{\text{PV}}$ refers to mass of raw *P. vulgaris*. The results are tabulated in Table 1.

Acidic and basic groups concentration was determined using Boehm's titration procedure. The xanthate-modified *P. vulgaris* were encountered with acid and bases (HCl, NaOH, $Na_2CO_3$, $NaHCO_3$). This basic interaction gives number of carboxylic; lactones and phenols as only carboxylic groups are neutralized by NaOH and $NaHCO_3$ counterbalance both lactones and carboxylic groups and their differences give number of phenols. Similarly, interaction with HCl gives number of basic groups. Results are arranged in Table 1 and comparison is displayed in Fig. 2.

For the identification of major functional groups on xanthate-modified *P. vulgaris*, Fourier-transform infrared spectroscopy (FTIR) was performed for both *P. vulgaris* and xanthate-modified *P. vulgaris*. These precise groups on the surface of biosorbent are responsible for the binding of metals and their removal [44]. In Fig. 3 FTIR showed that a peak of N–H and O–H was observed at 3,300 $cm^{-1}$ and many characteristics peaks were also observed in a range of 1,900–1,000 $cm^{-1}$. FTIR in Fig. 2 shows change in peaks in a range of 1,900–1,000 $cm^{-1}$ which confirmed the addition of modifier onto the surface of adsorbent.

The surfaces of unmodified and modified biomass were analyzed by SEM. The results showed in Fig. 4 that surface of unmodified biomass (Fig. 4a) was smooth as compared to the surface of modified biomass (Fig. 4b) and its surface was less exposed. On the other hand, the surface of modified biomass was very rough, and its surface was more exposed as compared to unmodified biomass. Modification of biomass made its surface rough which enhanced the removal of $Pb^{2+}$ and $Cd^{2+}$.

The elemental composition of xanthate-modified *P. vulgaris* was calculated in the form of weight percentage (wt.%) and displayed in Fig. 5. The sulfur content after the xanthation was 4.81% which indicates that xanthate group on *P. vulgaris* was incorporate successfully via method we have adopted for modification.

The point of zero charge on modified biomass was calculated by using $pH_{pzc}$ analysis. The biomass present in the solution at this point possessed zero charge [45]. The analysis showed that at pH 7.20 the net charge on biomass was "0". This showed that below this pH the charge on biomass was positive and above this pH the charge on

Table 1
Characterization of xanthate-modified *Phaseolus vulgaris*

| Characterization | Results |
|---|---|
| $pH_{pzc}$ | 7.20 |
| pwg (%) | |
| Acidic and basic groups (mmol/g) | Total acidic groups = 18.1 ± 0.02<br>Carboxylic groups = 8.9 ± 0.02<br>Lactones = 5.8 ± 0.02<br>Phenols = 3.4 ± 0.02<br>Total basic groups = 8.9 ± 0.02 |

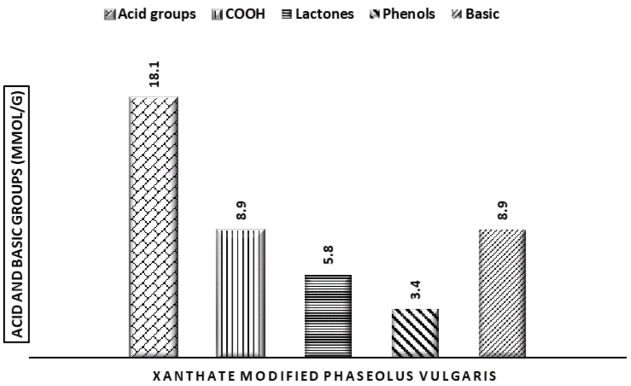


Fig. 2. Comparison of acidic and basic groups of xanthate-modified *Phaseolus vulgaris*.

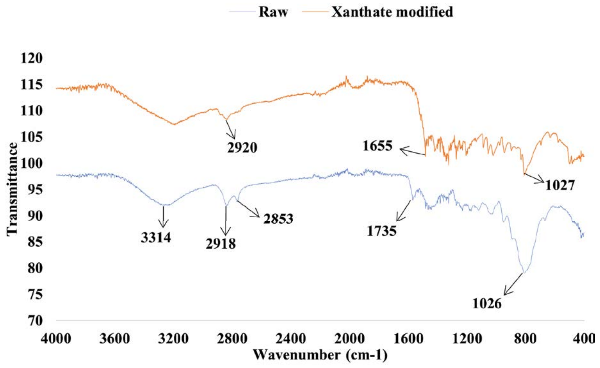


Fig. 3. Spectra of xanthate-modified *Phaseolus vulgaris* with comparison of raw *Phaseolus vulgaris*.

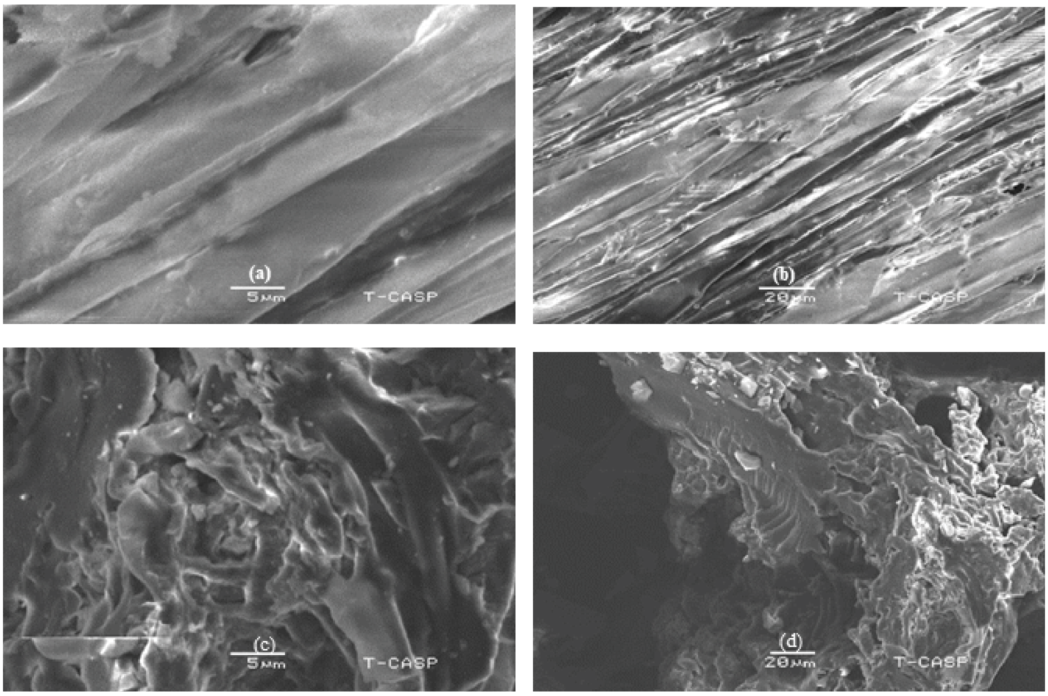
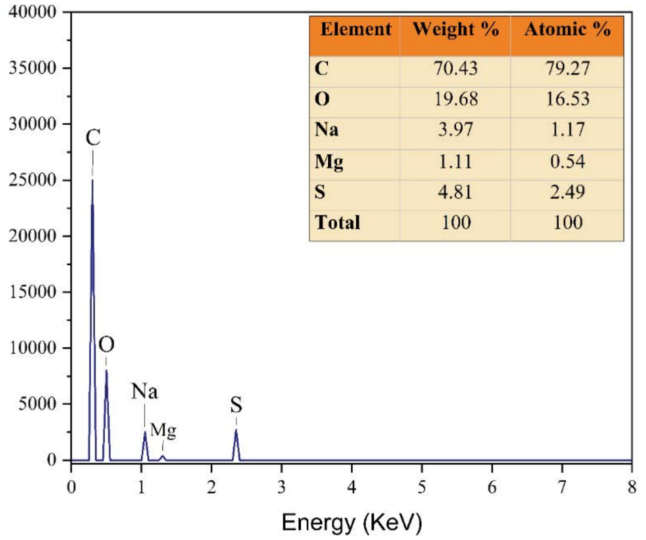


Fig. 4. Scanning electron microscopy image of raw *Phaseolus vulgaris* (a, b) and xanthate-modified *Phaseolus vulgaris* (c, d) at 5 and 20 µm.



| Element | Weight % | Atomic % |
|---|---|---|
| **C** | 70.43 | 79.27 |
| **O** | 19.68 | 16.53 |
| **Na** | 3.97 | 1.17 |
| **Mg** | 1.11 | 0.54 |
| **S** | 4.81 | 2.49 |
| **Total** | 100 | 100 |

Fig. 5. Energy-dispersive X-ray analysis of xanthate-modified *P. vulgaris* (wt.%).

biomass was negative. The graph between ΔpH and $pH_i$ (initial pH) gives the value of $pH_{pzc}$ (Fig. 6).

### 3.2. Impact and optimization of xanthate-modified P. vulgaris dosage

The impact of xanthate-modified *P. vulgaris* amount on the removal of lead and cadmium in one-component system was studied by varying the amount in range of 0.1–0.9 g. The initial concentration for both metals were taken as 50 mg/L. In one-component system, both lead and cadmium show that by increasing the amount of xanthate-modified *P. vulgaris*, removal percentage of $Pb^{2+}$ and $Cd^{2+}$ also increased (Fig. 7). As amount of xanthate-modified *P. vulgaris* increased, more binding sites will be available for attachment which in the end responsible for the high removal percentage [46]. The highest removal percentage recorded for lead was 90.25% at 0.9 g which increases from 78.01% at 0.1 g. Similarly in the case of cadmium removal percentage increases from 77.63% @ 0.1 g to 86.79% @ 0.9 g.

But by increasing the amount of adsorbent, adsorption capacity started to decrease. This trend was observed for both lead and cadmium because of the saturation and aggregation at binding sites.

Similarly, for two-components system, same trend was observed as of one-component for both lead and cadmium (Fig. 7). As there are two competing ions, interference by each other decreases the adsorption capacities and removal percentage for both lead and cadmium. The removal % of lead in two-component was observed as 85.76% @ 0.9 g which is low as compared to single system. Similarly for cadmium it was observed 81.03% @ 0.9 g. The competition between two ions causes the decrease in the trend as compared to single component system.

### 3.3. Impact and optimization of pH of metal solution

The sorption capacity of xanthate-modified *P. vulgaris* was explore by varying pH (1.0–10.0) for one-component system. Fig. 8 reveals that removal of lead and cadmium ions are highly dependent on the pH of solution. The sorption

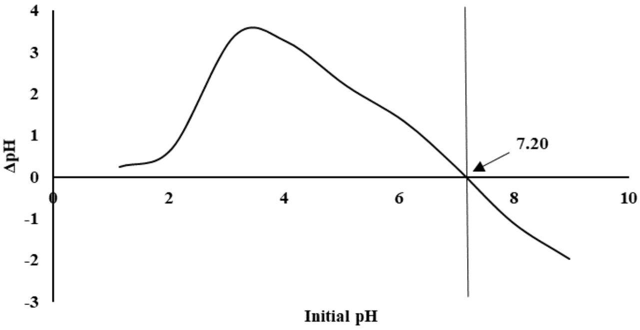


Fig. 6. Point of zero charge ($pH_{pzc}$) of xanthate-modified *Phaseolus vulgaris*.

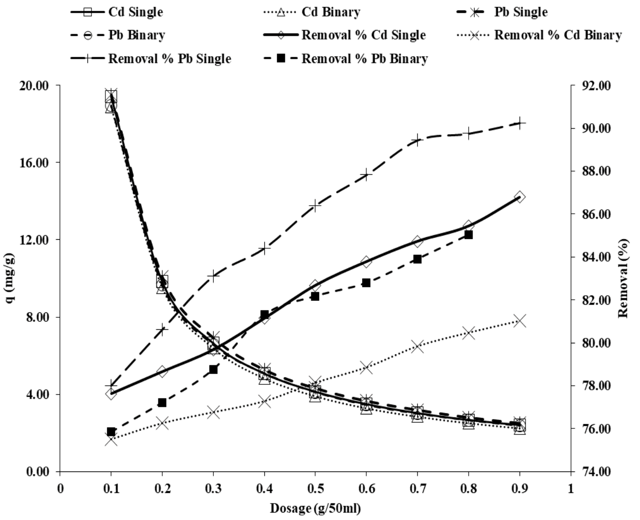


Fig. 7. Influence of the xanthate-modified *P. vulgaris* dosage upon the biosorption of Pb(II) and Cd(II) in the single and binary systems. Initial concentration of $Pb^{2+}$ and $Cd^{2+}$ 50 mg/L, adsorbent dosage 0.1–0.9 g, time 25 min.

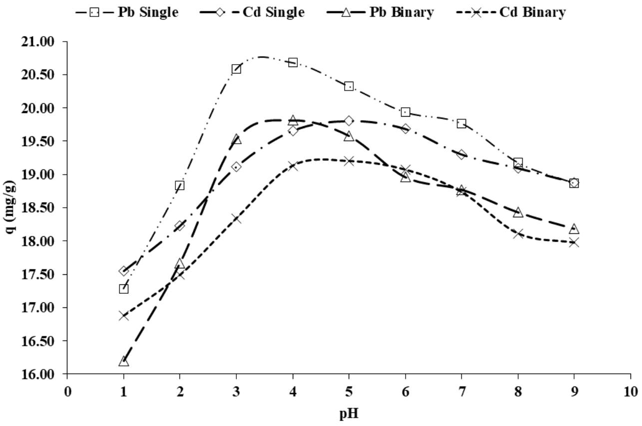


Fig. 8. Influence of the solution pH upon the biosorption of Pb(II) and Cd(II) in the single and binary systems. Initial concentration of $Pb^{2+}$ and $Cd^{2+}$ 50 mg/L, adsorbent dosage 0.1 g, time 25 min.

capacity for lead was maximum at pH 4.0 where it shows 82.73% removal in one-component system. The upper limit removal (98.21%) of cadmium was observed at pH 5.0. Hence, pH 4.0 and pH 5.0 were optimized for the removal of lead and cadmium in one-component system. As we can observe from Fig. 8, in high acidic conditions, metal solution is concentrated with protons which competes with lead and cadmium ions for binding sites which in the result make the surface protonated which repel the metal ions. Due to this reason, low adsorption was observed in extreme acidic conditions [47]. When pH start moving towards the basic conditions, deprotonation increase which increase the sorption of lead and cadmium consequently. However, in extreme basic conditions when pH becomes greater than 7.0, lead and cadmium starting to precipitate as hydroxides resulting in the low sorption capacity of both lead and cadmium in one-component system. In summary, the consequent measures of one and two-component systems give pH values of 4.0 and 5.0 for removal of lead and cadmium, respectively.

### *3.4. Impact and optimization of contact time*

The sorption of lead and cadmium ions by xanthate-modified *P. vulgaris* as a function of time was displayed in Fig. 9 for both one and two-component system. The rate of sorption increases steadily due to metals and adsorbent interaction. After a prolonged exposure, rate of biosorption becomes insignificant due to reducing numbers of binding sites.

The rate of biosorption for $Pb^{2+}$ and $Cd^{2+}$ was higher in beginning because of excess number of binding sites present on xanthate-modified *P. vulgaris* but with time active sites started to fill and unoccupied ones did not interact strongly Cd(II) and Pb(II). The interaction between metals (cadmium and lead) and active sites decreased because of repulsive forces present between the ions attached to the binding sites and ions present in the solution. As shown in Fig. 9, there is significant difference in biosorption capacity of lead at 5, 10, 15 and 20 min but after 20 min no noticeable change was seen. For cadmium at 5, 10, 15 and

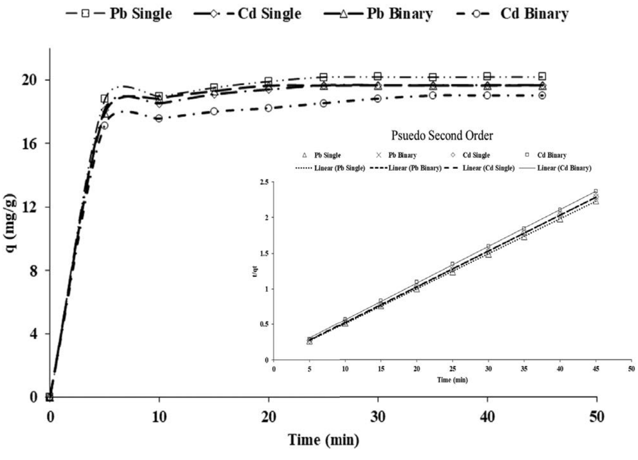


Fig. 9. Influence of the contact time upon the biosorption of Pb(II) and Cd(II) in the single and binary systems. Initial concentration of $Pb^{2+}$ and $Cd^{2+}$ 50 mg/L, time 5–45 min.

20 min, sorption capacity increases significantly but after 15 min it becomes constant.

The biosorption of $Pb^{2+}$ and $Cd^{2+}$ was very favourable in first 20 min. The biosorption of $Pb^{2+}$ and $Cd^{2+}$with xanthate-modified *P. vulgaris* was in range from 18.12–19.66 and 18.77–20.17 mg/g, respectively. This phenomenon may occur due to desorption and resorption of cadmium and lead ions. This observation was also supported by Aiyesanmi et al. [48] and Ghasemi and Mafi Gholami [49].

For binary system, the results are same as of single system but with lower biosorption abilities. The metal ions compete to pass through active sites for binding thus results in decreasing the force between solid–liquid phases in sorption system. This competition decreases the biosorption capacities for both $Pb^{2+}$ and $Cd^{2+}$.

### 3.5. Kinetic analysis of one and two-component system

Kinetic analysis was obtained from the time factor which helps us in the determination of adsorption rate. Kinetics analysis was observed by using two famous models, that is, pseudo-first-order and pseudo-second-order. Their appropriateness was determined through co-relation value ($R^2$) and by the assessment of experimental ($q_e$) and calculated ($q_c$) adsorption capacities.

The linear form of first [50]and second-order [51], respectively can be expressed as follows:

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{5}$$

where $q_e$ is adsorption capacity at equilibrium (mg/g), $q_t$ is adsorption capacity calculate from the data (mg/g) at time '$t$'. The rate constants of both pseudo-first-order and pseudo-second-order are represented by $k_1$ (min$^{-1}$) and $k_2$ (mg/g·min), respectively.

According to pseudo-first-order adsorption rate is proportional to the present number of binding sites. The linear graph between time ($x$-axis) and $\log(q_e - q_t)$ gives us the parameter of pseudo-first-order (Table 2) which helps to study the rate of reaction (Fig. 9). In case of lead, $R^2 = 0.8009$ and $q_e$ comes equal to '8.14 mg/g' which is lower than as compared to the experimental 'q' value ($q_t$ = 20.17 mg/g). Similarly, this situation was also in the lead two-component system, where $R^2 = 0.9991$ but $q_e$ is '4.044 mg/g' but $q_t$ is '19.64 mg/g'. In case of cadmium $R^2$ value for Cd in one-component system found to be 0.9678 and $q_e$ value found to be '3.22 mg/g' which were far away from experimental $q_t$ value (19.64 mg/g). Similarly, $R^2$ value for Cd binary system found to be 0.9378 and its calculated $q_e$ value '3.39 mg/g' were far away from experimental one '18.99 mg/g'. This calculated data showed that this model not fitted to experimental data.

The assumptions of pseudo-second-order reveals that adsorption rate is proportional to the square of available adsorption sites and concentration of metal ions. The linear regression between time ($x$-axis) and $t/q_t$ ($y$-axis) reveal the kinetic modelling (Fig. 9) giving us kinetics parameters (Table 2). In case of kinetics parameters of pseudo-second-order for lead, $R^2$ value for one and two-components found to be "0.9999". For both systems, the value of calculated $q_e$ (20.49 and 19.92 mg/g) was remarkably close to experimental $q_e$ (20.17 and 19.64 mg/g). In case of cadmium $R^2$ value for one and two-component system found to be "0.9999" and "0.9998", respectively. For one and two-component system of cadmium, the value of calculated $q_e$ (19.96 mg/g (one) and 19.46 mg/g (two)) found remarkably close to experimental $q_e$ (19.66 mg/g (one) and 18.99 mg/g (two)). The outcomes showed that kinetics data for xanthate-modified *P. vulgaris* adsorption fitted well in pseudo-second-order reaction kinetics for both lead and cadmium for both one and two-component system.

In addition, with kinetics parameters for both metals, adsorption capacities difference ($D$%) also tells us about the kinetics of adsorption. It is analyzed as:

$$D\% = \frac{q_{e(\text{cal})} - q_{e(\text{exp})}}{q_{e(\text{exp})}} \times 100 \tag{6}$$

As observed from data from Table 2 and Fig. 9, the $D$% is greater for the pseudo-first-order as compared to the pseudo-second-order and supported by lesser value of $R^2$ for pseudo-first-order and near to unity for pseudo-second-order for one and two-components for both lead and cadmium. This also made the strong point of kinetics data following the pseudo-second-order.

### 3.6. Equilibrium modelling

Equilibrium modellings are set of mathematical equations which describes the relation between sorbent and sorbate which helps us to find out about the amount of sorbent for a specific sorbate [52].

The equilibrium set of data comes from varying the amount of initial concentration (20–180 mg/L) of $Pb^{2+}$ ions

Table 2
Adsorption kinetics parameters for adsorption of Pb(II) and Cd(II) onto xanthate-modified *P. vulgaris*

| Metals | Pseudo-first-order | | | | | Pseudo-second-order | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $R^2$ | $k_1$ (min$^{-1}$) | $q_{e(\text{cal})}$ (mg/g) | $q_{e(\text{exp})}$ (mg/g) | $D$% | $R^2$ | $k_2$ | $q_{e(\text{cal})}$ (mg/g) | $q_{e(\text{exp})}$ (mg/g) | $D$% |
| $Pb_{\text{Single}}$ | 0.8009 | 0.21 | 8.14 | 20.17 | –59.64 | 0.9999 | 0.08 | 20.49 | 20.17 | 1.60 |
| $Cd_{\text{Single}}$ | 0.9678 | 0.12 | 3.22 | 19.66 | –83.61 | 0.9999 | 0.08 | 19.96 | 19.66 | 1.53 |
| $Pb_{\text{Binary}}$ | 0.9991 | 0.16 | 4.04 | 19.64 | –79.42 | 0.9999 | 0.11 | 19.92 | 19.64 | 1.43 |
| $Cd_{\text{Binary}}$ | 0.9378 | 0.09 | 3.39 | 18.99 | –82.14 | 0.9998 | 0.05 | 19.46 | 18.99 | 2.45 |

(one and two-component system) and $Cd^{2+}$ ions (one and two-component system). This data set is then assessed by using famous linear and non-linear mathematical models which include single parameter, that is, Langmuir and Freundlich.

Langmuir modeling [52,53] was utilized for the calculation of maximum adsorption capacity of xanthate-modified *P. vulgaris* ($q_{\max}$). This model assumes that lead and cadmium will form monolayer on the surface of xanthate-modified *P. vulgaris*. According to Langmuir when metal occupies the binding sites, there will be no further attachments on the surface and intermolecular forces between sites and metal ions starting to decrease with distance increase. Each binding site is independent, and any outside molecule will not interfere in the process occurring at a site.

Langmuir modelling was explained from linear graph (Fig. 10) plotted between $1/C_e$ ($x$-axis) and $1/q_e$ ($y$-axis). Langmuir parameters (Table 3) helps us for the calculation of maximum adsorption for both one and two-component system.

The $Y = mX + c$ form of this model is represented as:

$$\frac{1}{q_e} = \frac{1}{bq_{\max}}\frac{1}{C_e} + \frac{1}{q_{\max}} \tag{7}$$

Whereas non-linear form is expressed as:

$$q_e = \frac{bq_m C_e}{1 + bC_e} \tag{8}$$

where maximum adsorption uptake is represented as $q_{\max}$ (mg/g), '$b$' is Langmuir constant, equilibrium capacity is referred as $q_e$ (mg/g) and metal ion concentration is referred as $C_e$ (mg/g). The Langmuir parameters '$q_{\max}$' and '$b$' is calculated from the linear plot of Langmuir isotherm (Fig. 10).

A dimensionless constant factor $R_L$ gives the description of favorable and unfavorable adsorption process, that is, favorable $0 < R_L < 1$, unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$) [54]. It is calculated by given equation:

$$R_L = \frac{1}{1 + bC_o} \tag{9}$$

The other model discussed was Freundlich isotherm which helps to calculate the intensity of adsorption on the surface of adsorbent. it tells us about the multilayer metal ion adsorption fashion of the surface of sorbate in heterogenous manner [55].

The $Y = mX + c$ form of Freundlich model is given as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \tag{10}$$

Whereas non-linear type is written as:

$$q_e = K_f C_e^{1/n} \tag{11}$$

where adsorption capacity (mg/g) is given by Freundlich constant ($K_f$), $1/n$ is the adsorption intensity, uptake capacity

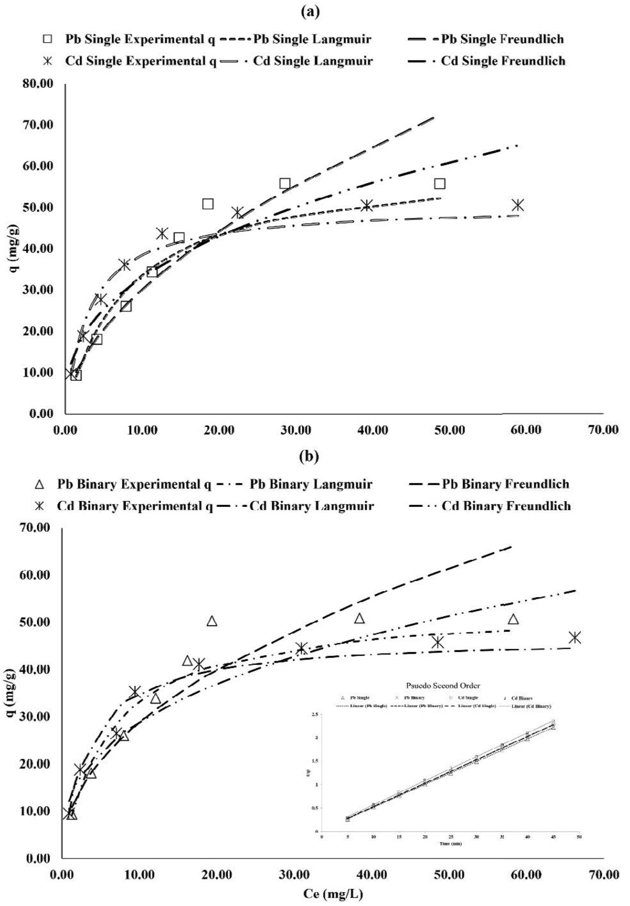


Fig. 10. Non-linear isotherms plot for the biosorption of Pb(II) and Cd(II) in the single and binary systems onto xanthate-modified *P. vulgaris* (a) for single and (b) for binary system depicting the Langmuir and Freundlich models.

Table 3
Adsorption isotherm parameters for adsorption of Pb(II) and Cd(II) onto xanthate-modified *P. vulgaris*

| Metals | Langmuir | | | | | Freundlich | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $R^2$ | $q_{\max}$ (mg/L) | $b$ | $R_L$ | RMSE | $R^2$ | $n$ | $1/n$ | $K_f$ | RMSE |
| $Pb_{Single}$ | 0.9831 | 60.98 | 0.12 | 0.29–0.05 | 1.70 | 0.9528 | 1.80 | 0.55 | 8.38 | 2.46 |
| $Cd_{Single}$ | 0.9887 | 50.51 | 0.31 | 0.14–0.02 | 1.01 | 0.9093 | 2.62 | 0.38 | 13.68 | 2.39 |
| $Pb_{Binary}$ | 0.9841 | 53.48 | 0.16 | 0.24–0.04 | 1.57 | 0.9278 | 2.12 | 0.47 | 9.70 | 2.54 |
| $Cd_{Binary}$ | 0.9929 | 46.95 | 0.29 | 0.15–0.02 | 0.82 | 0.9148 | 2.79 | 0.36 | 12.62 | 1.85 |

of sorbent is given by '$q_e$ (mg/g)', and '$C_e$' is metal ion concentration (mg/L). the major Freundlich constant '1/$n$' helps us to find the intensity of adsorption, that is, $1/n < 1$ = favorable adsorption system; $1/n > 1$ = unfavorable adsorption system. As bond between sorbent ad sorbate becomes stronger value of '$n$' increases. Additionally, '1/$n$' is heterogeneity factor whereas '$n$' displays the divergence from linearity. If $n > 1$ = physisorption; $n < 1$ = chemisorption and $n = 1$ indicates the linear adsorption [56].

In one and two-component system of lead $R^2$ was 0.9831 and 0.9841 correspondingly for Langmuir isotherm linear regression which is near to unity as compared to the Freundlich isotherm where it was 0.9528 and 0.9278, respectively. This correlation coefficient shows that sorption of lead by xanthate-modified *P. vulgaris* was purely monolayer absorption following the Langmuir isotherm. In case of cadmium same trend was observed for both one and two-component system depicting the data fit in Langmuir isotherm.

As equilibrium data does not fit well in Freundlich but as values tabulated in Table 3 the Freundlich constant '$n$' has higher values than unity in all the observed cases indicating the deviation from linearity and depicting the good adsorption characteristics of xanthate-modified *P. vulgaris*. The '$n$' value for $Pb^{2+}$ in one and two-component system was found to be 1.802 and 2.117, respectively. These n values in the range of 1–2 showed good evidence for adsorption. The '$n$' value for $Cd^{2+}$ in one and two-component system was found to be 2.615 and 2.789, respectively. These '$n$' values in the range of 1–2 showed good evidence for adsorption.

### 3.7. Root mean square error

Both the discussed models were compared by the values of root mean square error value (RMSE) which can be calculated as:

$$\text{RMSE} = \sqrt{\frac{\sum\left(q_{e(\text{cal})} - q_{e(\text{exp})}\right)^2}{N}} \tag{12}$$

This calculated value gives the error from linearity. As tabulated in Table 3, RMSE value for Langmuir model is less than that of Freundlich one which depicts that equilibrium data fitted well in Langmuir isotherm.

### 3.8. Thermodynamics study

Thermodynamics study helps to find the prospect of given adsorption system by xanthate-modified *P. vulgaris* and its potential to remove lead and cadmium from wastewater. Results tabulated in Table 4 and displayed in Fig. 11 show that adsorption capacity increases with the increase of temperature indicating the endothermic adsorption process.

In case of both lead and cadmium, for both one and two-component system increasing trend was observed but uptake capacity decreases in two-component system as compared to single system because of the competing ions of cadmium in case of lead and lead in case of cadmium.

Changes in temperature of the solution brought the considerable changes in the adsorption process. These changes affected the temperature dependent factors (enthalpy change ($\Delta H°$), free energy change ($\Delta G°$) and entropy changes ($\Delta S°$)) which were calculated by using Eq. (13).

$$\Delta G° = \Delta H° - T\Delta S° \tag{13}$$

Adsorption thermodynamics for lead one and two-component system was studied. Thermodynamic parameters were calculated as shown in Table 4. Negative value of $\Delta G°$ at all temperatures for both Pb one and two-component system indicated that reaction was spontaneous. The value of $\Delta H°$ was found positive in all cases which indicated that reaction was endothermic. The positive value of $\Delta S°$ indicated increased randomness on the surface of adsorbent.

Adsorption thermodynamics for cadmium one and two-component system was studied. Thermodynamic parameters were calculated as shown in Table 4. Negative

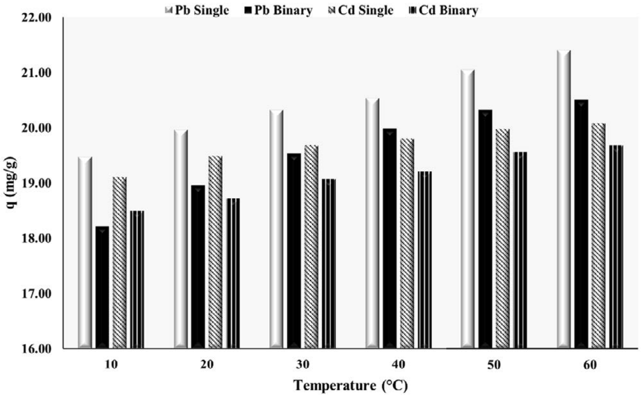


Fig. 11. Influence of the solution pH upon the biosorption of Pb(II) and Cd(II) in the single and binary systems. Initial concentration of $Pb^{2+}$ and $Cd^{2+}$ 50 mg/L, adsorbent dosage 0.1 g, time 5–45 min.

Table 4
Thermodynamics parameters for adsorption of Pb(II) and Cd(II) onto xanthate-modified *P. vulgaris*

| Temperature (K) | $\Delta G°$ (kj/mol) | | | | | | $\Delta H°$ | $\Delta S°$ |
|---|---|---|---|---|---|---|---|---|
| | 283.16 | 293.16 | 303.16 | 313.16 | 323.16 | 333.16 | | |
| $Pb_{\text{Single}}$ | –2.964 | –3.359 | –3.704 | –3.978 | –4.500 | –4.948 | 8.08 | 0.04 |
| $Cd_{\text{Single}}$ | –2.772 | –3.077 | –3.299 | –3.482 | –3.711 | –3.901 | 3.43 | 0.02 |
| $Pb_{\text{Binary}}$ | –2.324 | –2.787 | –3.210 | –3.599 | –3.949 | –4.209 | 8.36 | 0.04 |
| $Cd_{\text{Binary}}$ | –2.462 | –2.661 | –2.945 | –3.123 | –3.442 | –3.626 | 4.29 | 0.02 |

Table 5
Comparison of biosorption capacities with different utilized biosorbents

| Metals | Biosorbent | $q_{max}$ (mg/L) | References |
|---|---|---|---|
| Pb(II) | Xanthate-modified *Phaseolus vulgaris* | 60.98 | This study |
| | *Saccharum bengalense* | 4.43 | [57] |
| | *Sorghum bicolor* L. | 6.29 | [6] |
| | *Oryza sativa* seeds | 8.08 | [58] |
| | *Trifolium resupinatum* | 10.38 | [53] |
| | Pinecone powder | 16.34 | [59] |
| | Pigeon pea hulls powder | 23.64 | [60] |
| | Bamboo stem | 27.95 | [61] |
| | *Calophyllum inophyllum* seed husk | 34.51 | [62] |
| Cd(II) | Xanthate-modified *Phaseolus vulgaris* (This study) | 50.51 | This study |
| | *Arachis hypogaea* shells | 2.81 | [9] |
| | Castor seed hull | 6.98 | [63] |
| | *Sorghum bicolor* L. | 7.87 | [6] |
| | Bamboo stem | 12.34 | [61] |
| | *Triticum aestivum* (straw) | 14.56 | [64] |
| | Cashew nutshell | 22.11 | [65] |
| | Shea fruit shell | 25.44 | [66] |
| | Sawdust | 26.73 | [67] |

value of $\Delta G°$ at all temperatures for Cd one and two-component system indicated that reaction was spontaneous. The value of $\Delta H°$ was found positive in all cases which indicated that reaction was endothermic. The positive value of $\Delta S°$ indicated increased randomness on the surface of adsorbent.

### *3.9. Comparison of lead and cadmium adsorption onto xanthate-modified P. vulgaris with reported literature*

The biosorption capacities of the xanthate-modified *P. vulgaris* for lead and cadmium in one and two-component system compared in Table 5 with reported capacities of different biosorbents. The biosorption capacities for fourteen biosorbents for cadmium varied from 2.81 to 47 mg/g. From the reported material xanthate-modified *P. vulgaris* hold higher biosorption capacity of 50.51 mg/g for Cd(II). Similarly, the fourteen reported capacities for lead varied from 2.18 to 34.51 mg/g and xanthate-modified *P. vulgaris* out of all hold biosorption capacity of 60.98 mg/g for lead. These comparisons show that, out of all reported biosorbents xanthate-modified *P. vulgaris* hold higher capacity for the removal of Cd(II) and Pb(II).

## 4. Conclusion

The results of this biosorption study demonstrated that the xanthate-modified *P. vulgaris* was suitable and promising adsorbent for the removal of Cd(II) and Pb(II) from industrial effluents. In both single and binary systems, influence and optimization of different parameters like, xanthate-modified *P. vulgaris* dose, pH of solution, temperature and initial metal concentrations were studied. In binary system of Cd(II)–Pb(II) competitive adsorption was observed onto xanthate-modified *P. vulgaris*. The existence of Cd(II) helps increase the sorption of Pb(II) whereas, the presence of Pb(II) limits the sorption of Cd(II). From equilibrium isotherm data of Cd(II) and Pb(II) in single and binary system was well agreed to Langmuir isotherm indicating the monolayer adsorption. The kinetic data of adsorption onto xanthate-modified *P. vulgaris* fitted well in pseudo-second-order for both single and binary system. The thermodynamics study revealed that the adsorption process by xanthate-modified *P. vulgaris* for the removal of Cd(II) and Pb(II) was spontaneous and endothermic. These adsorption results shows that xanthate-modified *P. vulgaris* could be used as a promising adsorbent for the removal of cadmium and lead from the industrial waste.

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