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*Original Research*

# Chemically Modified Biomass from *Triticum aestivum* for Eco-Friendly Detoxification of Cd(II)- and Sn(II)-Contaminated Waters

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## Abstract

Eradication of toxic heavy metals from waters polluted due to urbanization and industrial effluents is a burning issue. There is a need to enhance research to find out new economical methods to overcome problems associated with current removal techniques. Use of novel modified biosorbents to increase metal removal efficiency through biosorption is the most suitable alternative. The present study is focused on removing cadmium and tin metal ions using acid-pretreated wheat straw (PWS) and urea-modified wheat straw (UMWS). The biosorption process is carried out in batch fashion to optimize the basic conditions of the process such as pH, amount of biosorbent, time of contact, agitation speed, and temperature. Langmuir isotherm, Freundlich isotherm, and Dubinin-Rudikish (D-R) model were applied to determine the maximum amount of metal ions adsorbed and the feasibility of the process. The maximum amount of cadmium and tin metal ions adsorbed using PWS is 33.55 (mg/g) and 47.84 (mg/g), whereas using UMWS is 74.62 (mg/g) and 64.10 (mg/g), respectively, as calculated by Langmuir model. Kinetic studies showed a better fit for pseudo 2nd-order, whereas intra-particle diffusion and Bangham's models partially proved macro pore diffusion as a rate-determining step. Thermodynamic studies confirmed that the process was spontaneous and endothermic with negative values of Gibb's free energy and positive values of enthalpy and entropy changes. It was found that modification enhanced the metal binding capacity up to more than 100%. As urea and wheat straw both are biodegradable, the process became eco-friendly.

**Keywords:** cadmium, tin, Langmuir isotherm, urea-modified, Bangham's model

## Introduction

Due to industrial and technological advancements, various environmental issues have sprung up. Among them, water contamination due to heavy metals and organic contents are the most threatening. Heavy metal species, which are persistent, highly toxic, non-thermo degradable, non-biodegradable, and can accumulate in body to a toxic level, are released through effluents due to industrial inefficiencies [1-3]. Heavy metal tin is mostly used as a protective layer to prevent corrosion and can contaminate food and water due to weathering effects. A concentration of 200-300 ppm of tin can be tolerable but it has been observed in the very recent past that more than 700 ppm concentration of tin is found in different water specimens [4]. This concentration of tin is highly toxic and can cause nausea and diarrhea, and can even damage bones and liver. Heavy metal cadmium is mostly released through mining, batter-

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ies, electroplating, alloy industries, smelting, fertilizers, and paint pigments [5, 6]. A meager concentration of cadmium is toxic enough to cause flu-like symptoms, cadmium blues, pulmonary edema, fever, chills, chest pain, dizziness, headache, weakness, osteoporosis, osteomalacia, kidney damage in very acute form, and occasional fits of coma [7]. The toxicity of cadmium can be gauged further by the fact that it causes renal toxicity, renal tubular dysfunction, and itai-itai in chronic form. In the perusal of these observations it has become a hot potato to remove these toxic heavy metals through feasible processes at point source emissions [8]. Several treatment methods that already have been suggested for heavy metals removal are ion exchange, chemical oxidation, chemical reduction, coagulations, solvent extraction, reverse osmosis, flotation, dialysis and electro dialysis, evaporative recovery, and electrochemical treatments [9]. A high cost of treatment, method inefficiency at low but toxic level of concentration, production of toxic sludge, and additional chemical cost are the major flaws. It reduces the afore-suggested methods to a low level of efficiency and proved biosorption is a more efficient, more economical and more useful method [10, 11]. The use of suitable biomass as that biosorbent to remove heavy metals is one alternative. Agricultural waste material can also be an efficient and economical, biosorbent used for removal of heavy metals [12, 13]. To increase metal removal efficiency by biosorbents, different methods of modifications in biosorbent have been used. There is a requirement for screening new biosorbents or modifications of biosorbents by changing in functional groups to increase the metal removal efficiency. In addition, the different biosorbent used are eco-friendly, metal can easily be-desorbed for reuse, there's no need to supply nutrients, and no additional chemicals are required. A variety of biosorbents have been used for various types of agriculture waste, plant and derived microorganisms such as endophytic fungus, marine algae, scenedesmus abundans, sawdust, banana peels, seaweed, bacteria, white-rot fungi, *Eichhornia crassipes*, and Myriophyllum triphyllumorchard for the removal of cadmium and tin metal ions. This shows that use of biosorbents for heavy metal removal is an efficient and economical method. However, use of microorganisms and some plant species need to be cultivated under special conditions, which require an extra investment [14-17].

Pakistan is one of the top wheat-producing countries. According to highlights of an economy survey, Pakistan produced 2.4 billion MT of wheat in 2013 (U.S. Department of Agriculture). Wheat straw is a waste/byproduct produced after harvesting the wheat. It is mostly used as an animal food and as a basic ingredient for paper and packing industry [18].

The objectives of the present study are to evaluate the comparative removal efficiencies of pre-treated wheat straw (PWS) and urea-modified wheat straw (UMWS) biomass for the toxic metals cadmium and tin. The effects of different parameters such as temperature, initial metal ion concentration, time of contact, agitation speed of rotary shaker, pH, and dose of adsorbent were also studied to optimize the conditions. To elaborate the process mechanism and to measure maximum adsorbed amount of metals ions, different equilibrium models such as the Langmuir model, Freundlich model, and Dubinin-Radushkevich model were applied. Reaction Kinetics was also estimated by Lagergren's pseudo 1$^{st}$-order, Ho & Mckays pseudo 2$^{nd}$-order, the intra-particle diffusion model, and Bangham's model. Thermodynamic studies were also performed to measure free energy change (Gibb's free energy), enthalpy change, entropy change, and spontaneity of the biosorption process.

## Materials and Methods

### Analytical Methods

All stock and standard solutions were prepared by dissolving specific quantities of respective metal salts in water. All chemicals used were of analytical grade (Sigma-Aldrich, Inc.,). All dilutions were done using double-distilled water. A rotary shaker (Aosheng, Os-100) was used and pH of solutions was adjusted using a digital pH meter (Hanna pH 211) with HCl (0.1M) and NaOH (0.1M) solutions as per requirement. Metal analysis was done using an atomic absorption spectrophotometer (Perkin Elmer, AAnalyst 100) at standard operating conditions. All experiments were performed in triplicate fashion and their mean values were considered as final readings.

### Collection and Pre-Treatment of Wheat Straw

Wheat straw (*Triticum aestivum*) was collected from the farmlands of the University of the Punjab, Lahore, Pakistan (31º32′59″N, 74º20′37″E). After cutting into small pieces, it was washed with double-distilled water until there was no visible color in the filtrate. Then it was dried in a drying oven (MINO/50) until constant mass and was further cut down into smaller pieces. It was ground to get fine powder using a grinder (Kenwood) and then screened to get particle size in 220-230 micrometers. The material was soaked in HCl (0.5M) solution for 3-4 hours to leach out already present metals. The processed material was washed repeatedly with double-distilled water. Residue was a dried in drying oven (Memmert, 100-800) until constant mass. This acid-treated biomass was called Pre-treated wheat straw (PWS) and stored in airtight glass containers.

### Modification of Pre-Treated Wheat Straw

Pretreated wheat straw was modified with urea in microwave oven (D 131, Dawlance) according to the method given elsewhere. Processed material was dried, stored in airtight glass bottles, and designated as urea-modified wheat straw (UMWS). Urea-modified material was found to possess greater biosorptin capacity, so this method was selected here [18-19].

### Batch Equilibrium Experiments

Stock solutions of Sn(II) and Cd(II) were prepared by dissolving specific amounts of tin nitrate and cadmium nitrate and these solutions were diluted to required concentrations. The effect of various parameters such as pH, time of contact, dose, temperature, and concentration of metal ions were studied by using concentration difference method. PWS (0.25-2.25 grams) was put separately in 250 mL Erlenmeyer flasks containing 100 mL solutions of Cd (30 mg/L) and Sn (30 mg/L) to determine optimum dose for biosorption at solution pH. These solutions were carried for 150 minutes on a rotary shaker (Aosheng, Os-100) with agitation speed 150 rpm. Solutions were filtered by whatmann filter paper and filtrates were brought to flame atomic absorption spectrophotometer to determine equilibrium residual concentration of Sn (II) and Cd (II) ions at standard operating conditions. The difference in final ($C_e$, mg/L) and initial concentration ($C_o$, mg/L) is the amount biosorbed by PWS. Metal removal percentage ($R$ %) and amount of metal adsorbed ($q_e$, mg/g) were determined using the following equations:

$$\%Removal = \frac{C_0 - C_e}{C_o} \times 100 \tag{1a}$$

$$q_e = \frac{C_o - C_e}{m} \times V \tag{1b}$$

...where $m$ is the mass of biomass in grams, $V$ is the volume of metal solution (L), and $q_e$ is the amount of metal biosorbed per unit mass of dried PWS (mg/g) at equilibrium.

The method was repeated to get optimum conditions for other parameters such as pH (2-10), temperature (293K-323K), agitation speed (25-225 rpm), time (25-225 minutes), and initial metal ions concentration (10-90 mg/L) for both tin and cadmium metal ions. It was done by changing progressively one parameter and keeping the remaining parameters constants with both type of biosorbents, PWS and UMWS for both metals. Once a parameter is optimized, the obtained values were fixed for further experiments.

## Results and Discussion

### Biosorbent Characterization (FTIR Analysis)

Fig. 1 shows FTIR spectra of all types of biomasses (WS, PWS, UMWS). Results proved the poly-functionality of the materials having different functional groups such as Hydroxyl, carbonyl and amines. Results also confirmed a change or addition in biomass functional groups among WS, PWS, and UMWS. The peaks at 1,632.9 cm$^{-1}$, 1,376.3 cm$^{-1}$, 1,051.9 cm$^{-1}$, and 793.7 cm$^{-1}$ show the presence of carbonyl, aliphatic nitro, aliphatic amines, and aromatic amines, respectively, in WS biomass. Whereas appearance of peaks at 2,893.2, 2,260.8, 1,508.3, 1,327.0, 1,253.7, 1,045.4, 827.0, and 2250.0 show the presence of hydroxyl, -CN, nitro, aromatic amines, carbonyl, nitrile, amines, and nitrites, respectively, at UMWS. These groups act as ligands and increase biosorption capacity for metal ions. The results revealed that the addition of these lone pairs of carrier groups will also increase the metal binding capacity of UMWS, hence increase percentage removal efficiency (Table 1).

### Effect of Amount of Biosorbent

Biosorption depends upon the amount of biosorbent as it affects the number of available binding sites, surface area and biosorbent:biosorbate ratio. The effect of the amount of biomass (PWS and UMWS) on the metal removal efficiency was studied in the range of 0.25-2.25 g/100 mL at solution pH (Fig. 2). Results revealed that percentage removal of metal depends upon the amount of biomass, as initially it increases with increases in the amount of biomass. There is an increase in biosorption from 25% (at 0.25 g) to 72% (at 1.75 g) for cadmium ions and 40% (at 0.25 g) to 75% (at 1.75 g) for tin ions with PWS. Whereas by using UMWS, the percentage metal removal increases from 41% (at 0.25g) to 97% (at 1.25 g) for cadmium ions and 40% (at an amount of 0.25 g) to 97% (at an amount 1.25 g) for tin and is reached at equilibrium. Thus the optimized doses of biomass (g/100mL) for Cd (II) and Sn (II) solutions are 1.75 g and 1.25 g with PWS and UMWS, respectively. The

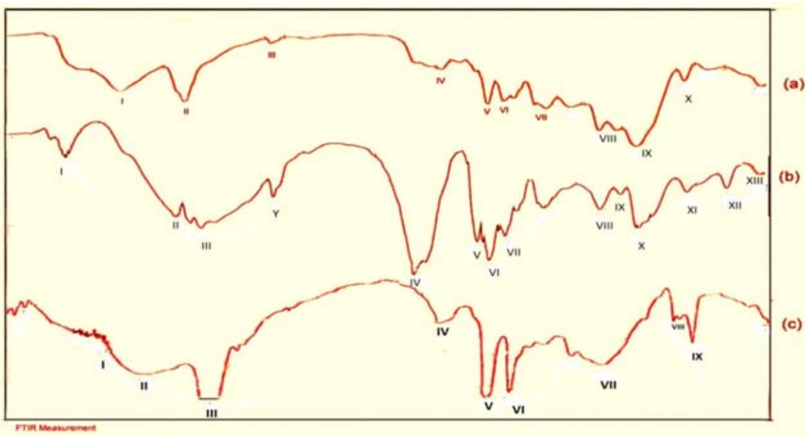

Fig. 1. FTIR Spectra images of WS, PWS, and UMWS (Biosorbents), x-axis show wavelength (cm$^{-1}$).

Table 1. FTIR spectra values with identification of poly functional groups of biomasses.

| Bands | WS (c) | PWS (a) | UMWS(b) |
|---|---|---|---|
| I | 3682.9, OH (Free hydroxyl, Alcohol+Phenol) | 3640.4, OH (Alcohol+Phenol) | 3286.7, OH (Alcohol+Phenol) |
| II | 3368.5, -NH (1º,2º Amines+Amides) | 2972.3, CH (Alkanes), O-H (Carboxylic acid) | 2893.2, CH (Alkanes), O-H (Carboxylic acid) |
| III | 2889.2, C-H (Alkanes) | 2810.2, H-C=O (Aldehydes) | 2260.8, CN (Nitriles), Alkynes |
| IV | 1632.9, Carbonyl (α,β unsaturated Aldehydes+Ketones | 1743.6, Carbonyl (Aldehydes, Esters) | 1653.0, Carbonyl (Aldehydes+Ketones) |
| V | 1459.8, CH (Alkanes), C-C (Aromatic rings) | 1550.7, N-O (Nitro compounds) | 1508.3, N-O (Nitro compounds) |
| VI | 1376.3, Aliphatic Nitro- | 1514.1, N-O (Nitro compounds) | 1458.1, C-C (Aromatics) |
| VII | 1051.9, C-N (Aliphatic Amines) | 1462.0, C-C, C-H (Alkanes), C-C (Aromatic), | 1327.0, C-N (Aromatic amines), N-O (Nitro) |
| VIII | 793.7, C-Cl (R-X), N-H (Amines), C-H (Aromatic) | 1107.1, C-N (Amines) | 1253.7, Co (Alcohol, aldehydes, Ketones, Ether) |
| IX | 723.0, Alkanes | 1047.3, C≡N (Amines) | 1159.2, CH (R-X), CN (Aliphatic amines) |
| X | | 777.3, C-H (Aromatic), R-X | 1045.4, C≡N |
| XI | | | 898.8, =C-H |
| XII | | | 827.0, N-H (1º,2º Amines), aromatic |
| XIII | | | 663, R-Cl, R-Br etc |
| Y | | | 2250.0, C≡N (Nitriles) |

increase in metal removal percentage initially with increase in biomass quantity was due to an increase in the number of active sites. As rate of biosorption depends upon uncovered surfaces or sites available for metal removal, at the start all sites were uncovered and rate was maximum. After the sites were covered, the percentage removal efficiency decreased and reached a stage when rate of biosorption become almost constant. After optimization, the decrease in percentage removal of metal ions (at high concentration of biomass) is due to partial aggregation of adsorbent, disturbance in metal ions or metal removal sites, and enhancement of adsorbent-adsorbent interaction as compared to adsorbate-adsorbent interaction [20, 21]. Furthermore, the greater increase in metal removal efficiency of UMWS as compared to PWS is due to the effect of modification. This confirms the addition of functional groups from urea biomass, which provide more sites for metal binding into the solution.

## Effect of pH

Study of the effect of pH for bisorption is a very important parameter as it causes a significant change in metal ions chemistry followed by metal ions removal efficiency. At low pH in acidic media solutions have an excess number of $H^+$ ions that occupy biosorbent active sites, resulting in protonation [22, 23]. Hence these positive metal sites oppose metal cations and there is less metal uptake due to enhancement of competition between $H^+$ ions and metal cations. At pH greater than 7, the solution has excess $OH^-$

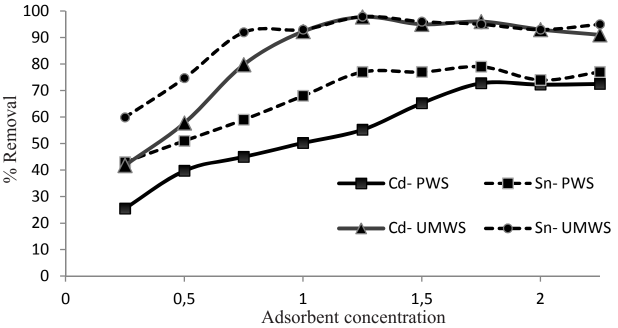

Fig. 2. Describe effect of biosorbent concentration on % removal efficiency of cadmium and tin ions using PWS and UMWS.

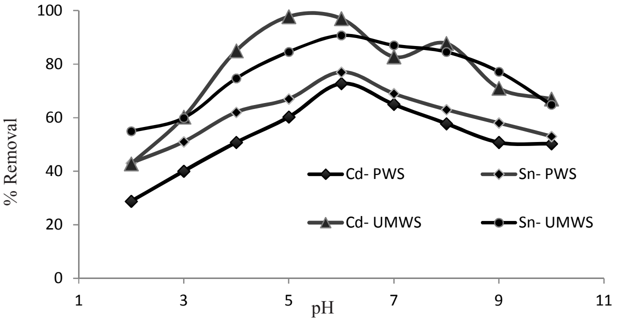

Fig. 3. Describe the effect of pH on % removal efficiency of cadmium and tin ions using PWS and UMWS.

Table 2. Values for Langmuir isotherm, Freundlich isotherm, and Dubinin-Radushkevich (D-R) model for the biosorption of cadmium and tin using PWS and UMWS.

| Metals | | PWS | | UMWS | |
|---|---|---|---|---|---|
| | | Cd | Sn | Cd | Sn |
| Langmuir Isotherm | | y=4.097x+0.0298 | y=0.1074x+0.0209 | y=1.4258x+0.0134 | y=0.4203x+0.0156 |
| | $R^2$ | 0.99 | 0.98 | 0.98 | 0.98 |
| | $b$ (L/mg) | 0.0072 | 0.1946 | 0.0093 | 0.0371 |
| | $q_{max}$ (mg/g) | 33.55 | 47.84 | 74.62 | 64.10 |
| | $R_L$ | 0.579-0.132 | 0.340-0.0541 | 0.518-0.106 | 0.729-0.230 |
| Freundlich Isotherm | | y=0.5607x-0.229 | y=1.053x+0.9772 | y=0.7138x+0.1284 | y=1.0281x+0.3394 |
| | $R^2$ | 0.9762 | 0.9554 | 0.9795 | 0.9573 |
| | $n$ (mg/g) | 1.78 | 0.94 | 1.40 | 0.97 |
| | $K_f$ (dm$^3$/g) | 1.69 | 9.48 | 1.34 | 2.18 |
| | $1/n$ | 0.56 | 1.05 | 0.71 | 1.02 |
| D-R Model | | y=-0.0002x+3.08 | $y=2\cdot10^{-7}x+2.076$ | $y=3\cdot10^{-5}x+3.5709$ | $y=7\cdot10^{-8}x+2.38$ |
| | $R^2$ | 0.728 | 0.788 | 0.702 | 0.930 |
| | $q_{max}$ (mg/g) | 21.75 | 7.97 | 35 | 10.80 |
| | $E_s$ (KJ/mol) | 0.05 | 1.58 | 0.129 | 2.67 |

ions, which create a competition between biosorbent donar sites and hydroxide ions. Hydroxide ions tend to precipitate with metals and reduce metal removal efficiency. Fig. 3 shows the effect of change in pH of solutions with PWS and UMWS for removal of cadmium and tin ions at a range of 2-10 pH. Results show that initially percentage removal of metal ions increase with increase in pH up to 6 (roughly 60-70%), then decreases with further increases in pH. The maximum percentage removal with PWS is 72.75% and 77% at pH 6 for both Cd(II) and Sn(II), respectively. Whereas by using UMWS, % removal is 97% at pH 5 and 92% at pH 6 for Cd(II) and Sn(II) ions, respectively. There is a 20-25% increase in metal removal percentage from PWS to UMWS [1, 22, 23].

## Effect of Agitation Speed

Agitation speed is a significant parameter that affects the rate of biosorption and metal ion removal capacity from solution. Fig. 4 shows behavior of biosorbent at different agitation speeds for metal ion uptake and establishment of equilibrium. Results show that biosorption increases when increasing the agitation speed initially. The maximum biosorbtion occurred at 125 rpm using PWS for both Sn(II) and Cd(II) metal ions. Urea-modified wheat straw (UMWS) showed maximum biosorption at 100 rpm for both metal ions. There is an increase in metal removal percentage averageing 50% from agitation speed 25 rpm to 150 rpm. This increase in metal removal percentage with increase in agitation speed shows that at low speed, biosorbent does not spread in the whole solution, hence biosorbent layers conglomerate and are not available for metal uptake. Therefore, due to agglomeration of particles, biosorption occurs by the top layers only and deep buried layers do not participate. Thus shaking speed should be enough to make sure that all active sites of biosorbents must be available for metal ion uptake. With increasing agitation speed, it may also decrease the film boundary layer surrounding biosorbent particles and enhance metal ion uptake due to diffusion rate of external film. The further decrease in metal removal percentage at higher agitation speeds is due to an increase in the random collisions between particles, detaching loosely bonded metal ions, vortex phenomena, and insufficient time for metal uptake by biosorbent, which makes biosorbtion difficult. Moreover, at a very high agitation speed loosely bonded metal ions also detach and again come to the solution. Similar results for other biosobents were also reported [25].

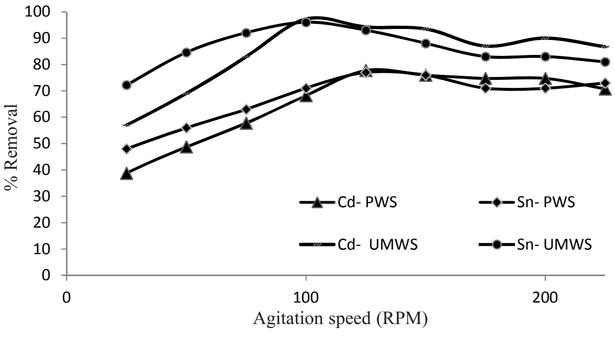

Fig. 4. The effects of agitation speed on % removal efficiency of cadmium and tin ions using PWS and UMWS.

## Biosorption Equilibrium Model

Biosorption equilibrium models were applied to study the concentration of sorbed species, attachment of metal ions with surfaces, and to calculate maximum amount of metal uptake. The three most common isotherms, namely Freundlich, Langmuir, and Dubinin-Radushkevich models were applied.

Langmuir isotherm can be represented by the following relationship:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{bq_{max}C_e} \qquad (2)$$

...where $q_{max}$ is the maximum capacity of sorption per unit mass of adsorbent (mg/g), $q_e$ is the amount of metal removed at equilibrium per unit mass of adsorbent (mg/g), and $C_e$ represents concentration of metal ions in solution at equilibrium (mg/L). Here $b$ (L/mg) is the sorption coefficient or Langmuir sorption constant, which is related to apparent adsorption energy [26]. Langmuir assumed homogenous monolayer adsorption on the adsorbent surface with a finite number of identical active sites and no interaction between different layers [27].

Table 2 represents different parameters of Langmuir isotherm calculated by slope and intercepts of graph between $1/q_e$ and $1/C_e$ with straight line using equation 2

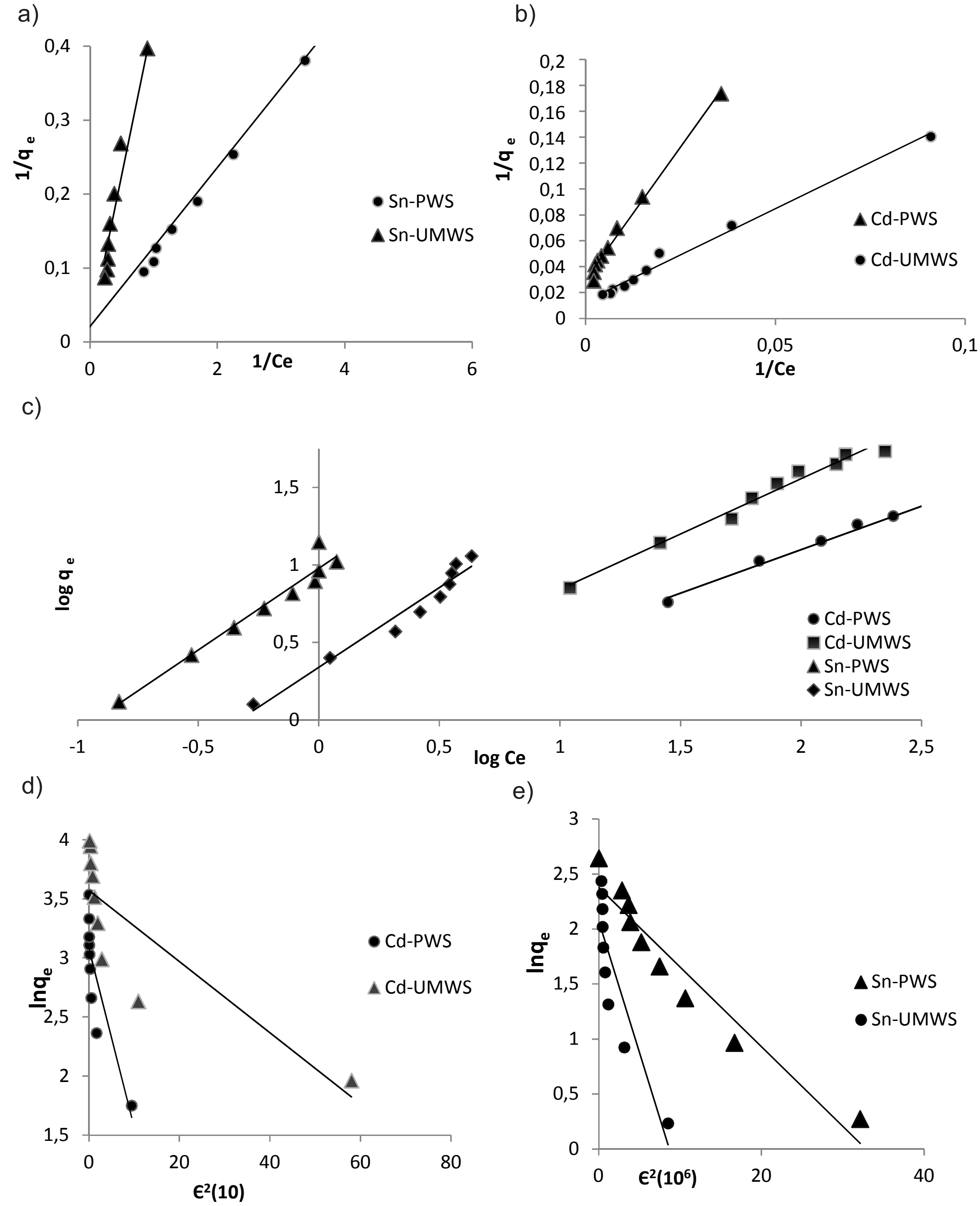

Fig. 5. a) and b) Linear plot of Langmuir isotherm for the adsorption of tin and cadmium metal ions using PWS and UMWS; c) linear plot Freundlich isotherm model for biosorption of cadmium and tin using PWS and UMWS; d) and e) Linear plot of D-R model for biosorption of cadmium and tin metal ions on PWS and UMWS.

(Figs. 5a and b). Values of $q_{max}$ for cadmium and tin metal ions with PWS are 33.55 (mg/g) and 47.84 (mg/g), respectively. The $q_{max}$ values with UMWS for cadmium and tin metal ions are 74.62 (mg/g) and 64.10 (mg/g), respectively. Results showed there is an increase in amount of 41.07 (mg/g), more than 100%, for cadmium and 16.26 (mg/g), about 70%, for tin metal ions while moving from PWS to UMWS, respectively. The significant increase in metal uptake amount shows that UMWS has greater ability of biosorption compared to PWS. The coefficient of determination ($R^2$) values is equal to or greater than 0.98 for both metal ions, which again shows the better fit of the Langmuir isotherm followed by the monolayer homogenous adsorption process.

Significant characteristics of Langmuir isotherm model can be represented by a dimensionless constant called equilibrium parameter ($R_L$). The $R_L$ values describe the shape and feasibility of Langmuir isotherm model. The mathematical expression for $R_L$ is [28, 29]:

$$R_L = \frac{1}{1+bC_o} \tag{3}$$

...where $b$ (L/mg) is sorption coefficient and $C_o$ is the initial metal ion concentration (mg/L). The value of $R_L$ calculated for both cadmium and tin metal ions is represented in Table 2. Results shows that all the values for both biosorbents, PWS and UMWS, are greater than zero and less than one, which describes Langmuir isotherm model as favorable. As Value of $R_L > 1$ indicates, the isotherm model is unfavorable; $R_L$=1 indicates it is linear; $0<R_L<1$ shows the model is favorable; and $R_L$=0 irreversible [18, 30].

The linear form of Freundlich isotherm can be represented as:

$$log q_e = \ log K_f \ + \frac{1}{n} log C_e \tag{4}$$

An empirical equation of Freundlich isotherm model described the adsorption by a heterogeneous surface [29-31]. Where $n$ is an empirical parameter depending upon the extent of heterogeneity, $K_f$ (L/g) is a binding constant that depends upon maximum adsorption capacity and empirical factor 1/$n$ related to the intensity of adsorption. Values of $n$ and $K_f$ were calculated from the slope and intercept of the linear Freundlich plot of log $q_e$ versus log $C_e$ using equation 4 (Fig. 5c). Table 2 represents values of 1/$n$, $K_f$, $R^2$ and $n$ for the Freundlich isotherm. Values of $n$ (1.78, 1.40) and 1/$n$ (0.56, 0.71) for cadmium metal ions using PWS and UMWS, respectively, shows the favorability of the Freundlich isotherm model. Whereas for tin metal ions values of $n$ (0.94, 0.97) and 1/$n$ (1.05, 1.02) using PWS and UMWS, respectively, indicate not a better fit of Freundlich isotherm. As the values of n in the range of 1-10 and 1/$n$, less than 1 shows significant adsorption at low amount of biosorbent. Again, the correlation co-efficient ($R^2$) value for all experiments, which are less than 0.98, revealed that Freundlich isotherm is not a much better fit as compared to Langmuir isotherm.

Dubinin-Radushkevich isotherm (D-R) model applied to analyze whether the nature of cadmium and tin metal ions biosorption using PWS and UMWS is physical or chemical. The linear form of D-R model is:

$$ln\, q_e = ln\, q_{max} - \beta \varepsilon^2 \tag{5}$$

...where $\beta$ (mol$^2$/kJ$^2$) is Dubinin-Radushkevich coefficient linked with mean free energy and $\varepsilon$ is Polanyi potential (J/mol). Values of $\beta$ and $q_{max}$ were calculated using linear plot of ln$q_e$ versus $\varepsilon^2$ (Figs. 5d and e). Here:

$$\varepsilon = RTln(1 + \frac{1}{C_e}) \tag{6}$$

The $q_{max}$ values for cadmium and tin metal ions using PWS are 21.75 mg/g and 7.97 mg/g, whereas 35.0 mg/g and 10.80 mg/g by using UMWS, respectively. The mean free energy ($E_s$) of biosorption for cadmium and tin using PWS and UMWS was calculated using equation 7.

$$E_S = \frac{1}{\sqrt{2\beta}} \tag{7}$$

The values of $E_s$ were calculated as 0.05 and 0.129 using PWS, whereas 1.58 and 2.67 KJ/mol fused UMWS for cadmium and tin metal ions, respectively (Table 2). Results show adsorption of cadmium and tin on PWS and UMWS is just a type of physical adsorption. The adsorption process will be chemisorptions for $8 < E_s < 16$ kJ/mol and physical adsorption for $E_s < 8$ kJ/mol. The values of coefficient of determination ($R^2$) show a poor fit of the data to the Dubinin-Radushkevich model as compared to two other models [18, 19]. As this model is not being followed by the biosorption system, the nature of biosorption is not ultimate. Further studies are required to establish the fact about the nature of biosorption. Overall data shows a better fit for Langmuir model as determined by the values of coefficient of determination. Hence the process occurs at some homogenous sites on the biosorbent used in the monolayer biosorption process.

## Adsorption Thermodynamics

An increase or decrease in temperature causes a change in metal ions uptake efficiency. This is very significant to analyze the mechanism and suitability of biosorption by its free energy change ($\Delta G^o$), entropy change ($\Delta S^o$), and enthalpy change ($\Delta H^o$). These factors can also help to determine the feasibility and spontaneity of the adsorption process [32]. The apparent equilibrium constant of biosorption is given as [33]:

$$K_C = \frac{C_{\alpha d,e}}{C_e} \tag{8}$$

...where $C_{\alpha d,e}$ (mg/L) is concentration of adsorbate on adsorbent at equilibrium. By using $K_c$ we determined the value of $\Delta G^o$ as:

$$\Delta G^o = -RTln\,K_c \tag{9}$$

Enthalpy and entropy change can be determined by Vant's Hoff equation:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{10}$$

...where $R$ (kJ/mol K) is general gas constant, $\Delta G^o$ (kJ/mol) is the standard free energy, and $\Delta S^o$ (J/mol·k) is standard entropy change. Fig. 6a shows a change in percentage removal of metal ions with respect to temperature. There is a 30-40% increase in metal removal efficiency from 293K to 313K (Fig. 6a) showing that the adsorption process is endothermic and feasible for relatively hot waters. As industrial waste waters are released at relatively high temperatures, so the endothermic nature of the process under study may get the attraction of engineers to develop treatment technology using biomass from Triticum for Cd(II) and Sn(II) ions. A decrease in percentage removal of metal ions after optimum temperature may be due to the fact that K.E. particles move with greater speed, and interaction between adsorbent-adsorbate decreased [34].

Fig. 6b shows a Linear plot of $\Delta G^o$ versus temperature. Change in enthalpy and entropy were calculated by intercept and slope using equation 10. Results show that the value of $\Delta G^o$ decreased with an increase in temperature, indicating a better adsorption at relatively elevated temperatures. Positive value of $\Delta H^o$ represents that process is endothermic, which again supports greater adsorption at high temperatures. Value of $\Delta S^o$ is also positive for all parameters showing an increase in randomness and spontaneity of the adsorption process (Table 3). The positive value of $\Delta S^o$ also confirmed change in biomass structure and replacement of other molecules previously adsorbed or already present, which causes increased randomness at solid-solute interface [35, 36].

Table 3. Values of thermodynamic parameters of cadmium and tin adsorption on PWS and UMWS.

| Metal | Temperature (K) | $K_D$ (L/g) | $\Delta G^o$ (kJ/mol) | $\Delta H^o$ (kJ/mol) | $\Delta S^o$ (J/mol·K) |
|---|---|---|---|---|---|
| Cd (PWS) | 293 | 1.36 | -0.76 | +5.90 | +61.2 |
| | 303 | 2.10 | -1.87 | | |
| | 313 | 2.77 | -2.65 | | |
| | 323 | 2.66 | -2.63 | | |
| Sn (PWS) | 293 | 1.74 | -1.35 | +1.16 | +45.2 |
| | 303 | 2.44 | -2.25 | | |
| | 313 | 2.76 | -2.64 | | |
| | 323 | 2.76 | -2.73 | | |
| Cd (UMWS) | 293 | 2.77 | -2.48 | +7.53 | +266 |
| | 303 | 7.88 | -5.20 | | |
| | 313 | 7.91 | -9.81 | | |
| | 323 | 8.21 | -9.83 | | |
| Sn (UMWS) | 293 | 3.37 | -2.96 | +6.53 | +233 |
| | 303 | 6.04 | -4.53 | | |
| | 313 | 12.4 | -8.97 | | |
| | 323 | 13.6 | -9.25 | | |

## Adsorption Kinetics-Time Factor

To elaborate adsorption kinetics it is required to study metal ion removal efficiency with change in time of contact, as equilibrium time is very significant to study the effectiveness of the biosorbtion process. Fig. 7 shows the effect of contact time on the biosorption of Cd(II) and Sn(II) metal ions by PWS and UMWS. Results revealed that there is a rapid increase in amounts of metal uptake in the first 20 minutes, i.e., almost 20-25% using PWS and 30-35% using UMWS, followed by equilibrium state in the first 100 minutes, which is the optimum time. UMWS shows 30% greater removal efficiency as compared to PWS as already described in the effect of biosorbent amount and effect of agitation speed sections. Maximum sorption capacity initially can be due to the presence of more sorption sites [37].

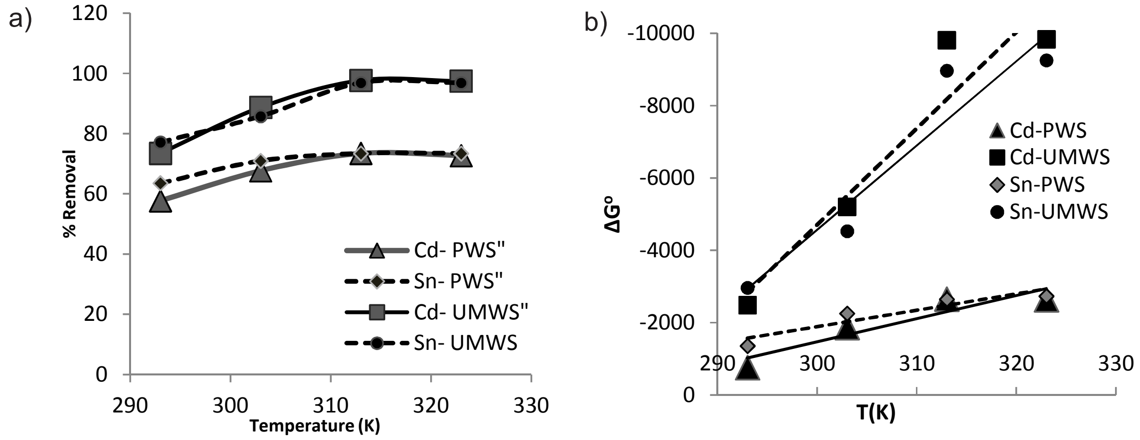

Fig. 6 a) Effect of temperature on % Removal of cadmium and tin using PWS and UMWS; b) Graph versus Gibbs free energy and temperature, thermodynamic parameters.

Table 4. Values and constants for kinetics models for biosorption of cadmium and tin metal ions using PWS and UMWS.

| Biosorbent Type | | PWS | | UMWS | |
|---|---|---|---|---|---|
| Heavy Metals | | Cd | Sn | Cd | Sn |
| Pseudo 1st-order | Slope | -0.005 | -0.003 | -0.008 | 0.006 |
| | Intercept | 0.537 | 0.089 | 0.446 | -0.139 |
| | $R^2$ | 0.328 | 0.153 | 0.259 | 0.882 |
| | $K_1$ ($min^{-1}$) | 0.005 | 0.003 | 0.008 | -0.006 |
| | $q_e$ (mg/g) | 3.44 | 1.22 | 2.79 | 1.37 |
| | $q_e$ Experimental (mg/g) | 11.8 | 2.98 | 15.68 | 4.00 |
| Pseudo 2nd-order | $R^2$ | 0.98 | 0.97 | 0.99 | 0.99 |
| | Slope | 0.079 | 0.343 | 0.006 | 0.256 |
| | Intercept | 1.505 | 3.017 | 0.028 | 0.878 |
| | $K_2$ (mg/g·min) | 0.0042 | 0.0391 | 0.1556 | 0.0748 |
| | $q_e$ (mg/g) | 12.51 | 2.91 | 15.15 | 3.90 |
| IPD Model | $R^2$ | 0.2961 | 0.7591 | 0.0009 | 0.8346 |
| | Slope | 0.446 | 0.069 | -0.010 | 0.0712 |
| | Intercept | 6.125 | 2.347 | 13.88 | 2.706 |
| Bangham's Model | $R^2$ | 0.4204 | 0.7419 | 0.0031 | 0.8475 |
| | $K_0$ [mL/(g/L)] | 11.51 | 6.57 | 14.77 | 6.71 |
| | $\alpha$ | 0.4494 | 0.2382 | 0.0206 | 0.3049 |

Four different models were applied to study biosorption reaction kinetics in detail.

The linear equation for Lagergren's pseudo 1st-order is [37]:

$$ln\,(q_e - q_t) = lnq_e - k_1 t \tag{11}$$

...where $q_e$ (mg/g) is the amount of metal adsorbed at equilibrium and $q_t$ (mg/g) is the amount of metal adsorbed at a particular time $t$, $k_1$ (1/min) and is the 1st-order rate constant. Values of $q_e$ and $k_1$ were calculated by intercept and slope of linear plot between ln($q_e$-$q_t$) and time using equation 11 (Fig. 8a). Results show that there is greater difference between the amounts of metal uptake as calculated by pseudo 1st-order ($q_{cal}$) and the experimental metal uptake ($q_{exp}$). The value of coefficient of determination ($R^2$) also shows (Table 4) not a better follow of pseudo 1st order kinetics for the biosorption of cadmium and tin metal ions using PWS and UMWS.

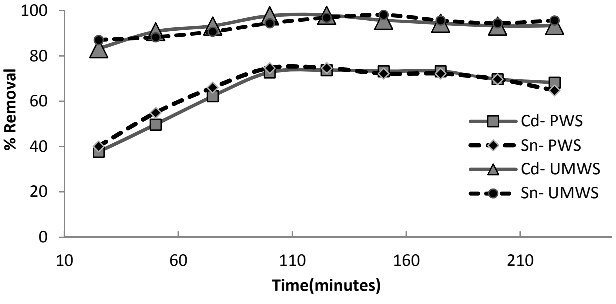

Fig. 7. Effect of Time of contact on biosorption of cadmium and tin metal ions using PWS and UMWS.

Ho and McKay's pseudo 2nd-order linear equation is [37]:

$$\frac{t}{q_t} = \frac{1}{k_2(q_e)^2} + \frac{t}{q_e} \tag{12}$$

...where $k_2$ (mg/g·min) is the 2nd-order rate constant. Rate constant for pseudo 2nd-order can be determined by linear plot of $t/q_t$ versus $t$, which gives slope equal to $1/q_e$ and intercept as $1/k_2(q_e)^2$ (Fig. 8b). The amount of metal uptake ($q_e$) for 2nd-order kinetics were also measured, which are very close to experimental metal uptake ($q_{exp}$) values, which shows reaction following this kinetic model (Table 4). Values of correlation factor ($R^2$) are 0.98, 0.97, 0.99, and 0.99 for cadmium and tin metal ions using PWS and UMWS, which again show a better fit of the equilibrium data for pseudo 2nd-order kinetics [18, 23, 25].

To determine the rate-controlling step of biosorption of cadmium and tin metal ions using PWS and UMWS, intraparticle diffusion model was applied. The linear equation for intra-particle diffusion model is represented as:

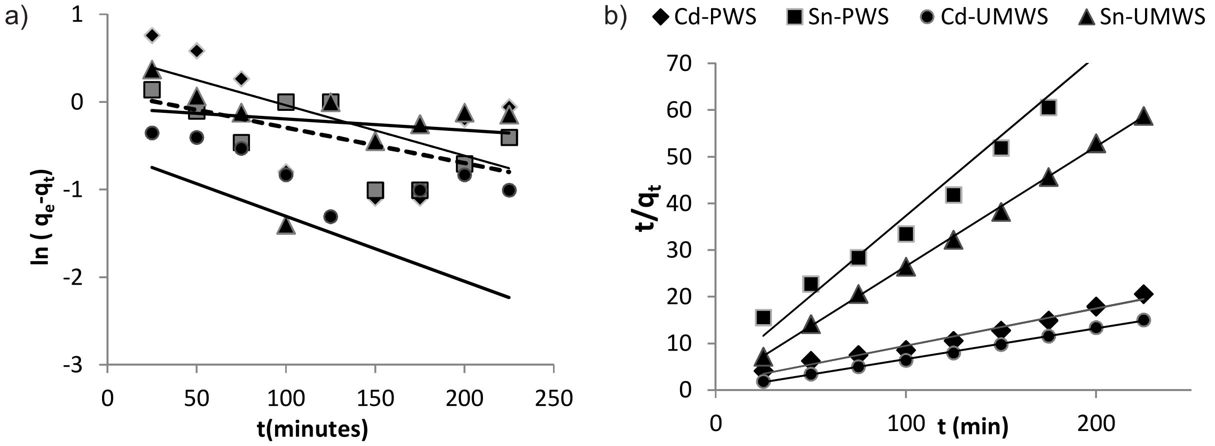

Fig. 8. a) Linear plot of Lagergren's pseudo 1st-order kinetics, b) A Linear plot of Ho & Mckays pseudo 2nd-order kinetics for bisorption of cadmium and tin metal ions on PWS and UMWS.

$$q_t = k_{int}\, t^{1/2} + c \tag{13}$$

...where $q_t$ (mg/g) is the amount of metal adsorbed for a particular time $t$, $k_{int}$ (mg·g$^{-1}$·min$^{-1/2}$) is intra-particle rate constant and c is the intercept. The multi linearity in the plot may represent the possibility of three steps. The first sharper portion represents the diffusion of solute particles through boundary layer or diffusion of adsorbate (metal ions) from solution to the surface of adsorbent. Then there is a gradual adsorption stage in the 2nd step where the rate-limiting step is intra-particle diffusion. Then there is a slow-down of the process attributed to low solute concentration in the third portion [5, 6, 11]. According to intra-particle diffusion model, if intra-particle diffusion is involved then the plot of metal uptake amount ($q_t$) versus $t^{0.5}$ must be linear. Intra-particle diffusion will be the rate-determining step if a straight line passes through the origin. Intra-particle diffusion may not be the only rate-determining step and rate of adsorption may be controlled somehow through boundary layer control if a straight line does not pass through the origin [38]. The rate parameter ($K_p$) for intra-particle diffusion can be derived using slop of the linear portion from the plot. Ideas about thickness of boundary layer may be obtained by the intercept of linear plot, i.e., the boundary layer effect increases with increasing intercepts [5, 39]. Fig. 9a shows a linear plot of $q_t$ versus $t^{0.5}$ for the biosorption of cadmium and tin metal ions using PWS and UMWS. The straight-line portion of linear plot for cadmium metal ions shows macro pore diffusion and utilization of readily available adsorbing sites on the surface of biomass. Whereas for tin metal ions it shows boundary layer control, which may be due to the greater size of tin ions as compared to cadmium ions [40].

Bangham's model was applied to confirm whether adsorption of metal ions is diffusion-controlled or not [40]. The linear form of Bangham's model can be written as:

$$\left[\log\left\{\log\left(\frac{C_o}{C_o - q_t m}\right)\right\}\right] = \log\left(\frac{K_o m}{2.303V}\right) + \alpha \log(t) \tag{14}$$

...where $C_o$ shows initial adsorbate concentration (mg/L), $q_t$ is the amount of metal uptake (mg/g) at time $t$, $V$ is the volume of solution (mL), $m$ is weight of the biomass, and $\alpha$ and $K_o$ [mL/(g/L)] are constants. Values of $\alpha$ and $K_o$ were calculated from linear plot of [log{log ($C_o$/$C_o$-$q_t m$)}] versus $t$ (Fig. 9b). The values of coefficient of determination ($R^2$)

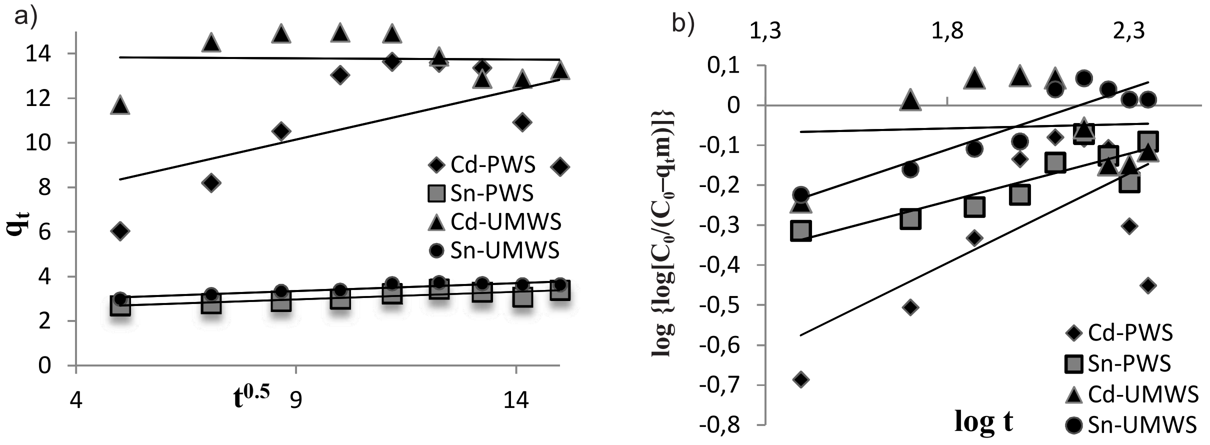

Fig. 9. a) Linear plot of intra-particle diffusion model, b) A Linear plot of Bangham's model for bisorption of cadmium and tin metal ions on PWS and UMWS.

values show equilibrium data is a poor fit to Bangham's model and biosorption of metal ions on pores of the surface of PWS and UMWS is not the only rate-determining step (Table 4).

## Conclusion

Our study revealed that biosorption capacity of both pre-treated wheat straw (PWS) and urea-modified wheat straw absorbents is very high for the removal of Cd(II) and Sn(II) metal ions. However, UMWS shows greater metal removal efficiency as compared to PWS due to modification in functional groups as confirmed by FTIR analysis. Urea was used in modification as it is easily available and economical. Modification with urea is also eco-friendly as its degradation further enhances the nitrogen content of the soil and fertility. Furthermore, urea causes the addition of some lone pair carriers' functional groups in biomass on modification. These groups, which have a lone pair of electrons, act as ligands and enhance the metal binding process and amount of metal adsorbed finally. Metal ions removal efficiency can further increase by further modification of its functional groups through novel methods. Isotherm models were applied, which proved homogenous single layer adsorption. The order of fit of isotherm as determined by coefficient of determination was Langmuir < Freundlich < Dubinin-Radushkevich models. Kinetics models explained that biosorption of cadmium and tin metal ions using both PWS and UMWS followed pseudo 2nd-order kinetics. Intraparticle diffusion mechanism also was proven by intra-particle diffusion model whereas experimental data was not a better fit on Bangham's model. Thermodynamic parameters showed that biosorption of cadmium and tin metal ions are spontaneous and endothermic. Hence, overall it proves that PWS and UMWS are good biosorbents for removal of cadmium and tin metal ions.

## References

1. ARIEF VO., TRILESTARI K., SUNARSO J., INDRASWATI N., ISMADJI S. Recent Progress on Biosorption of Heavy Metals from Liquids Using Low Cost Biosorbents: Characterization, Biosorption Parameters and Mechanism Studies. Clean-Soil Air Water. **36**, (12), 937, **2008**.
2. KRATOCHVIL D., VOLESKY B. Advances in the biosorption of heavy metals. Water Res. **32**, 2760, **1998**.
3. PINO G H., MESQUITA L M S., TOREM M L., PINTO G A S. Biosorption of cadmium by green coconut shell powder. Miner. Eng. **19**, 380, **2006**.
4. MATHEICKAL J T., QIMING Y U., WOODBURN G M. Biosorption of Cadmium (II) from Aqueous Solutions by Pre-Treated Biomass of Marine Algae *Durvillaea Potatorum*. Water Res. **33**, (2), 335, **1999**.
5. WASEWAR KL., KUMAR S., PRASAD B. Adsorption of Tin Using Granular Activated Carbon. J. Environ. Protect. Science. **3**, 41, **2009**.
6. PAZIRANDEH M., WELLS B M., RYAN R L. Development Of Bacterium-Based Heavy Metal Biosorbents: Enhanced Uptake Of Cadmium And Mercury By *Escherichia Coli* Expressing a Metal Binding Motif. Appl. Environ. Microbio. **64**, (10), 4068, **1998**.
7. MAHVI A H., GHOLAMI FAND., NAZMARA S. Cadmium Biosorption from Wastewater by Ulmus Leaves and their Ash. Eur. J. Sci. Res. **23**, (2), 197, **2008**.
8. VOLESKY B., HOLAN Z R. Biosorption of Heavy Metals. Biotechnol. Prog. **11**, 235, **2008**.
9. DANG V B H., DOAN H D., DANG-VU T., LOHI A. Equilibrium and kinetics of biosorption of cadmium(II) and copper(II) ions by wheat straw. Bioresource Technol. **100**, 211, **2009**.
10. FIGUERA MM., VOLESKY B., AZARIAN K., SIMINELLI V S Y. Biosorption column performance with metal mixture. Environ. Sci. Technol. **34**, 4320, **2009**.
11. PREETHA B., VIRUTHAGIRI T. Biosorption of zinc (II) by *Rhizopus arrhizus*: equilibrium and kinetic modeling. African J. Biotechnol. **4**, (6), 506, **2005**.
12. ERGOZHIN., EE., KALIEVA BK., NIKITINA AI., KABULOVA GK., BEKTENOV NA. New Phosphorus-Containing Sorbents Based On Wheat Straw and Glycidyl Methacrylate For $Hg^{2+}$ Removal. Russ. J. Appl. Chem. **83**, (6), 965, **2010**.
13. ARVELAKIS S., CROCKER C., FOLKEDAHL B., PAVLISH J., SPLIETHOFF H. Activated Carbon from Biomass for Mercury Capture: Effect of the Leaching Pretreatment on the Capture Efficiency. Energy Fuels. **24**, 4445, **2010**.
14. ZHANG W., YAN H., LING H., JIANG Z., DONG L., KAN X., YANG H., LI A., CHENG R. Removal of dyes from aqueous solutions by straw based adsorbents: Batch and column studies. Chem. Eng. J. **168**, (3), 1120, **2011**.
15. PIETROBELLI J M T A., MÓDENES A N., FAGUNDES-KLEN M R., ESPINOZA-QUIÑONES F R. Cadmium, Copper and Zinc Biosorption Study by Non-Living Egeria densa Biomass. Water Air Soil Poll. **202**, 385, **2009**.
16. SAIKAEW W., KAEWSARN P., SAIKAEW W. Agricultural Waste for Biosorption of Cadmium Ions from Aqueous Solutions. World Academy Sci. Eng. Technol. **56**, 287, **2009**.
17. TERRY P.A., STONE W. Biosorption of cadmium and copper contaminated water by Scenedesmus abundans. Chemosphere. **47**, 249, **2002**.
18. FARROQ U., KOZINKSI J., KHAN MA., ATHAR M. Biosorption of heavy metal ions using wheat straw biosorbent – A Review of the recent literature. Bioresource Technol. **101**, (14), 5043, **2010**.
19. FAROOQ U., KHAN MA., ATHAR M., SAKINA M., AHMAD M. Environmentally Benign Urea-modifed *Triticum aestivum* Biomass for Lead (II) Elimination from Aqueous Solutions. Clean-Soil, Air, Water. **38**, 49, **2010**.
20. MUHAMAD H., DOAN H., LOHI A. Batch and continuous fixed-bed column biosorption of $Cd^{2+}$ and $Cu^{2+}$. Chem. Eng. J. **158**, **2010**.
21. FILIPOVIC-KOVACEVIC Z., SIPOS L., BRISKI F. Biosorption of Chromium, Copper, Nickel and Zinc Ions onto Fungal Pellets of *Aspergillus niger* 405 from Aqueous Solutions. Food Tech. B. **38**, (3), 211, **2000**.
22. LAWTHER J M., SUN R., BANKS B. Extraction, fractionation and characterization of structural polysaccharides from wheat straw. J. Agric. Food Chem. **43**, 667, **1995**.
23. GARDEA-TORRESDEY JL., BECKER-HAPAK MK., HOSEA JM., DARNALL DW. Effect of chemical modification of algal carboxyl groups on metal ion binding. Environ.Sci. Technol. **24**, 1372, **1990**.

24. KADIRVELU K., THAMARAISELVI K., NAMASIVAYAM C. Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Bioresource Technol. **76**, 63, **2001**.
25. SURYAN S., AHLUWALIA S S. Biosorption of heavy metals by paper mill waste from aqueous solution. Int. J. Environ. Sci. **2**, (3), 1331, **2012**.
26. EL-SAYED G.O., DESSOUKI H.A., IBRAHI S.S. Bio-Sorption of Ni (II) and Cd (II) Ions from Aqueous Solutions onto Rice Straw. Chem Sci J. **9**, 1, **2010**.
27. HAN R., ZHANG L., SONG C., ZHANG M., ZHU H., ZHANG L. Characterization of modified wheat straw, kinetic and equilibrium study about copper ion and methylene blue adsorption in batch mode. Carbohydrate Polymers. **79**, 1140, **2010**.
28. MCKAY G., BLAIR H.S., GARDENER JR. Adsorption of dyes on chitin I Equilibrium studies. J. App Polymer sci. **27**, 3043, **1982**.
29. BAIG K.S., DOAN H.D., WU J. Multicomponent isotherms for biosorption of $Ni^{2+}$ and $Zn^{2+}$. Desalination. **249**, 429, **2009**.
30. HALL K.R., EAGLETON LC., ACRIVOS A., VERMEULEN T. Pore- and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. Ind. Eng. Chem. Fund. **5**, 212, **1966**.
31. LADEIRA A C. Q., CIMINELLI V S. T. Adsorption and desorption of arsenic on an oxisol and its constituents. Water Res. **38**, 2087, **2004**.
32. BREIEROVA E., VAJCZIKOVA I., SASINKOVAV., STRATILOVA E., FISERA M., GREGOR T., SAJBIDOR J. Biosorption of Cadmium Ions by Different Yeast Species. Z. Naturforch. Pak. J. Phytopathol. **57**, (C), 634, **2002**.
33. PATTANAYAK J., MONDAL K., MATHEW S., LALVANI S B. A parametric evaluation of the removal of As(V) and As(III) by carbon based adsorbents. Carbon. **38**, 589, **2000**.
34. YANG J., VOLESKY B. Bio-sorption Of Uranium on Sargassum Biomass. Water Res. **33**, (15), 3357, **1999**.
35. ARBANAH M., MIRADATULNAJWA MR., KUHALIM KH. Biosorption of Cr(III), Fe(II), Cu(II) and Zn(II) Ions from Liquid Laboratory Chemical Waste by *Pleurotus ostreatus*. Int. J. Biotech. Well. Indus. **1**, 152, **2012**.
36. XIAO X., LUO S., ZENG G., WEI W., WAN Y., CHEN L., GUO H., CAO Z., YANG L., CHEN J., XI Q. 36. Biosorption of cadmium by endophytic fungus (EF) Microsphaeropsis sp. LSE10 isolated from cadmium hyperaccumulator *Solanum nigrum* L. Bioresource Technol. **101**, 1668, **2010**.
37. HO YS., M CKAY G. Kinetic model for the sorption of dye from aruous solution by wood. Process safety Env. Prot. **76**, (B), 183, **1998**.
38. BAILEY S. E., OLIN T. J., BRICKA R. M., ADRIAN D. D. A review of potentially low-cost sorbents for heavy metals. Water Res. **33**, 2469, **1999**.
39. GUIBAL E., MILOT C., TOBIN J.M. Metal-anion sorption by chitosan beads: equilibrium and kinetic studies. Industrial and engineering chemistry Res. **37**, 1454, **1998**.
40. SUBHA R., NAMASIVAYAM C. Modelling of adsorption isotherms and kinetics of 2, 4, 6-trichlorophenol onto micro porous $ZnCl_2$ acticated coir pith carbon. J. Env. Engg. **18**, (4), 275, **2008**.