

Use of wheat straw for effective binding of metal ions via a novel modification

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Abstract—An innovative biacetyl-modified *Triticum aestivum* (BMTA) was prepared and its biosorption efficiency was investigated for the removal of Pb(II) and Cr(III) ions from synthesized single and binary metal solutions. The characterization using infrared spectrum, surface area determination and potentiometric titrations indicated an increased acid content of the biomass, indicating BMTA as a potential choice for the binding of metal ions at a relatively low pH. The isoelectric point was found to be at pH 4.5. Various biosorption parameters were optimized. Langmuir model best fitted the experimental equilibrium data with q_{max} 27.39 mg/g for Pb(II) ions and 24.69 mg/g for Cr(III) ions in single metal system and 24.21 mg/g for Pb(II) and 12.97 mg/g for Cr(III) ions in binary system, respectively. The kinetics was described by pseudo-second-order model both in single and binary metal system. The studies indicated relatively selective biosorption of Pb(II) ions by BMTA compared to other metal ions.

Keywords: Biacetyl, Wheat Straw, Lead, Chromium, Selective Biosorption

INTRODUCTION

Biosorption involves the sequestering of soluble metal species as a result of the attachment of metals by non-living biomass cells [1]. Biosorbents are the biological materials containing a number of polar functional groups such as -OH, -CHO, -COOH, -NH₂ and -SH having high affinity for heavy metal ions [2]. During the process of biosorption, metal immobilization by different parts of the cell can occur via various non-metabolic processes including complexation, ion exchange, adsorption, diffusion and precipitation. The type of mechanism followed differs depending on the species used, the origin and processing of the biomass and the solution chemistry [3].

The biosorbent materials are accessible in huge amounts mainly at proximities of the contaminated effluents, such as food industries wastes (fermentation waste [4]), microorganisms (bacteria [5], algae [6], yeast [7] and molds [8]) and agricultural residues [9]. Because of their low price and the high availability, various agricultural waste materials such as wheat stem [10], rice husk [11], grape stalk waste [12], loquat bark [13] and mango tree sawdust [11] and natural materials like chitosan [14] have been investigated, either in their natural form or after some physical or chemical modification, for the removal of toxic metal ions from aqueous media.

A number of physical and chemical methods have been employed to increase the biosorption capacity, to have information about the metal binding sites, and to incorporate known functional groups into the biomass [15,16]. Thus, modification results in the increase of sorption capacity of adsorbents by providing greater exposed

metal-binding sites as compared to unmodified adsorbents [17]. The chemically modified adsorbent offers increase in the available surface area. The surface chemistry is changed after chemical treatment due to the incorporation of new functional groups. These modified functional groups act as complexing or chelating agents for metal ions [18].

Contamination of aquatic systems owing to the presence of hazardous metal ions has become a dilemma of global concern. Heavy metals can pose health hazards to human and aquatic lives if their concentrations exceed certain safe limits [19]. Lead(II) and chromium(III) ions are toxic and carcinogenic and also cause damaging effects on respiratory and nervous system as well as on gastrointestinal tract. The safe limits of Pb(II) and Cr(III) ions are 0.5 mg/L and 1.0 mg/L, respectively, in effluent water [20].

Wheat straw is an agricultural waste which can be used as a cost-effective adsorbent for a number of pollutants including metal ions. Wheat is herbaceous annual plant that grows between 2 and 4 feet (0.6 to 1.2 meters) tall. Wheat (*Triticum aestivum*) is one of the major crops grown throughout the world and is the most important staple food for a large part of the world's human population. In Pakistan, production of wheat is 24000 (1000MT) per year and thus is a huge source of wheat straw [21].

The present study explores the effectiveness of an agricultural by-product, wheat straw, in its biacetyl-treated form for the removal of Pb(II) and Cr(III) ions from their single and binary metal solution using a batch process. Studies are based on the identification of functional groups which are involved in the attachment of metal ions and the evaluation of metal ion binding process in terms of binding capacity. The sorption isotherms have been used for assessing biosorbent capacities and three commonly used equilibrium models (Langmuir, Freundlich and Dubinin-Radushkevich models) have been fitted to the experimental data.

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MATERIALS AND METHODS

1. Collection and Modification of Wheat Straw

The dried wheat straw (*Triticum aestivum*) was collected from the agricultural area of University of the Punjab Lahore, Pakistan. It was washed with water to remove the dust and solid particles. The air dried wheat straw (WS) was pulverized and screened using sieve (80 mesh ASTM) to get particle size less than 80 mesh. The powdered WS was soaked in distilled water for 24 hours, filtered and washed with distilled water till the filtrate appeared to be colorless. After this washing, biosorbent was dried in an oven (110 °C) till constant mass. The known amount of dried biomass (5 g) was taken in a beaker (100 mL) and biacetyl (Merck, Germany) was added in excess and mixed with glass rod properly. This mixture was kept overnight for complete reaction and then it was washed using distilled water till no visible color appeared in filtrate. The residue was air dried and preserved in air tight labeled jars. This modified biomass was designated as biacetyl modified *Triticum aestivum* (BMTA).

2. Characterization of BMTA

The biacetyl modified *Triticum aestivum* (BMTA) was characterized using potentiometric titration, BET surface area, point of zero charge pH (pH_{pzc}) and FTIR analysis. Boehm's potentiometric titrations [22] were employed to quantify the acidic and basic active sites present on the surface of BMTA biomass. The KBr disc method was used to scan FTIR spectra in range of 4,000-400 cm^{-1} with the help of FTIR spectrophotometer (Spectrum RX-1, Perkin Elmer). BET surface area was determined using Chemisorb 2750 (Micromeritics).

3. Batch Process

All the solutions were prepared from chemical reagents of analytical grade (Merck, Germany) and double distilled water was used for all solution preparation/dilution. Metal solutions were prepared using lead and chromium nitrates. The glassware used was thoroughly washed with chromic acid, caustic soda, soda ash, tap water, distilled water, in that order, and dried in an oven prior to use.

To evaluate the biosorption efficiency of BMTA using single and binary metal system, laboratory batch mode studies were performed by optimizing the experimental factors including effects of contact time, pH and initial concentration. The specific amount of biosorbent (100 mg) was added to metal solution of known concentration (50 mg/L, 50 mL) at predefined pH and room temperature in a conical flask (100 mL) and allowed for specified time period. Sodium hydroxide solution (NaOH, 0.01 M) and/or nitric acid solution (HNO₃, 0.01 M) were used for adjusting predefined pH of the solution. To facilitate biosorption process, the flasks were kept for shaking on an orbital shaker at 125 rpm. After specific time interval, the suspensions were filtered and filtrates were analyzed for metal ions concentration (C_e , mg/L) using an atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 100) under standard operating conditions. One of the experimental factors/parameters was optimized at every step and kept constant in further experiments. The difference of initial (C_o , mg/L) and equilibrium metal ion concentration (C_e , mg/L) was considered to be sorbed by the biosorbent. Blank determinations were also performed and no detectable adsorption of metal ions by the glass-ware was observed.

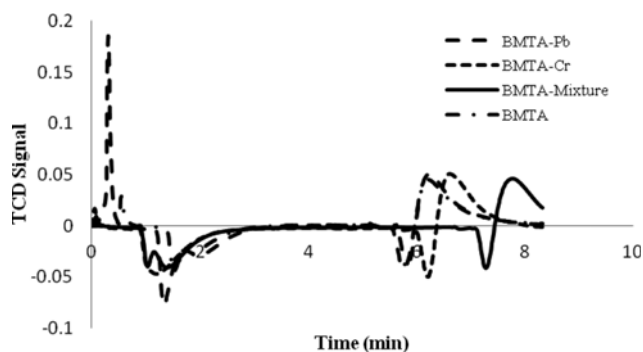


Fig. 1. BET surface area curves for BMTA, Pb(II) loaded BMTA, Cr(III) loaded BMTA and mixture loaded BMTA.

Sorption capacity (q_i or q_e , mg/g) of metals was determined by applying the following equation:

$$q_i \text{ or } q_e = \frac{C_o - C_e}{m} \times V \quad (1)$$

where m (g) is the mass of BMTA and V (L) is the volume of the metal solution used for the experiment.

RESULTS AND DISCUSSION

1. Characterization of BMTA Biomass

The modified biomass BMTA was characterized using various available techniques. Brunauer, Emmett and Teller (BET) method was used to determine the surface area based on chemisorption process (Fig. 1). The surface area of BMTA was found to be 7.4207 m^2/g and the monolayer volume was 1.705 cm^3/g . On comparing the surface area of BMTA (7.4207 m^2/g) with simple wheat straw (8.17 m^2/g [15]), the decrease in surface area of biomass was observed. This decrease might be due to the cross-linking of biacetyl with the straw forming the channels. The surface areas of metal-loaded biosorbent were found to increase from 7.4207 m^2/g to 15.0114 m^2/g (Pb-loaded), 14.195 m^2/g (Cr-loaded) and 17.99 m^2/g (mixture-loaded). The pH_{pzc} value for BMTA biosorbent was found to be 4.5. At this pH, biosorbent is neutral and optimum pH value for the metal ions might be equal to or greater than pH_{pzc} . The total acidic and basic functional groups were determined by Boehm's method using potentiometric titrations. The method is based on the fact that sodium bicarbonate (NaHCO₃) only neutralizes -COOH groups, sodium carbonate (Na₂CO₃) neutralizes -COOH groups and lactones, and sodium hydroxide (NaOH) can neutralize -COOH groups, lactones and phenols. The concentration of acidic sites including carboxylic, phenolic and lactonic was found to be 35.5 mmol/g. Modification of wheat straw using biacetyl increased the number of acidic functional group as indicated by the pH_{pzc} value of BMTA (4.5) in comparison to simple wheat straw, i.e., 6.1 [23]. The total concentration of basic groups can be determined by neutralizing them with acid, and for BMTA, it was 3.1 mmol/g. Table 1 summarizes the results for characterization of BMTA.

The FTIR spectrum of BMTA biomass is shown Fig. 2. A broader peak ranging 3,500-3,000 cm^{-1} centered at 3,200 cm^{-1} indicates the O-H stretching. The appearance of sharp peaks around 1,700-1,650

Table 1. Characterization of biacetyl modified *Triticum aestivum*

Property	Results
BET surface area	BMTA surface area=7.4207 m ² /g
	Monolayer volume=1.705 cm ³ /g
	BMTA-Pb surface area=15.0114 m ² /g
	Monolayer volume=3.448 cm ³ /g
	BMTA-Cr surface area=14.195 m ² /g
	Monolayer volume=3.261 cm ³ /g
	BMTA-(Pb+Cr)=17.996 m ² /g
	Monolayer volume=4.134 cm ³ /g
pH _{pzc}	4.5
Acidic and basic functional groups	Total acidic functional groups=35.5 mmol/g
	Lactonic acid groups=6.8 mmol/g
	Phenolic groups=16.7 mmol/g
	Carboxylic acid groups=12.0 mmol/g
	Total basic functional groups=3.1 mmol/g

cm⁻¹ is due to the C=O stretching of carbonyl group representing the presence of aldehydes or ketones. The peak at 1,692 cm⁻¹ is characteristic peak of α, β unsaturated ketones. The peaks ranging 1,600-1,450 cm⁻¹ correspond to the presence of aromatic ring system. The peaks around 1,490-1,150 cm⁻¹ are attributed to the presence of methyl and methylene group. The peak at 1,032 cm⁻¹ represents silicates. It can be concluded that the biacetyl modified *Triticum aestivum* (BMTA) is poly functional and may have high capacity for the sorption of metal ions.

2. Effect of Time of Contact

The study of effect of contact time is very crucial as it provides information about the minimum time required to adsorb maximum amount of the metal ions, from the solution onto the biosorbent. It has been reported repeatedly that adsorption passes through two steps [24]. In the first step, sharp increase in the adsorption capacity has been observed at the start of the process due to high availability of active binding sites in biomass. In the second step, the

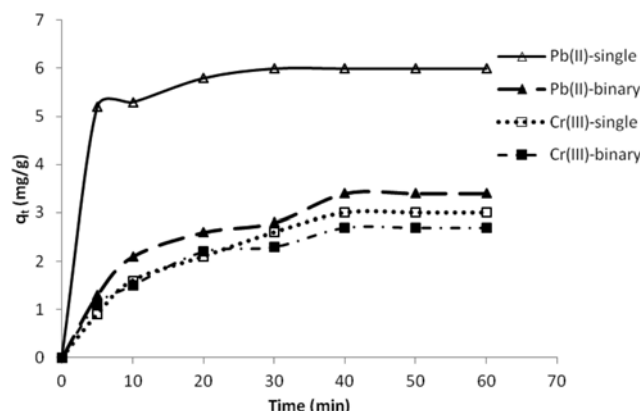


Fig. 3. Effect of contact time on the biosorption of Pb(II) and Cr(III) ions on BMTA in single and binary metal system (50 mg/L, 50 mL, 500 mg biomass for both metal ions in single and binary system).

adsorption capacity changes at slower rate with increase in time till there is no significant change in q_t value because of enrichment of the sorbent. The same trend was observed in all single and binary metal systems as shown in Fig. 3. The optimum time for the maximum sorption of Pb(II) and Cr(III) ions in single metal system was found to be 30 and 40 minutes, respectively. In case of binary metal solution, the optimum time for Pb(II) ions was increased from 30 to 40 minutes and equilibrium time of Cr(III) ions remained the same, 40 minutes. The q_t value for Pb(II) ions has been decreased from 6 to 3.4 mg/g (43% decrease) while q_t value for Cr(III) ions reduced from 3 to 2.7 mg/g (10% decrease). This decrease in the q_t values could be explained on the basis of the competitive repulsive interactions between the metal ions under studied conditions. Cr(III) had a smaller size and greater charge, whereas the charge on large sized Pb(II) ions was relatively small. Thus, it could be inferred that the decrease q_t value for Pb(II) was greater than that for Cr(III). The total capacity of biomass was also decreased as a result of possible repulsive interactions between both positively charged metal

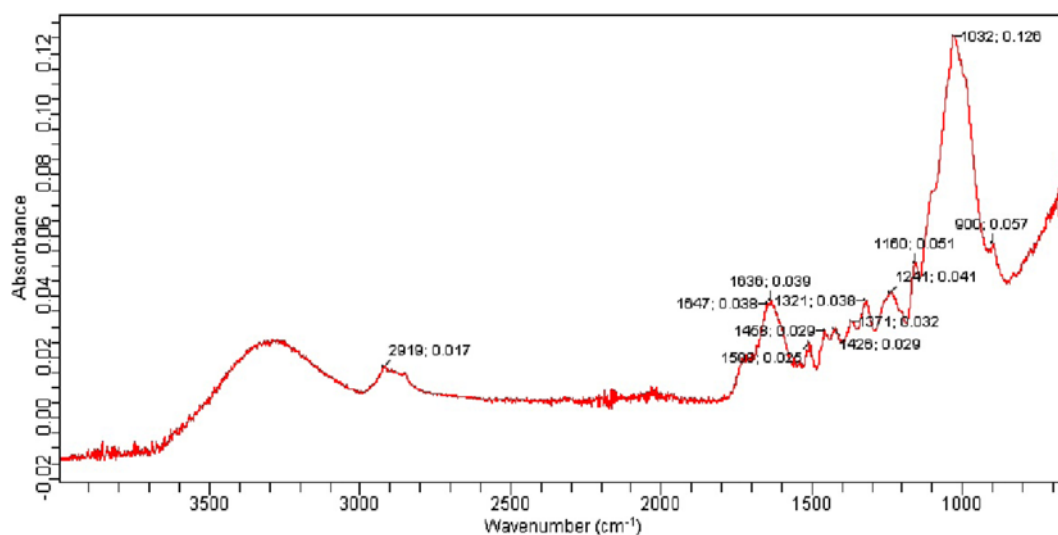


Fig. 2. FTIR spectrum for BMTA (refer to the text for peak description).

Table 2. Kinetic parameters for the biosorptive removal of Pb(II) and Cr(III) in single and binary metal solutions by BMTA

Model	Parameter	Pb(II)		Cr(III)	
		Single	Binary	Single	Binary
Pseudo first order	k_1 (min^{-1})	0.062	0.048	0.056	0.06
	$q_{e(\text{calc})}$ (mg/g)	1.044 (6.00)*	1.089 (3.40)*	1.077 (3.00)*	2.089 (2.70)*
	R^2	0.921	0.947	0.834	0.983
	D (%)	-82.58	-67.96	-64.07	-22.65
Pseudo second order	k_2 ($\text{g mg}^{-1}\text{min}^{-1}$)	0.1509	0.0234	0.0167	0.0305
	$q_{e(\text{calc})}$ (mg/g)	6.1349 (6.00)*	4.0650 (3.40)*	3.891 (3.00)*	3.2258 (2.70)*
	R^2	0.999	0.992	0.990	0.994
	D (%)	2.24	19.56	29.70	19.47
Intraparticle diffusion	K_{IPD} ($\text{mg g}^{-1}\text{min}^{-1}$)	0.160	0.390	0.377	0.302
	R^2	0.837	0.934	0.926	0.921

* $q_{e(\text{exp})}$

ions adsorbed on biomass.

3. Kinetics Modeling

The optimum time helps in evaluating the rate of biosorption process. It is also necessary to recognize the type of sorption mechanism in a given system. Kinetic models are used to investigate the mechanism of biosorption and its potential rate determining steps. In addition, the kinetics of metal uptake provides essential information about the conditions required for designing full-scale batch metal removal processes. Such models are always derived on the basis of three consecutive steps [34]: 1) diffusion occurring across the liquid film which surrounds the adsorbent particles (external or film diffusion); 2) diffusion in the liquid phase enclosed in the pores and/or along the pore walls, (internal or intra-particle diffusion); and 3) adsorption and desorption between the adsorbate species and active binding sites on biosorbent (mass action). Adsorption models originate from the kinetics of chemical reaction based on the whole process of adsorption devoid of considering the above mentioned steps.

Lagergren suggested pseudo-first-order (PFO) kinetics for the adsorption studies of solid and liquid systems [25]. Pseudo-first-order kinetics is based on the fact that the biosorption rate is proportional to the number of vacant binding sites on the biosorbent. The linear form of pseudo-first-order kinetics is expressed as follows:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2)$$

A linear plot should be obtained when $\ln(q_e - q_t)$ is drawn against time (t). The theoretical value of sorption capacity at equilibrium (q_e) and k_1 (rate constant) can be calculated from the value of slope and intercept. Sorption of metal will follow pseudo-first-order kinetics, if coefficient of determination (R^2) has value greater than 0.98 and smaller percentage difference ($D\%$) between calculated and experimental q_e values.

Percentage difference for sorption capacity can be calculated from the formula.

$$D\% = \left(\frac{q_{e(\text{cal})} - q_{e(\text{exp})}}{q_{e(\text{exp})}} \right) \times 100 \quad (3)$$

The parameters for the pseudo-first-order kinetics are given in

Table 2 calculated from $\ln(q_e - q_t)$ vs t plots (Figure not shown). The smaller R^2 values and greater $D\%$ for the sorption of Pb(II) and Cr(III) ions in single and binary metal system showed that pseudo-first-order kinetics was not being followed.

Ho's pseudo-second-order (PSO) kinetics is based on the assumption that rate of biosorption is proportional to the square of the number of free active sorption sites on the surface of biosorbent [26]. The linear form of pseudo-second-order model is expressed as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

A straight line should be obtained on plotting ' t/q_t ' against time ' t '. The value of the intercept gives the value of model adsorption capacity ($q_{e(\text{calc})}$), and from slope the rate constant (k_2) can be calculated.

It was observed from Fig. 4 and the parameters in Table 2 that the greater R^2 value, and comparison of calculated and experimental sorption capacities (smaller $D\%$ value) suggested that pseudo-second-order kinetics was being followed by the biosorption of Pb(II) ions in both single and binary metal system. It seemed that bio-

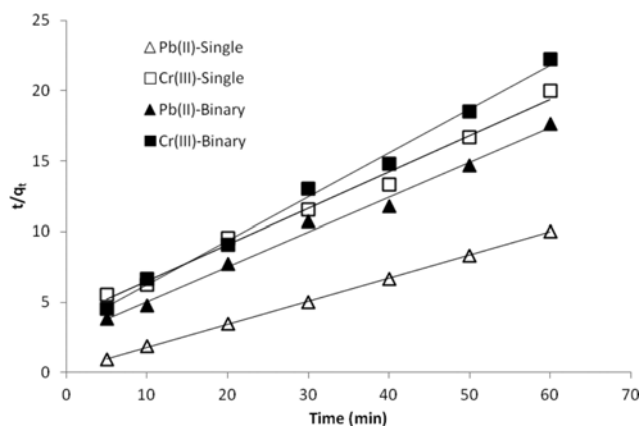


Fig. 4. Pseudo second order kinetic model for biosorptive removal of Pb(II) and Cr(III) ions by BMTA (50 mg/L, 50 mL, 500 mg biomass for both metal ions in single and binary system).

sorption of Cr(III) in binary system followed PFO ($R^2 > 0.98$), but the greater correlation ($R^2 > 0.99$) and smaller D% value indicated a better fit for PSO model.

Weber-Morris suggested intra-particle diffusion model to describe the rate-limiting step for adsorption process [27]. The linear form of intra-particle diffusion model can be expressed as follows:

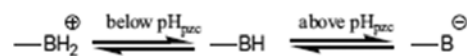
$$q_t = K_{IPD} \sqrt{t} + C \quad (5)$$

A plot of q_t versus \sqrt{t} should be a straight line with a slope equal to K_{IPD} . However, if the intra-particle diffusion is the only rate-limiting step, it is essential for the q_t versus \sqrt{t} plot to pass through the origin. It is not always the case and adsorption kinetics may also be controlled by the process of film diffusion and intra-particle diffusion simultaneously. If the straight line curve does not pass through the origin, the intra-particle diffusion is not the only rate-limiting step, indicating that the process is controlled by more than one mechanism. It was observed that the curve did not pass through origin in all four cases (intercept C is not zero). The values of intercept C and K_{IPD} suggested that the rate-determining step for the biosorption of Pb(II) and Cr(III) ions in single and binary metal system on BMTA biomass was controlled by interparticle diffusion as well as by boundary layer diffusion.

4. Effect of pH

The pH of an aqueous solution is found to be the most important parameter for efficient biosorption. Sorption is the comparative ability of H^+ ions and M^{n+} ions to attach with active binding sites located on the biosorbent. The ionization of chemically active sites on the biomass and speciation of metal ions, both are affected by the manipulation of pH [21]. The presence of various functional groups namely -COOH, -OH, -CONH₂ etc was confirmed from FTIR analysis. The behavior of each of these functional groups varies with the change in pH of solution. Such a behavior is linked with the isoelectric pH (pH_{pzc}) of the material. The protonation of BMTA occurs below pH_{pzc} and deprotonation occurs above pH_{pzc} . So far as the effective biosorption of positively charged metal ions is considered, the material needs to be negatively charged [21]. Hence an optimum pH is expected to be above pH_{pzc} of BMTA ($pH_{pzc} = 4.5$). The lower value of pH_{pzc} provides a relatively longer pH range

in which BMTA is negatively charged. Hence, this may be employed to remove metal ions at a relatively higher acidic pH.



The optimum pH for the maximum sorption of Pb(II) and Cr(III) ions in single metal system was found to be 5 and 6 pH, respectively (Fig. 5). Depending upon the nature of competition for adsorption, the equilibrium pH may increase or decrease in a binary metal system as compared to single metal system. In this case optimum pH for Pb(II) ions increased from 5 to 6 pH, while optimum pH for Cr(III) ions remained the same.

5. Effect of Concentration

In batch biosorption process, the initial concentration of metal ions in the solution plays a fundamental role as a driving force to surmount the mass transfer resistance between the aqueous and solid phases. Thus, the quantity of M^{n+} ions adsorbed is expected to be higher with a higher initial concentration till the enrichment of the available binding sites. In present studies, it was observed (Fig. 6) that at the start of experiment, biosorption rate of Pb(II) using single metal system was higher due to the greater availability of binding sites. It decreased afterwards till no significant decrease was observed because of the enrichment of all active sites. Same trend was observed in other three cases. The maximum q_e values were 26 mg/g for Pb(II) ions and 12.35 mg/g for Cr(III) ions in single metal system. The sorption capacity of Pb(II) ions and Cr(III) was decreased from 26 mg/g to 19.25 mg/g and 12.35 mg/g to 7.5 mg/g, respectively, using binary metal system. As a result of the competition between the metal ions for adsorption onto a specified number of binary sites, the binding capacities for these ions decreased in a multi-metal system. The greater q_e value for Pb(II) ions as compared to that for Cr(III) ions suggested the high affinity of BMTA for Pb(II) ions.

6. Equilibrium Modeling

Sorption isotherms are plots between the sorption uptake (q_e) and the final equilibrium concentration (C_e) of the residual sorbate remaining in the solution. The sorption models give an idea about position of equilibrium and the relationship between the amounts of substance adsorbed on the adsorbent and amount of adsorbate remained in the solution at constant temperature [28].

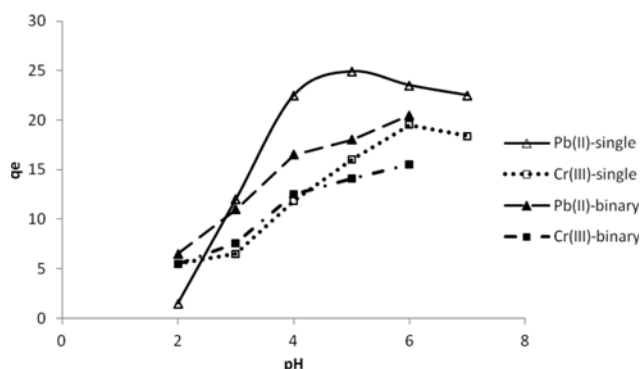


Fig. 5. Effect of initial pH on the biosorption of Pb(II) and Cr(III) ions on BMTA in single and binary metal systems (50 mg/L, 50 mL, 100 mg biomass for both metal ions in single and binary system).

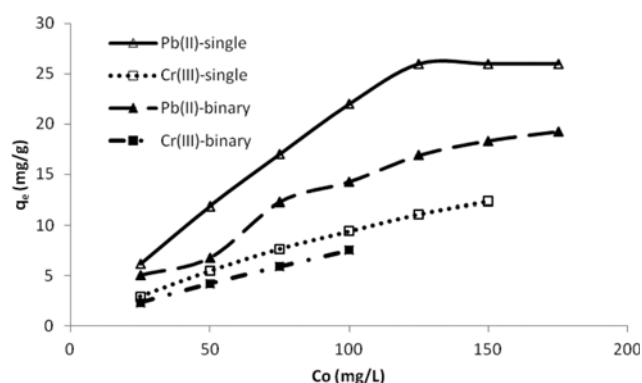


Fig. 6. Effect of initial concentration on the biosorption of Pb(II) and Cr(III) ions on BMTA in single and binary metal system.

Table 3. Equilibrium models for biosorptive removal of Pb(II) and Cr(III) by BMTA in single and binary metal systems

Model	Parameters	Pb(II)		Cr(III)	
		Single	Binary	Single	Binary
Langmuir	q_{max} (mg/g)	27.39	24.21	24.69	12.97
	K_L (L/mg)	0.3826	0.0397	0.0099	0.0148
	R_L	0.0147-0.0946	0.1258-0.5019	0.4000-0.8000	0.4020-0.7289
	R^2	0.9975	0.9895	0.9989	0.9881
Freundlich	K_F (mg/g) $^{1-1/n}$	8.6902	2.3159	0.4703	0.3815
	$1/n$	0.3142	0.4789	0.7209	0.672
	R^2	0.9331	0.9843	0.9925	0.9746
D-R	q_{DR} (mmol/g)	0.1472	0.1021	0.2317	0.1482
	q_{DR} (mg/g)	30.46	21.13	12.05	7.70
	β (mol ² /J ²)	7×10^{-9}	2×10^{-8}	9×10^{-8}	9×10^{-8}
	E (kJ/mol)	8.45	5.0	2.35	2.35
	R^2	0.984	0.9728	0.9612	0.9725

The Langmuir adsorption model is based on the assumption that maximum adsorption corresponds to the formation of a saturated monolayer of metal ions on the homogenous surface, with no mutual interactions between the sorbed metal ions [29]. The linear form of Langmuir model can be expressed as

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_L q_{max}} \quad (6)$$

where q_{max} is the monolayer sorption capacity (mg/g) and K_L is Langmuir constant. When a graph is plotted between C_e/q_e and C_e , a straight line with slope of $1/q_{max}$ and an intercept of $1/K_L q_{max}$ is obtained. The Langmuir parameters are given in Table 3 determined from Fig. 7. It was observed that the q_{max} is greater for Pb(II) ions than that of Cr(III) ions in single metal system while in case of binary metal system q_{max} value of Pb(II) ions decreases from 27.39 to 24.21 mg/g and for Cr(III) ions q_{max} decreased from 24.69 to 12.975 mg/g. So, in the presence of Pb(II) ions, a larger decrease in q_{max} values for Cr(III) ions was observed due to the competitive biosorption. The feasibility of Langmuir isotherm can be expressed by dimensionless separation factor or the equilibrium parameter. It can be calculated from Langmuir model using the formula

$$R_L = \frac{1}{1 + K_L C_o} \quad (7)$$

R_L explains both the shape and feasibility of the isotherm [21]. The value of R_L can be used to predict whether a sorption system is favorable or unfavorable. If R_L value is greater than 1, then adsorption process is unfavorable. The process is favorable if the value of R_L is $0 < R_L < 1$. If R_L value is equal to 1 then linear sorption is suggested. R_L value of '0' shows the irreversible sorption of adsorbate. It can be inferred from the R^2 and R_L values that Langmuir model was being followed by the biosorption of Pb(II) and Cr(III) ions and adsorption process is favorable in both single and binary metal systems.

The Freundlich model is an empirical equation employed to describe a heterogeneous system for adsorption. It is based on the multi-layered adsorption of molecules. There is exponential decrease in sorption capacity, on saturation of biosorbent active binding sites. The linear form of Freundlich model can be expressed as follows:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (8)$$

where K_F is Freundlich constant and $1/n$ is heterogeneity factor. Freundlich constant (K_F) is related to the binding energies of adsorbate molecules (metal ions in present studies) and heterogeneity factor ($1/n$) suggests the feasibility of multi-layered adsorption. If n is greater than 1, adsorption takes place favorably. Linear adsorption will be observed if n is equal to 1. A graph was plotted between $\ln q_e$ and $\ln C_e$ (figure not shown, slope and intercept given in Table 3). Freundlich parameters were calculated using intercept and slope of the curve and given in Table 3.

It can be inferred from the R^2 value that the biosorption of Pb(II) and Cr(III) ions on BMTA biomass did not follow Freundlich model both in single and binary metal system. It seemed that Cr(III) in single metal system followed Freundlich model ($R^2=0.9925$); a comparison of R^2 values for Langmuir ($R^2=0.9989$) and Freundlich models showed that Langmuir model was a better fit.

Dubinin-Radushkevich (D-R) equilibrium model is used to cal-

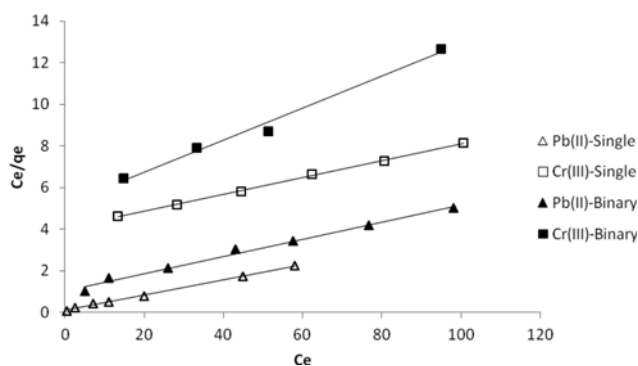
**Fig. 7. Langmuir plots for biosorption of Pb(II) and Cr(III) by BMTA.**

Table 4. Comparison of capacities of different biosorbents for Pb(II) and Cr(III) ions

Biosorbent	Metal ion	Equilibrium time (min)	pH	q_{max} (mg/g)	Kinetics	Equilibrium	Reference
<i>Triticum aestivum</i> (untreated)	Pb(II) ^a	15	6	0.85	PSO	F	[23,31]
Waste beer yeast	Pb(II) ^a	60	6	5.71	--	L	[7]
Waste beer yeast	Pb(II) ^b	60	6	2.90	--	--	[7]
NaOH treated <i>A. niger</i>	Pb(II) ^a	6 hr	4	3.81	PSO	F	[32]
NaOH treated <i>A. niger</i>	Pb(II) ^b	6 hr	4	2.87, 1.83	--	--	[32]
<i>S. bangalense</i>	Pb(II) ^a	40	5.5	12.65	PSO	L	[33]
<i>Arecha catechu</i>	Pb(II) ^a	25	2-7	11.723	PSO	L, F	[34]
<i>Phaseolus aureus</i>	Pb(II) ^a	60	6	21.8	PSO	L	[35]
Biacetyl treated <i>Triticum aestivum</i>	Pb(II) ^a	30	5	27.39	PSO	L, DR	Present study
Biacetyl treated <i>Triticum aestivum</i>	Pb(II) ^b	40	6	24.21	PSO	L, F	Present study
<i>Ficus benghalensis</i> L	Pb(II) ^a	20	6	28.63	PSO	L	[36]
<i>Moringa olifera</i> bark	Pb(II) ^a	30	5	34.6	PSO	F	[37]
<i>Ficus carcia</i>	Pb(II) ^a	80	5	37.74	PSO	L	[38]
<i>Cladophora rivularis</i>	Pb(II) ^a	30	4	48.13	----	F	[39]
Wheat bran	Pb(II) ^a	20	5	63.9	--	--	[4]
<i>Agave lechugilla</i>	Cr(III) ^a	12 hr	4	21.32	--	L, F	[40]
<i>Triticum aestivum</i>	Cr(III) ^a	20	6	3.45	PSO	F	[23]
HCl treated Sorghum straw	Cr(III) ^a	--	4	6.96	--	L, F	[41]
HCl treated Agave bagasse	Cr(III) ^a	--	4	11.44	--	L, F	[41]
HCl treated Oats straw	Cr(III) ^a	--	4	12.97	--	L, F	[41]
Biacetyl treated <i>Triticum aestivum</i>	Cr(III) ^a	40	6	24.69	PSO	L, F	Present study
Biacetyl treated <i>Triticum aestivum</i>	Cr(III) ^b	40	6	12.97	PSO	L	Present study
Wheat bran	Cr(III) ^a	20	5	87.0	--	--	[4]

^aSingle metal system^bBinary metal system

PSO; Pseudo second order, L; Langmuir, F; Freundlich, DR; Dubinin-Radushkevich

culate the mean free energy (E , kJ/mol) of adsorption. Linear form of D-R model is

$$\ln q_e = \ln q_{DR} - \beta \varepsilon^2 \quad (9)$$

where, q_{DR} is the biosorption capacity from D-R model and ε is the Polanyi potential ($\varepsilon = RT \ln(1 + 1/C_e)$), R being the ideal gas constant and T being temperature in absolute units. The mean free energy is determined from

$$E = \frac{1}{\sqrt{2\beta}} \quad (10)$$

Mean free energy gives the idea of physical or chemical nature of sorption process. The adsorption will be physical if E is less than 8 kJ/mol, and if value of E is greater than 16 kJ/mol, it indicates chemical adsorption. An intermediate value indicates an ion-exchange mechanism [21]. A graph between $\ln q_e$ and ε^2 gives the values of q_{DR} and β from intercept and slope, respectively. The R^2 value shows that biosorption of Pb(II) and Cr(III) ions on biomass does not follow D-R model in both single and binary metal system. Value of E for Pb(II) ions and Cr(III) ions suggests that biosorption of both metal ions was physical (Table 3). From the R^2 value for Pb(II) in single metal system, it seemed that it followed D-R model ($R^2 = 0.984$). A comparison of different studied models for Pb(II) indicated that Langmuir model was a better fit ($R^2 = 0.9975$). The maximum biosorption capacity, as determined by both mod-

els, was close to each other, indicating that biosorption of Pb(II) by BMTA was more ion-exchange than physiosorption. However, further insight is required to establish the 'true' mechanism involved.

The comparison of equilibrium models showed that Langmuir model was the best fit among the studied ones. However, a decrease in q_{max} values in binary metal systems pointed to the fact that there existed a competition between adsorbate species before adsorption.

7. Comparison of Biosorption Capacities

The biosorption capacities of the biacetyl modified *Triticum aestivum* has been compared with other biosorbents as well as unmodified *Triticum aestivum*. Table 4 shows such a comparison that was performed in terms of equilibrium time, pH of solution, biosorption capacity and equilibrium and kinetic models. Biacetyl modification caused a significant change in the biosorption capacity for the single metal ions. For Pb(II), capacity increased from 0.85 mg/g to 27.39 mg/g for single (3122% increase) and 24.21 mg/g (278% increase) for binary system. Similarly for Cr(III), the capacity increased from 3.45 mg/g to 24.69 mg/g for single (615% increase) and 12.97 mg/g (275% increase) for binary system. The increase was due to modification only and in accordance with reported literature [30]. The increase in the capacity was greater than the increase in the equilibrium time in comparison to those for unmodified biomass. The biosorption capacity of BMTA was found to be greater than a number of studied biosorbents in single and binary metal systems. Hence, it can be inferred that BMTA could be a poten-

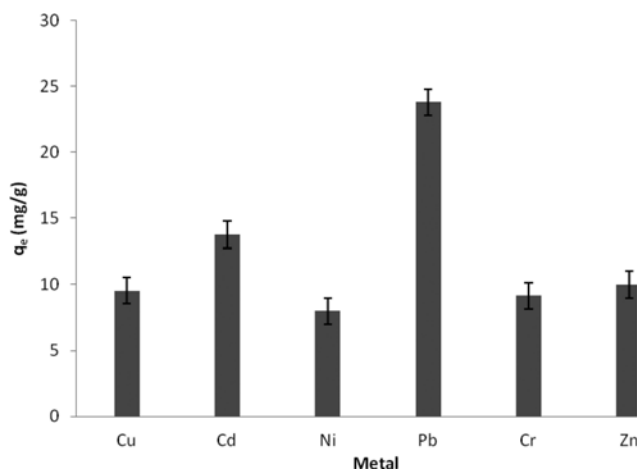


Fig. 8. Selectivity of biosorption of Pb(II) ions with respect to other studied ions by BMTA.

tial biosorbent for biosorptive removal of metal ions.

8. Selectivity of Metals

We investigated sorption capacity of BMTA using single and binary metal system. While comparing the q_{max} values, it was inferred that BMTA might be a good option for the removal of Pb(II) and Cr(III) ions in single metal system. In case of binary metal system, competitive biosorption takes place between Pb(II) and Cr(III) ions, and appreciable decrease in the sorption capacity for Cr(III) ions was observed in the presence of Pb(II) ions. BMTA was found to have relatively greater affinity for Pb(II) ions than other metal ions (Fig. 8). This affinity might be related to the larger size of Pb(II) ions, which resulted in the coverage of more area and volume on BMTA surface. This is the first study, to the best of our knowledge, to point to the use of the modified agricultural material as selective adsorbent for some metal ion. BMTA can be suggested as a relatively selective biosorbent for Pb(II) ions. However, a further detailed study is required to establish the fact.

CONCLUSION

An innovative biacetyl modified *Triticum aestivum* biosorbent was prepared and its sorption capacity was investigated for the removal of Pb(II) and Cr(III) ions in single as well as in binary metal systems. Comparative batch studies were conducted and various biosorption parameters were optimized. The optimum time of contact for Pb(II) and Cr(III) ions in single metal system was 30 and 40 min, respectively, with a slight increase (40 min) for Pb(II) in binary metal system. Optimum pH for Pb(II) and Cr(III) ions in single metal system was 5 and 6, respectively while pH 6 was found to be optimum pH for binary metal system. The maximum biosorption capacities for Pb(II) and Cr(III) ions in single metal system were 27.39 mg/g and 24.69 mg/g, respectively, while for binary metal system the values were 24.21 mg/g and 12.97 mg/g respectively. The sorption capacity for Cr(III) ions decreased significantly in binary mixture. Kinetic modeling revealed biosorption of Pb(II) and Cr(III) ions on BMTA was described by pseudo-second-order kinetics both in single and binary metal systems. Langmuir equilibrium model was the best fit for biosorption studies of Pb(II) and

Cr(III) ions both in single and binary metal system. FTIR analysis, potentiometric titration and pH_{pzc} (4.5) revealed that BMTA was a poly functional biosorbent with more acidic contents. Due to the increased acid content, BMTA may be a good choice for the removal of metal ions at a relatively lower pH. The results showed relatively selective binding for Pb(II) ions compared to other metals. The present studies are a step forward for the selective removal of Pb(II) ions in multi-metal system.

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