

Simultaneous removal of Pb(II), Cd(II) and Cu(II) from aqueous solutions by adsorption on *Triticum aestivum* – a green approach

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Abstract

The presence of heavy metals in industrial effluents as a single component is generally very rare. The present study provides information about adsorption behaviour of lead, cadmium and copper in single and multi-component system using *triticum aestivum* (wheat straw) as adsorbent. It has been shown that adsorption of a certain metal ion is greatly affected by the presence of other metal ions. Effects of process parameters (adsorbent dose, contact time, pH, agitation speed etc.) have been studied. pH 4-6 have been found suitable for metal removal. Adsorption mechanism has been evaluated using five adsorption isotherm models (Langmuir, Freundlich, Temkin, Harkin-Jura and Halsey Isotherms). Removal of cadmium in multi-component system is greater as compared in single component system indicating the metal competition for adsorption sites. Kinetic and thermodynamic parameters have also been calculated and obtained results were found closely related to the reported literature. Positive values of ΔH° for lead, cadmium and copper shows feasibility of the process and the spontaneous nature of adsorption.

Keywords: *Triticum aestivum*; Multi-component adsorption; Adsorption isotherms; Second-order kinetics; Thermodynamics; Activation energy

Introduction

Heavy metals are considered to be major source causing both water and soil pollution and their levels are increasing day by day [1]. Industrial activities continuously release heavy metals to the aquatic environment which are considered to be highly toxic and may seriously damage natural aqueous environment [2,3].

Among the heavy metals, cadmium is considered to be one of the most toxic. Cadmium pollution in environment is due to various industrial sources such as electroplating, smelting, pigments, plastics, battery, mining and refining processes [4,5]. Due to its bioaccumulation property, cadmium is recognized as a human carcinogen [6]. Intake in very small amounts can also cause health problems such as hypertension. The permissible USEPA limit of divalent cadmium ions in water is 5ppb [7].

Lead, another heavy metal, has been regarded as a persistent environmental pollutant [8]. Inorganic lead arising from a number of industrial and mining sources occur in water in the divalent state [9]. Almost all of its compounds are considered to be toxic which usually affects the gastrointestinal tract and nervous system [10]. The Permissible limit setted by USEPA is 5ppb.

Copper is one of the most widely used metals and is reported to be present in metal bearing industrial effluents [11]. The suggested USEPA limit of cupric ions in industrial effluents is 1.3ppm [12]. Long term exposure causes irritation of nose, mouth and eyes, stomachache, neurotoxicity and lung cancer [13].

Various conventional methods widely utilized for the removal of these heavy metals from waste water includes reduction, precipitation, ion-exchange, filtration, electrochemical treatment etc. [14-17]. Most of these methods are either costly or ineffective for metals removal especially when metals are present in large volumes of water at relatively low concentration [18].

The search for cost-effective technologies involving the removal of toxic metals from water has attracted attention to adsorption [19,20].

The noticeable advantages of this method are high metal removal efficiency, low investment and operational cost, minimization of chemical sludge and regeneration of the adsorbent. Mechanism of adsorption involves ion exchange, chelation and surface binding by physical and chemical linkages. Agricultural wastes have proved to be very useful and low cost adsorbents for the removal of metals [21]. The interaction between adsorbent and metal occurs due to the presence of polymeric groups like cellulose, pectin, proteins etc.[22].

Wheat straw (*Triticum aestivum*) is one of the low cost adsorbent chiefly available in Pakistan. Its cellulosic structure makes it a natural biopolymer with ion exchange property, hence makes it good adsorbent for metal ions. Some varieties of it have already been used for metal adsorption [23,24].

In the present study, an effort had been made to remove lead, cadmium and copper from industrial waste water using wheat straw as adsorbent. The preliminary study included the condition optimization (contact time, adsorbent dose, pH, agitation speed and temperature) for these metals individually as well as when simultaneously present in synthetic samples as the presence of only one metal ion in natural waters is very rare. Multi-component solutions are also mostly encountered in industrial operation mode systems releasing a mixture of heavy metals in industrial wastewater. Thus need arises to investigate the adsorption behavior of heavy metals from multi-component solutions in order to pursuit the industrial wastewater treatment problems. The difference in single component and multi-component adsorption was taken into account in this study. The obtained equilibrium data was evaluated

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Received July 04, 2011; Accepted August 09, 2011; Published August 31, 2011

Citation: Ali SZ, Athar M, Salman M, Din MI (2011) Simultaneous removal of Pb(II), Cd(II) and Cu(II) from aqueous solutions by adsorption on *Triticum aestivum* – a green approach. Hydrol Current Res 2:118. doi:10.4172/2157-7587.1000118

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using various adsorption isotherms models i.e. Langmuir, Freundlich, Harkin-Jura, Temkin and Halsey. Kinetic and thermodynamic studies were also used to evaluate adsorption mechanism.

Material and Methods

Preparation of adsorbent

Wheat straw was collected from local markets of Lahore, Pakistan. It was then washed to remove dust and particles other than wheat straw and then air dried. Dried wheat straw was then ground to mesh range 40-60 (ASTM). It was then washed with distilled water for further purification from any foreign material and then oven dried at 105-110°C.

Stock solution and standards

Stock solutions (1000mg/L) of Pb(II), Cd(II) and Cu(II) were prepared by using appropriate quantities of lead nitrate (Merck), cadmium nitrate (Merck) and copper nitrate (Sigma-Aldrich). Standard solutions Pb(II), Cd(II) and Cu(II) of desired concentrations (5-50mg/L) were prepared by successive dilutions of their respective stock solutions.

Equipment and apparatus

Digital pH-meter (HANNA, Model-8417) was used for pH adjustments. HCl (0.1M), NaOH (0.1M) along with standard buffers were used to maintain the desired pH. Perkin Elmer atomic absorption spectrometer (Model-AAAnalyst 100) was used to determine the concentrations of Pb, Cd and Cu at 283.3nm, 228.8nm and 324.8nm. FTIR (Perkin Elmer Spectrum-RX1) was used to characterize the adsorbent. Orbital shaker with time control (VORTEX Model-OSM-747) was used for homogenization of reaction mixture.

Study of process parameters

Using the initial concentration of 50mg/L for all three analytes; (Pb(II), Cd(II) and Cu(II)); a series of experiments were performed to check the effects of various process parameters (adsorbent dose, contact time, pH, and agitation speed) on metal adsorption. The effect of a certain parameter was studied by varying it gradually keeping all other parameters constant. The glass ware used in the study was successively washed with acid and distilled water and then oven dried at 105°C for 1h. After adsorption under certain conditions, the contents under observation were filtered and the filtrates were subjected to atomic absorption spectrometer for the analysis of metal ion concentration.

The effect of adsorbent dose was studied by varying the adsorbent amount from 0.2g/50mL to 1.8g/50mL. Variation of pH was made from 1-9 to investigate the optimum pH for metal adsorption. The effect of contact time and agitation speed on metal adsorption was studied under gradually varied conditions of 1-45min and 50-250rpm for contact time and agitation speed respectively. Effect of temperature was also studied for the temperature range 293-353 K.

Study of adsorption isotherms

Solutions of varying concentration (20, 30, 40, 50, 60, 70, 80, and 90mg/L) of all three analytes were prepared by successively diluting their respective stock solutions. Adsorption of metal ions from all these solution was carried out under the optimum conditions obtained from the study of process parameters. Langmuir (Equation 1), Freundlich (Equation 2), Temkin (Equation 3), Harkin-Jura (Equation 4) and Halsey (Equation 5) isotherms were plotted and their corresponding parameters were calculated from their respective plots.

Results and Discussion

Characterization of adsorbent

Ground, dried wheat straw (*Triticum aestivum*) was subjected to FTIR analysis for its characterization in terms of functional groups (adsorption sites). The characteristic functional group present in wheat straw was C=O (1650.8cm⁻¹) as investigated from the data illustrated in Figure 1 [25].

Effect of adsorbent dose

The effect of adsorbent dose on Pb(II), Cd(II) and Cu(II) was studied by varying the adsorbent amount from 0.2 to 1.8g/50mL of all analytes individually at neutral pH for time interval of 15min. Observed trend due to variation in adsorbent dose is illustrated in Figure 2. Maximum adsorption of Pb(II), Cd(II) and Cu(II) were 91.5%, 90.18% and 75.08% for the dose of 0.4g/50mL for lead and 0.6g/50mL for cadmium and copper. The increase in adsorption with the increase in adsorbent dose is due to the fact that more active sites are available for metal adsorption. It was also observed that after certain addition of dose the adsorption of metals decreases or remains constant with further increase in adsorbent dose, which indicated the adsorption mechanism to be reversible and that there exist chemical equilibrium between adsorbent and sorbate.

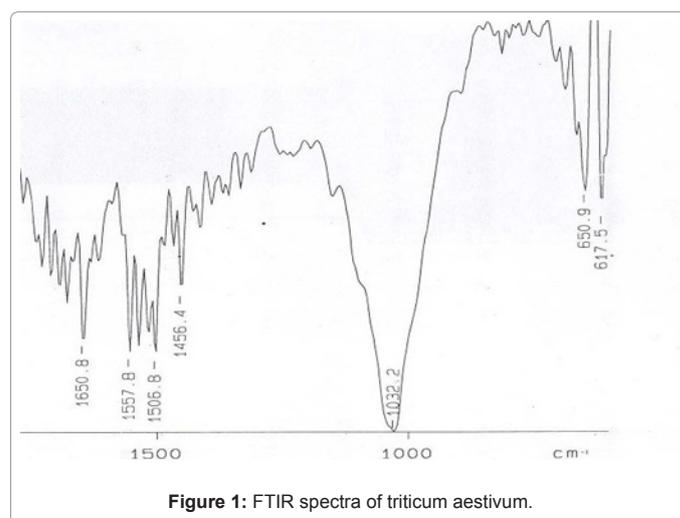


Figure 1: FTIR spectra of triticum aestivum.

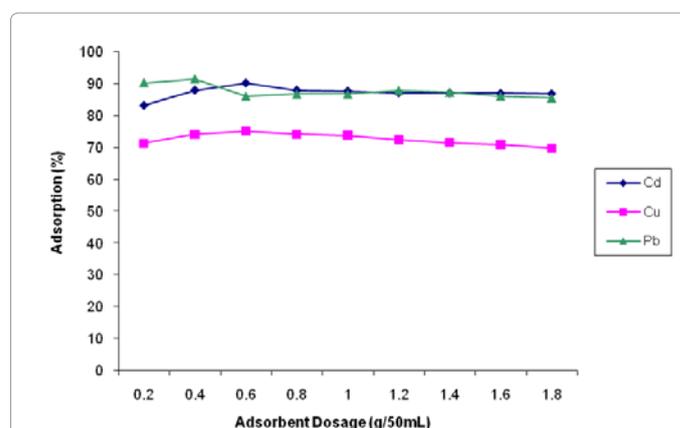


Figure 2: Effect of the adsorbent dose on adsorption of Pb(II), Cd(II) and Cu(II). (metal concentration: 50 mg/L; contact time: 15 min; agitation speed: 100 rpm; temperature: 30°C).

The study also includes the adsorbent dose factor for multi-component system containing all three analytes in same solution in same ratio i.e. 1:1:1. The percentage removal for Pb(II), Cd(II) and Cu(II) (90.30%, 74.72%, 69.46% respectively) showed difference when compared with single component system, which indicated the competition of metal ions for adsorption sites.

Effect of pH and agitation speed: pH is considered as an important parameter in the adsorption studies of metals as it controls the adsorption at the adsorbent-solution interface. It affects both the biomass and the metal ions present in the solution. Experiments were conducted varying the solution pH from 1-9 while rest of the factors were kept constant. The maximum removal of all analytes was observed at pH range 4-6 as illustrated in Figure 3. At basic pH (>7) analytes precipitated out as the respective hydroxides which makes adsorption of these analytes with biomass difficult. Minimum adsorption of analytes was also observed at truly acidic pH range (<3) due to the repulsion of cations with highly protonated adsorbent. The maximum removal efficiency 93.92%, 97.36% and 75% was obtained for Pb(II), Cd(II) and Cu(II), respectively, at pH range 4-6. So conclusion can be made that optimum pH range for the removal of Pb(II), Cd(II) and Cu(II) from a multi-component sample should be 4-6. Almost similar results of optimum pH for Pb(II), Cd(II) and Cu(II) binding for various adsorbents have been reported [24,26,27].

Experiments were also conducted to check the effect of agitation speed on adsorption of metal ion and shown in Figure 4. Optimum agitation speed for Pb(II) and Cd(II) was found to be 100 rpm, and for Cu(II) 75 rpm with percentage adsorption as 91.5%, 88.76% and 79.6%, respectively. It is because at very slow agitation speed the adsorbent accumulates at the bottom reducing the contact surface area of the adsorbent with sorbate. Also at very high speed, centrifugal forces operate resulting in desorption of the adsorbate.

Adsorption isotherms: Adsorption mechanism and relationship between the concentration of the sorbed ions and adsorption capacity of adsorbent were investigated using various adsorption isotherm models.

Langmuir (Equation 1), Freundlich (Equation 2), Temkin (Equation 3), Harkin-Jura (Equation 4) and Halsey (Equation 5)

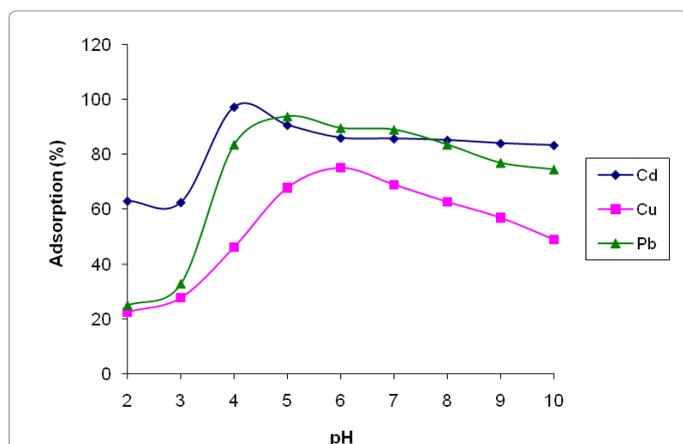


Figure 3: Effect of pH on adsorption of Pb(II), Cd(II) and Cu(II) onto raw wheat straw. (metal concentration: 50 mg/L; contact time: 15 min; agitation speed: 100 rpm; temperature: 303 K; dose: 0.4g/50mL for Pb(II), 0.6g/50mL for Cd(II) and Cu(II)).

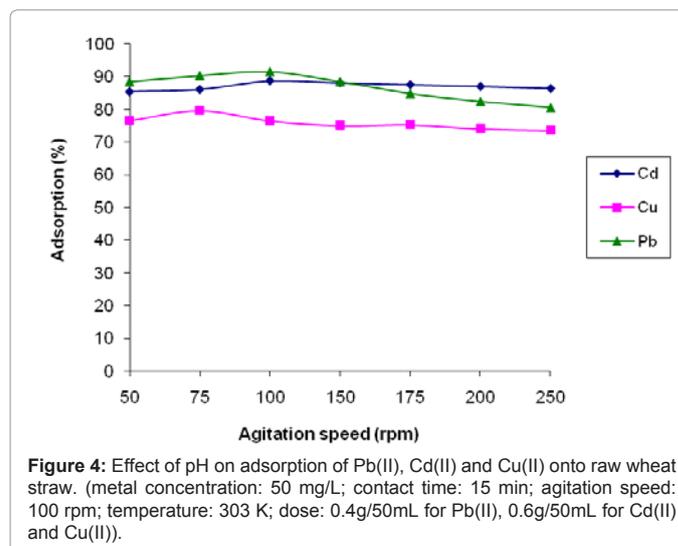


Figure 4: Effect of pH on adsorption of Pb(II), Cd(II) and Cu(II) onto raw wheat straw. (metal concentration: 50 mg/L; contact time: 15 min; agitation speed: 100 rpm; temperature: 303 K; dose: 0.4g/50mL for Pb(II), 0.6g/50mL for Cd(II) and Cu(II)).

isotherms were used for the said purpose and their respective linear forms are as under:

$$C_e / q_e = C_e / q_{\max} + 1 / b q_{\max} \quad (1)$$

$$\log q_e = \log K_f + 1 / n \log C_e \quad (2)$$

$$q_e = K_T \ln C_e + B_T \quad (3)$$

$$1 / q_e^2 = B / A - 1 / A \log C_e \quad (4)$$

$$\ln q_e = 1 / n \ln K - 1 / n \ln C_e \quad (5)$$

where q_e and q_{\max} are the equilibrium and maximum uptake capacities (mg/g), respectively. b is related to free energy of adsorption and represents the Langmuir adsorption constant. C_e is the equilibrium metal ion concentration in solution (mg/L). K_f is the Freundlich constant related to adsorption capacity (mg/g) while $1/n$ represents the adsorption intensity. B_T and K_T are Temkin isotherm parameters; B_T (kJ/mol) gives the idea of heat of adsorption.

Adsorption isotherm studies for Pb(II), Cd(II) and Cu(II) were carried using multi-component system containing these ions in the ratio 1:1:1. The equilibrium data was analyzed by regression analysis to evaluate the goodness of fit for Langmuir, Freundlich, Temkin, Harkin-Jura and Halsey isotherm models. Adsorption isotherm parameters are illustrated in Table 1 for all the isotherm models calculated from the respective plot along with their correlation coefficients.

Monolayer coverage of adsorbate on the outer surface of the adsorbent is predicted by the Langmuir isotherm model [28]. Correlation coefficients, 0.96, 0.86 and 0.89, for all the analytes; Pb(II), Cd(II) and Cu(II), respectively shows the goodness of fit for the Langmuir model. Maximum uptake capacities for Pb(II), Cd(II) and Cu(II) were 3.865 mg/g, 4.746 mg/g and 4.585 mg/g which indicate that in multi-component system cadmium uptake is greater as compared to copper and lead.

Freundlich model was investigated for adsorption capacity (K_f) and adsorption intensity (n). K_f values as calculated from the intercept were 1.8×10^{-3} mg/g, 1.07 mg/g and 1.66 mg/g for Pb(II), Cd(II) and Cu(II) respectively, showing appreciable affinity of raw wheat straw for cadmium and copper as compared to lead. The value of n ranging from 1-10 shows favorable adsorption [29]. 'n' value for Pb(II), Cd(II) and

	Single Component System			Multi-component system		
Metal	R ²	q _{max} (mg/g)	b	R ²	q _{max} (mg/g)	b
Langmiur Isotherm Parameters						
Lead	0.98	90.09	0.0089	0.96	3.86	0.079
Cadmium	0.99	23.20	0.0165	0.86	4.75	0.271
Copper	0.98	21.01	0.0156	0.89	4.58	1.600
Metal	R ²	K _f (mg/g)	1/n	R ²	K _f (mg/g)	1/n
Freundlich Isotherm Parameters						
Lead	0.98	0.82	0.98	0.99	1.8e ⁻³	2.07
Cadmium	0.99	0.90	0.38	0.89	1.09	2.04
Copper	0.97	0.39	1.16	0.99	1.66	2.63
Metal	R ²	K _T	B _T (kJ/mol)	R ²	K _T	B _T (kJ/mol)
Temkin Isotherm Parameters						
Lead	0.93	5.19	3.55	0.97	0.94	0.77
Cadmium	0.95	3.77	3.31	0.75	0.51	0.43
Copper	0.96	2.56	2.77	0.93	0.78	0.98
Metal	R ²	A	B	R ²	A	B
Harkin-Jura Isotherms						
Lead	0.80	3.51	1.00	0.92	0.65	1.09
Cadmium	0.85	1.35	1.02	0.98	0.35	0.48
Copper	0.83	3.51	1.29	0.93	0.26	0.34
Metal	R ²	K	n	R ²	K	n
Halsey Isotherms						
Lead	0.98	1.21	0.98	0.99	1.89	0.48
Cadmium	0.99	2.24	0.88	0.89	1.04	0.54
Copper	0.97	3.02	1.16	0.99	145.9	3.83

Table 1: Comparison of Langmuir, Freundlich, Temkin, Harkin's-Jura and Halsey isotherm constants for single and multi-component adsorption of Pb (II), Cd (II) and Cu (II) on raw wheat straw at room temperature (30°C).

Cu(II) was found to be 2.07, 2.04 and 2.63, respectively. R² values, 0.99, 0.89 and 0.99 for Pb(II), Cd(II) and Cu(II), showed the better fitness of Freundlich model as compared to the Langmuir model indicating the multilayer formation on heterogeneous surface of the adsorbent.

Temkin parameters K_T and B_T were obtained to study the adsorption potential and heat of adsorption. K_T values obtained from Temkin isotherm model; 0.93, 0.51 and 0.78; depicted satisfactory adsorption potential for Pb, Cd and Cu. Also the B_T values for Pb(II), Cd(II) and Cu(II), 0.77 kJ/mol, 0.43 kJ/mol and 0.97 kJ/mol (less than 8) suggests weak interaction between metal ions and raw wheat straw indicating that process would be physisorption [28].

Harkin's-Jura isotherm is based upon the assumption of presence of multilayer adsorption with the existence of heterogeneous pore distribution. Correlation factor close to 1 i.e., 0.92, 0.98 and 0.93 for Pb(II), Cd(II) and Cu(II) supported multilayer adsorption.

Halsey adsorption isotherm agrees with the multilayer adsorption and the best fitting of experimental data, R² values 0.99, 0.89 and 0.99 for Pb(II), Cd(II) and Cu(II), affirmed the heteroporous nature of the raw wheat straw.

Formerly discussed adsorption isotherms were also investigated for all the analytes (Pb(II), Cd(II) and Cu(II)) when they were present as single component i.e., in the absence of other metal ions and calculated isotherm parameters are presented in Table 1.

Adsorption capacity represented by Freundlich and Langmuir constants; K_f and q_{max}, for the single components have higher values than in multi-component system. Adsorption potential obtained from Temkin isotherm model also showed higher value for the single

component system whereas B_T values indicated somewhat stronger forces between adsorbent and adsorbate species in single component as compared to multi-component system. Harkin's-Jura and Halsey models supported multilayer adsorption in both cases.

R-L factor: Favorability of adsorption process is predicted by a dimensionless parameter known as separation factor or equilibrium parameter (R_L), obtained from Langmuir adsorption isotherm model. R_L factor is determined using equation: [11]

$$R_L = 1 / (1 + bC_0) \quad (6)$$

where b is the Langmuir constant and C₀ is the initial liquid phase concentration of analytes (Pb, Cd and Cu). Adsorption process is explained by R_L values as R_L>1 shows unfavorable, R_L=1 gives linear, 0<R_L<1 signifies favorable and R_L=0 depicts unfavorable adsorption [11].

R_L values for single component; 0.69, 0.55, and 0.56; and multi-component system; 0.20, 0.07, and 0.01; for Pb(II), Cd(II) and Cu(II), respectively, were found to be greater than zero and less than 1 describing adsorption process as favorable. However, the decrease in R_L value was observed in multi-component system.

D-K-R model: Characteristics of adsorption can also be studied by applying the Dubinin-Kaganer-Radushkevich (D-K-R) model whose linear form is as under:

$$\ln q_e = \ln q_m - \beta \epsilon^2 \quad (7)$$

where q_m is the theoretical saturation capacity (mg/g), β is the constant related to mean free adsorption energy (mol²/J²), and ε is the polyani potential, calculated as:

$$\varepsilon = RT \ln(1+1/C_e) \quad (8)$$

β was further used to calculate the mean free adsorption energy using the following equation:

$$E = 1/\sqrt{2\beta} \quad (9)$$

The values of q_m , β , E and R^2 for Pb(II), Cd(II) and Cu(II) obtained from the linear plot of Equation 7. are computed in the Table 2. E values (kJ/mol) less than 8 imply the presence of physical and Vander waal's forces indicating physisorption. Values in between 8-16 indicate ion exchange mechanism whereas $E > 16$ depicts particle diffusion [30]. The E values for Pb(II), Cd(II) and Cu(II) under study described physisorption as the operating phenomenon. These results were in good agreement with those of Temkin isotherm model.

Effect of contact time – kinetic studies: Contact time shows a marked influence on the adsorption efficiency and is used to elucidate the kinetics of the adsorption process. The effect of contact time on the percentage adsorption of analytes (Pb(II), Cd(II) and Cu(II)) indicated sharp increase in adsorption within first 25 min for all the analytes. Rapid increase in adsorption in lesser time revealed physical nature of binding. No or small increase in adsorption was observed after equilibrium was established.

Reaction kinetics was investigated to describe the rate of adsorption and kinetic models were used for the optimization of effluent treatment models. The mechanism of Pb(II), Cd(II) and Cu(II) adsorption by raw wheat straw was analyzed by pseudo-first order, pseudo-second order and intra-particle diffusion kinetic model.

The linear equation of the pseudo-first order model is given as:

$$1/q_t = 1/q_e + k_1/q_e t \quad (10)$$

Metal	D-K-R Equation Parameters				Energy of Activation		
	R^2	q_m (mg/g)	β (mol ² /J ²)	E (kJ/mol)	R^2	E_a (kJ/mol)	A
Lead	0.92	8.88	$3e^{-06}$	0.41	0.99	4.89	9.88
Cadmium	0.88	5.84	$3e^{-06}$	0.41	0.95	3.49	179.9
Copper	0.81	4.53	$5e^{-06}$	0.32	0.95	3.39	16.45

Table 2: D-K-R and Arrhenius parameters for the adsorption of Pb (II), Cd (II) and Cu (II) onto raw wheat straw.

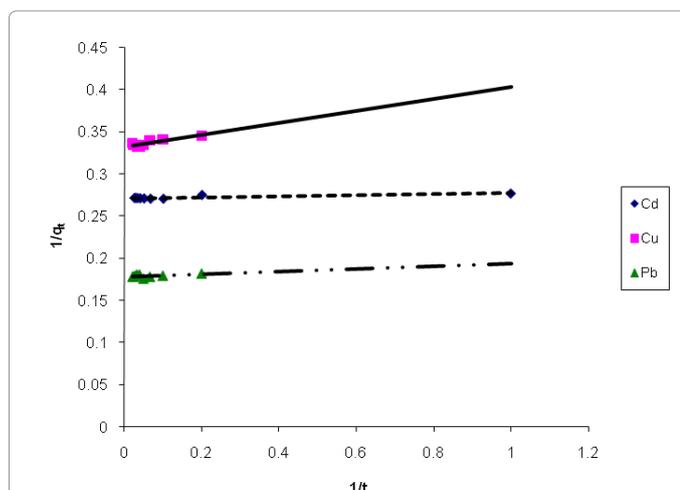


Figure 5: Pseudo first-order kinetic plot for the adsorption of Pb(II), Cd(II) and Cu(II) on raw wheat straw. (metal concentration: 50 mg/L; dose 0.4g/50mL for Pb(II), 0.6 g/50mL for Cd(II) and Cu(II); contact time: 20 min for Pb(II), 10 min for Cd(II), 25 min for Cu(II); temperature: 303 K).

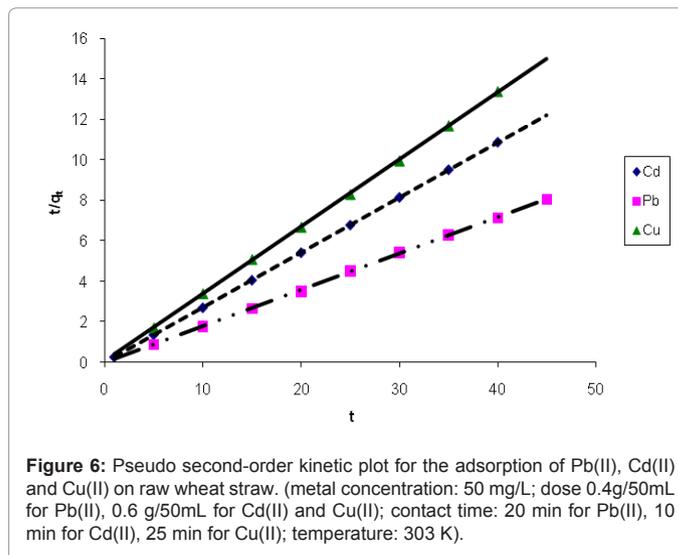


Figure 6: Pseudo second-order kinetic plot for the adsorption of Pb(II), Cd(II) and Cu(II) on raw wheat straw. (metal concentration: 50 mg/L; dose 0.4g/50mL for Pb(II), 0.6 g/50mL for Cd(II) and Cu(II); contact time: 20 min for Pb(II), 10 min for Cd(II), 25 min for Cu(II); temperature: 303 K).

Metals	Pseudo First-Order			Experimental q_e (mg/g)	Pseudo Second-Order		
	q_e (mg/g)	k_1 (min ⁻¹)	R^2		q_e (mg/g)	k_2 (min ⁻¹)	R^2
Lead	5.60	0.086	0.24	5.68	5.59	4.20	0.99
Cadmium	3.68	0.022	0.73	3.69	3.68	45.45	0.99
Copper	3.01	0.212	0.78	3.01	3.02	1.41	0.99

Table 3: Comparison of rate constants, q_e and correlation coefficients of pseudo first-order and pseudo second-order kinetic models.

where q_e and q_t (mg/g) refer to the amount of metals sorbed on raw wheat straw at equilibrium and t (min), respectively; k_1 being the first order rate constant (min⁻¹) calculated from the slope of the linear curve plotted between $1/q_t$ and $1/t$ (Figure 5).

Equation describing the pseudo-second order model can be written as follows in linear form:

$$t/q_t = 1/k_2 (q_e^2) + t/q_e \quad (11)$$

where k_2 is the second order rate constant. The k_2 and q_e values were determined from the intercept and slope of t/q_t versus t linear plot shown in Figure 6.

Kinetic data is given in Table 3. R^2 values determined for the pseudo-first order ($R^2 < 0.97$) and pseudo-second order ($R^2 > 0.98$) clearly showed a perfect fit for pseudo-second order model as compared to pseudo-first order model whereas q_e values calculated from both models were very close to the experimental values for the three analytes, Pb(II), Cd(II) and Cu(II). Thus adsorption of these metal ions was governed by the pseudo-second order kinetics.

Another kinetic model was suggested by Weber and Morris to identify the diffusion mechanisms and rate controlling steps affecting the adsorption process, known as intra-particle diffusion model [31]. Rate constant for Pb(II), Cd(II) and Cu(II) in single as well as in multi-component system was determined using the following linearized equation:

$$\text{Log}R = \text{log}k_{id} + a \text{log}t \quad (12)$$

where R is the percent of sorbate sorbed, t is the contact time (min), a is the gradient of linear plot which depicts the adsorption mechanism and k_{id} is the intra-particle diffusion rate constant. It is taken as rate factor i.e., percent of sorbate sorbed per unit time (mgg⁻¹ min^{-1(1/2)}).

Linear curve of $\log R$ versus $\log t$, Figure 7, gave the intra-particle diffusion model parameters, represented in Table 4 for single as well as multi-component system. Larger k_{id} values illustrate better adsorption related to improve bonding between sorbate and adsorbent particles [32]. The k_{id} values were reduced to some extent in the multi-component system as compared to single component system. Smaller R^2 values ($R^2 < 0.97$) evinced experimental data don't fit the model very well. Boundary layer diffusion and intra-particle diffusion is distinguished by the linearity of the plot. Particle diffusion is indicated by a straight line passing through the origin, whereas boundary layer diffusion is obvious in other conditions [24]. The plots for all analytes (Pb(II), Cd(II) and Cu(II)) in single as well as in multi-component system were neither linear nor passing through the origin indicating that boundary layer diffusion was the rate limiting bioadsorption process. The values of Pb, Cd and Cu in both systems were found to be less than unity presented in Table 4.

Activation energy: Activation energy is regarded as an important parameter as it depicts the strength and nature of forces present between sorbate and adsorbent. The activation energy E_a was calculated by the linearized Arrhenius equation given as:

$$\ln k = \ln A - E_a / RT \quad (13)$$

where E_a is the activation energy of adsorption (kJ/mol), k is the rate constant, A is the Arrhenius constant, R is the ideal gas constant ($8.3134 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the temperature of the medium (K).

k_2 , the rate constant which controls the process, obtained from the pseudo-second order kinetic studies was used as k in this study and activation energy values for Pb(II), Cd(II) and Cu(II) were obtained by plotting $\ln k_2$ versus $1/T$.

Table 2 presents Arrhenius parameters, E_a values and R^2 values for the analytes. Small values of E_a (not more than 4.2 kJ/mol) are obtained

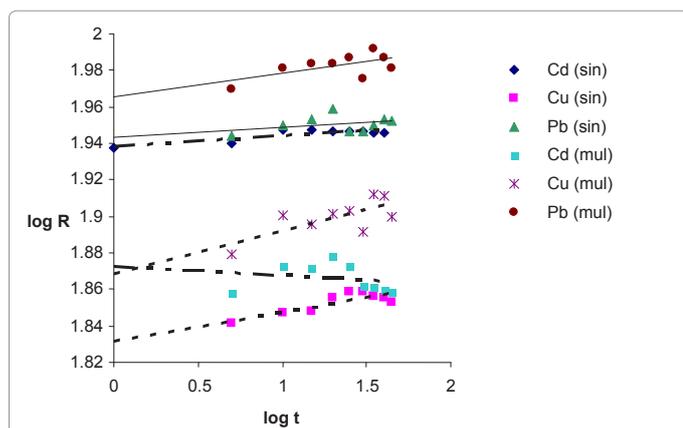


Figure 7: Intra-particle diffusion model for the adsorption of Pb(II), Cd(II) and Cu(II) on raw wheat straw in single and multi-component system. (metal concentration: 50 mg/L; dose 0.4g/50mL for Pb(II), 0.6 g/50mL for Cd(II) and Cu(II); contact time: 20 min for Pb(II), 10 min for Cd(II), 25 min for Cu(II); temperature: 303 K).

	Single component system			Multi-component system		
Metal	R^2	A	$k_{id}(\text{mgg}^{-1} \text{ min}^{-1/2})$	R^2	a	$k_{id}(\text{mgg}^{-1} \text{ min}^{-1/2})$
Lead	0.14	0.0052	87.82	0.38	0.0128	92.34
Cadmium	0.72	0.0057	86.80	0.04	0.0050	74.56
Copper	0.72	0.0159	67.87	0.51	0.0232	73.90

Table 4: Intra-particle diffusion model parameters for the adsorption of Pb (II), Cd (II) and Cu (II) on raw wheat straw in single and multi-component system.

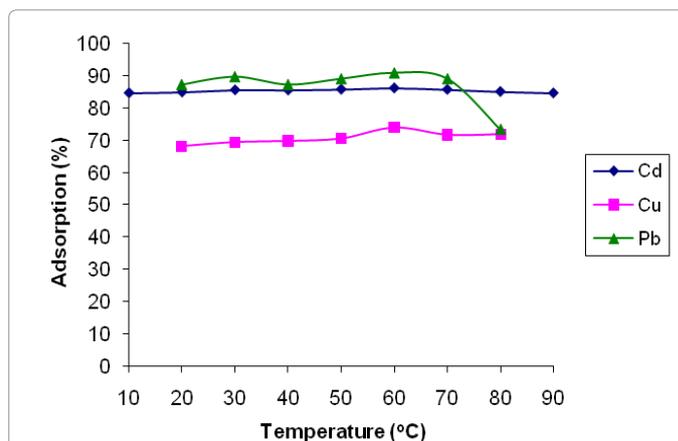


Figure 8: Effect of temperature for the adsorption of Pb(II), Cd(II) and Cu(II) on raw wheat straw. (metal concentration: 50 mg/L; dose 0.4g/50mL for Pb(II), 0.6 g/50mL for Cd(II) and Cu(II); contact time: 20 min for Pb(II), 10 min for Cd(II), 25 min for Cu(II)).

when the forces involved in physical adsorption are weak. The E_a values lies between 8.4 and 83.7 kJ/mol when strong forces results in chemical adsorption [33]. Values of E_a for Pb(II), Cd(II) and Cu(II) indicated physical adsorption and the positive value of the activation energy suggested that the rise in solution temperature favors the adsorption of Pb(II), Cd(II) and Cu(II) onto raw wheat straw.

Effect of temperature – thermodynamic parameters:

Determination of thermodynamic parameters was carried out by studying the effect of change in temperature on the adsorption of Pb(II), Cd(II) and Cu(II) by the raw wheat straw. Figure 8 depicts the influence of temperature on the adsorption, showing increased adsorption capacity with temperature. Increased adsorption capacity at high temperature indicated the adsorption process to be endothermic in nature for all the metals and suggested that raw wheat straw can effectively be used for their adsorption or removal from aqueous solution at high temperatures. 90.9%, 86.2% and 73.9% adsorption of Pb(II), Cd(II) and Cu(II) was observed at 333K (60°C), respectively.

Thermodynamic parameters like changes in free energy (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) were studied to investigate the nature of the process and these parameters were evaluated using the equations:

$$\Delta G^\circ = -RT \ln K_D \quad (14)$$

$$\ln K_D = \Delta S^\circ / R - \Delta H^\circ / RT \quad (15)$$

where R is the universal gas constant ($8.3134 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature of the medium (K), and K_D is the distribution coefficient, obtained from equation:

$$K_D = q_e / C_e \quad (16)$$

where q_e is the equilibrium amount of metal sorbed (mg/g) and C_e is the concentration of metal in solution at equilibrium (mg/ L) [34,35].

Thermodynamic parameters obtained from equation 15 are given in Table 5. The negative values of ΔG° for the adsorption of Pb(II), Cd(II) and Cu(II) by raw wheat straw at the studied temperature range confirmed the feasibility of the process and the spontaneous nature of adsorption. Increase in feasibility of adsorption at elevated temperatures was shown by the increase in the value of ΔG° with temperature, thus affirming the endothermic nature of adsorption. The positive values

Metals	Temp. (K)	K_d (L/g)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol)
Lead	293	1.857704	-1.51	3.52	17.01
	303	1.906353	-1.62		
	313	1.960069	-1.75		
	323	2.019689	-1.89		
	333	2.248626	-2.24		
Cadmium	293	1.468543	-0.94	0.62	5.33
	303	1.494568	-1.01		
	313	1.492969	-1.04		
	323	1.502696	-1.09		
	333	1.520531	-1.16		
Copper	293	1.178228	-0.39	0.84	4.19
	303	1.188998	-0.44		
	313	1.192058	-0.46		
	323	1.199153	-0.49		
	333	1.236442	-0.59		

Table 5: Thermodynamic parameters for the adsorption of Pb (II), Cd (II) and Cu (II) onto raw wheat straw ($C_0=50\text{mg/L}$).

of ΔH° also corroborated this statement. Increased randomness at the solid-solution interface during the adsorption of metal ions was shown by the positive values of ΔS° which reflected the affinity of raw wheat straw for Pb(II), Cd(II) and Cu(II) ions.

Effect of ionic interaction: Multi-component systems (containing more than one metal) are found to be much complicated when dealing with adsorption because of the solute-surface interactions and competition of metal ions with each other. Decrease in K_f and q_{max} values in the multi-component system corroborated this observation. The effect of ionic interaction on the adsorption process may be represented by the ratio of the adsorption capacity (obtained from Langmuir isotherm) of one metal ion in the presence of the other metal ions, Q^{mix} , to the adsorption capacity (obtained from Langmuir isotherm) of same metal ion when it is present alone in the solution, Q° , such that for:

$Q^{\text{mix}}/Q^\circ > 1$; adsorption is promoted by the presence of other metal ions,

$Q^{\text{mix}}/Q^\circ = 1$; no observable net interaction,

$Q^{\text{mix}}/Q^\circ < 1$; adsorption is suppressed by the presence of other metal ions [36].

The Q^{mix}/Q° values; 0.043 for Pb(II), 0.205 for Cd(II), and 0.210 for Cu(II); were found to be <1 showing ionic interactions and were agreeable with those obtained from adsorption isotherms in the presence and absence of various metal ions. Values increased in the order $\text{Cd} < \text{Cu} < \text{Pb}$ for the adsorption of Pb(II), Cd(II) and Cu(II) in multi-component system.

Conclusion

The aim of the study was to evaluate the application of a cost-effective adsorbent towards water pollution remediation, which is frequently available in Pakistan and most of the other countries. The results of this study indicated that *Triticum aestivum* (wheat straw) proved to be an effective adsorbent for the uptake of toxic metals, lead, cadmium and copper from aqueous solutions in single as well as in multi-component systems. The optimum parameters for equilibrium study were calculated, which indicated that optimum adsorption occurred at slightly acidic condition i.e. pH 4-6. Maximum uptake capacities for Pb(II), Cd(II) and Cu(II) were 3.865 mg/g, 4.746 mg/g and 4.585 mg/g which indicate that in multi-component system cadmium uptake is

greater as compared to copper and lead showing its competition for adsorption sites as compared to other metal ion (Pb(II) and Cu(II)). The kinetic study showed that adsorption mechanism was obeyed a pseudo second-order kinetic model. Thermodynamic parameters like ΔG° , ΔS° and ΔH° were also determined. The values indicated that adsorption mechanism was spontaneous and energetically feasible. Enthalpy values also showed that the adsorption process was an endothermic process.

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