

Competitive sorption of nickel, copper, lead and cadmium on okra leaves (*Abelmoschus esculentus*)

Khaskheli M.I.^{1,*}, Memon S.Q.¹, Jatoi W.B.², Chandio Z.A.¹, Shar G.K.², Malik A.¹ and Khan S.³

¹M. A. Kazi Institute of Chemistry, University of Sindh, Jamshoro 76080, Pakistan.

²Institute of Chemistry, Shah Abdul Latif University Khairpur Mirs, Pakistan.

³Molecular Biology (Genetics) Laboratory Medical Research Centre, LUMHS, Jamshoro, Pakistan

Received: 22/02/2016, Accepted: 11/04/2017, Available online: 26/09/2017

*to whom all correspondence should be addressed:

e-mail: kumailmazhar@gmail.com

Abstract

In this study, potential of okra leaves for the removal of Ni(II), Cu(II), Pb(II) and Cd(II) from the mixed metal aqueous solution were evaluated. The data were analyzed by Freundlich, Langmuir, D-R, Flory-Huggins and Halsey adsorption models. Pseudo first order rate, Pseudo second order rate, Morris-Weber and Elovich equations were employed to understand the kinetics of the reaction. The characterization of the adsorbent was carried out by EDX and FTIR techniques. The order of maximum metal uptake calculated by D-R isotherm was Cu(II) > Pb(II) > Cd(II) and Ni(II), 453 mg g⁻¹, 81 mg g⁻¹, 13.82 mg g⁻¹ and 1 mg g⁻¹ respectively, with the energy of adsorption in the range of 9-15 for Ni(II) and Cd(II) expected for the ion exchange nature of adsorption and 7-8 for Cu(II) and Pb(II) showing the physical nature of adsorption. The calculated thermodynamic parameters like Gibbs free energy and enthalpy change demonstrate that adsorption process was spontaneous and endothermic in nature. Further it was observed that all four metal ions could be adsorbed at pH 6 with detection limits of 0.04-0.1 µg L⁻¹. The method was successfully applied for the removal of these metal ions from the ground water, tap water and wastewater samples collected from different areas of Pakistan.

Keywords: Okra leaves; Removal; Metals; D-R isotherm; Kinetics

1. Introduction

Ground water contamination with heavy metals wastes is the greatest threat for government agencies, industry and communities (Jaeyoung *et al.*, 2009). Industrial activities and the processing of ore mining are the major sources through which these toxic metals have been introduced into the environment (Fuller *et al.*, 2002). Literature survey indicates that Ni(II), Cu(II), Cd(II) and Pb(II) are some of the potential pollutants of the environment. Cadmium, nickel and lead are known as toxic heavy metals, posing a serious threat to plant, animal, human and environment (Ashenef, 2014). According to W.H.O, maximum contamination levels of copper, cadmium, nickel and lead in drinking water are

2 mg g⁻¹, 0.003 mg g⁻¹, 0.07 mg g⁻¹ and 0.01 mg g⁻¹ respectively (W.H.O, 2011). Lead heads the list of environmental threats because even at extremely low concentrations it causes brain damage in children (Ahmedna *et al.*, 2004). Cadmium is non-essential, non-beneficial and recognized as an occupational health hazard for many decades and increasing number of studies have shown early adverse health effects on the kidney (Kefela *et al.*, 1999; Chandio *et al.*, 2013). Cadmium ions are not biodegradable and easily accumulate in human tissues (Evangelin *et al.*, 2014). The inhalation of nickel and its compounds can lead to serious problems, including respiratory cancer, skin allergies, dermatitis, lung fibrosis, headaches, nausea, vomiting, chest pain, dry cough and shortness of breath (Chandio *et al.*, 2013). The toxic effects of copper are well documented by Sobecka (Sobecka, 2001).

Chemical precipitation, reverse osmosis, ion-exchange, filtration and evaporative recovery are most commonly using methods and effective for the treatment of liquid effluents containing high concentration of metal ions. However, these technologies are usually expensive and become inefficient for treatment of effluents containing metal ions in the range of 100 mg L⁻¹ (Suman *et al.*, 2008). Over the last few years, adsorption has been shown to be an economically and environmentally feasible method for removal of metal ions from ground water and wastewater (Khaskheli *et al.*, 2011). The biggest barrier in the application of this process by the industries is the high cost of adsorbents presently available for commercial use. It is, therefore, important to explore new adsorbents for metals removal and recovery from such effluents, and thus reduce the concentration of these metal ions to the safe levels.

Okra (*Abelmoschus esculentus*), a flowering plant belongs to mallow family Malvaceae, is a tropical perennial crop growing 3 to 6 feet tall. It is believed to have originated in Ethiopia. In recent years, it has become an important commercial crop, especially in south, where thousands of tons of the pods are grown (Olajide, 2009). In current study an effort has been made to develop an efficient, cheap and environmental friendly method to remove nickel, copper,

lead and cadmium using okra leaves as an adsorbent. Table 1 shows a comparison of the capacities of different sorbent materials with proposed sorbent. It can be shown that okra leaves have comparable capacity values with most of the

sorbents reported in the literature. In order to check the practical applicability of a method it has been used for removal of all four metal ions from real water systems.

Table 1. Comparison of sorption capacities of various sorbents for Cu(II), Cd(II), Ni(II) and Pb(II)

Adsorbent	pH				Capacity (mg g ⁻¹) Based on Langmuir isotherm				Applications	References
	Pb(II))	Cd(II))	Cu(II))	Ni(II)	Pb(II)	Cd(II)	Cu(II)	Ni(II)		
Wheat bran	5	5	5	5	62.0	21.0	15.0	12.0	Not applied	Farajzadeh and Monji, 2004
Barley straw	6		6.6		23.2	-	4.64	-	Not applied	Pehilvan <i>et al.</i> , 2009
Tartaric acid modified rice husk	-	-	-	-	108	-	29.0	-	Not applied	Wong <i>et al.</i> , 2003
Coffee husk	-	6	7	-	-	6.85	7.50	-	Not applied	Oliveira <i>et al.</i> , 2008
Waste black tea	-	-	-	5	-	-	-	90.91	wastewater	Malakahmad <i>et al.</i> , 2016
HCl treated oak sawdust	7	7	7	7	-	-	3.60	3.37	Waste water	Argun <i>et al.</i> , 2007
Dairy sludge	-	-	-	-	149	66.7	-	-	Not applied	Sassi <i>et al.</i> , 2010
Treated Geobacillus	4.5	6	7.5	-	32.3	42.9	50	-	Industrial waste water	Chatterjee <i>et al.</i> , 2010
marine algae	6	6	6	-	232.6	88.5	92.6	-	Waste water	Feng and Jatoi, 2004
Functionalized HLS biomass	-	-	-	-	-	52.8	-	23.6	Not applied	Panda <i>et al.</i> , 2008
Pristine biomass	-	-	-	-	-	35.0	-	15.7	Not applied	
Orange peel cellulose Unmodified	5-7	-	-	-	-	55.1	-	27.0	Not applied	Li <i>et al.</i> , 2008
Grape stalk waste	5.5	5.5	5.5	5.5	49.9	27.9	-	-	Not applied	Martinez <i>et al.</i> , 2006
Hazelnut shell	-	-	-	-	16.23	5.42	-	3.83	Not applied	Bulut and Tez, 2007
Almond shell	-	-	-	-	3.43	3.18	-	3.11	Not applied	
Holly oak(stem)	-	-	-	-	0.75	0.36	0.21	0.58	Not applied	Parsad and Freltas, 2000
Brewery biomass	5	5.5	5.5	-	96.4	14.3	48.9	-	Not applied	Kim <i>et al.</i> , 2005
Sawdust of walnut	-	-	-	-	6.66	4.90	-	2.79	Waste water	Bulut and Tez, 2007
Sawdust of deciduous trees	3.5-5.5	-	-	-	-	3.50	9.90	4.60	Mine water, Electroplating water, metal industry	Bozic <i>et al.</i> , 2009
Phaseolus aureus hull carbon	6	8	7	-	21.8	15.7	19.5	-	Not applied	Rao <i>et al.</i> , 2009
Olive stone waste	5.5-6	-	-	-	9.26	7.73	2.02	2.13	Not applied	Fiol <i>et al.</i> , 2006
NaOH treated Reed biomass	4	7	7	7	0.083	0.019	0.156	0.135	Not applied	Southichak <i>et al.</i> , 2006
*Okra leave (present work)	6	6	6	6	81.0	18.8	453	2.16	Drinking and waste water	This study

*D-R capacity

2. Experimental

2.1. Materials and methods

All chemicals used were of analytical grade and supplied by Merck (Darmstadt, Germany). A stock standard solution of all four metal ions was prepared by dissolving the appropriate amount of their salts in deionized water (conductivity <0.5_Scm⁻¹). Buffer solutions of pH 1–3, 4–6 and 7–9 were prepared by mixing appropriate ratios of 0.1M HCl and KCl, 0.5M acetic acid and sodium acetate and 0.5M ammonia and NH₄Cl solutions respectively.

2.2. Chemical analysis

Perkins-Elmer Atomic Absorption Spectrophotometer (AA-800) was used to quantify metal ions using recommended conditions. All pH measurements were carried out by Thermo Scientific Orion 5 Star (pH. ISE. Cond. DO Benchtop, 8102BNUP; Made in USA) PH-meter. Shaking Incubator Model 1-40000 Irmeco GmbH (Geesthacht/Germany) was

used for batch experiments. Peristaltic pump (Gilson, Made in France) was used for column study.

2.3. Batch sorption study of Ni(II), Cu(II), Cd(II) and Pb(II)

A weighed amount of Okra leaves was equilibrated with 20 mL solution containing 10 mg mL⁻¹ of each Ni(II), Cu(II), Cd(II) and Pb(II) at pH 6 and ionic strength (0.001 mol L⁻¹) at 25±1°C. The sorbent was filtered and the equilibrium concentration was determined.

2.4. Sorption of metal ions (Ni (II), Cu(II), Cd(II) and Pb(II)) by column method

A fixed bed study was carried out in a glass column made up of glass. A glass column of 18 cm length and 1.2 cm diameter was selected for the study. Small amount of glass wool was placed in the bottom to avoid the wastage of sorbent from the lower end of the column. Then slurry in water of 0.5 g of sorbent was poured and column filled up to the 2.5 cm. pH 6 maintained metals ion solution was pumped through the embedded column by peristaltic

pump controlling the flow rate 1-6 mL min⁻¹. The passing of the solution at an optimized flow rate, continued till no sorption of metal ion occurred or biomass in the column was fully saturated with metal ions means breakthrough was achieved. Then a suitable amount of leaching agent (H₂SO₄) was eluted through the column having metal loaded sorbent. Consequently, metal analysis of eluted sample solutions collected at regular intervals of time after sorption and desorption were done with an Atomic Absorption spectrometer. Column studies were conducted at room temperature (25 °C). Finally, breakthrough curves were drawn from the observed results.

Data manipulation

The percent sorption of all four metal ions was determined using the following equation: %Sorption = $\frac{C_0 - C_f}{C_0}$ (Bazrafshan *et al.*, 2012).

Where

C₀ = Concentration of solution before sorption (mol L⁻¹)

C_f = Concentration of solution after sorption (mol L⁻¹)

3. Results and discussion

3.1. Characterization of sorbent

3.1.1. Energy Dispersive X-ray Analysis (EDX) of metal loaded okra leaves

The surface study of okra leaves before and after the sorption of metal ions was carried out. Both figures Fig.1a and Fig. 1b show the elemental analysis of okra leaves before and after the sorption respectively. In Fig.1a okra leaves sorbent contains a number of elements including carbon, oxygen, sodium, aluminum and calcium. While peaks of Cu(II), Cd(II), Ni(II) and Pb(II) appeared in the EDX spectrum of okra leaves (Fig. 1b) shows the retention of these metal ions.

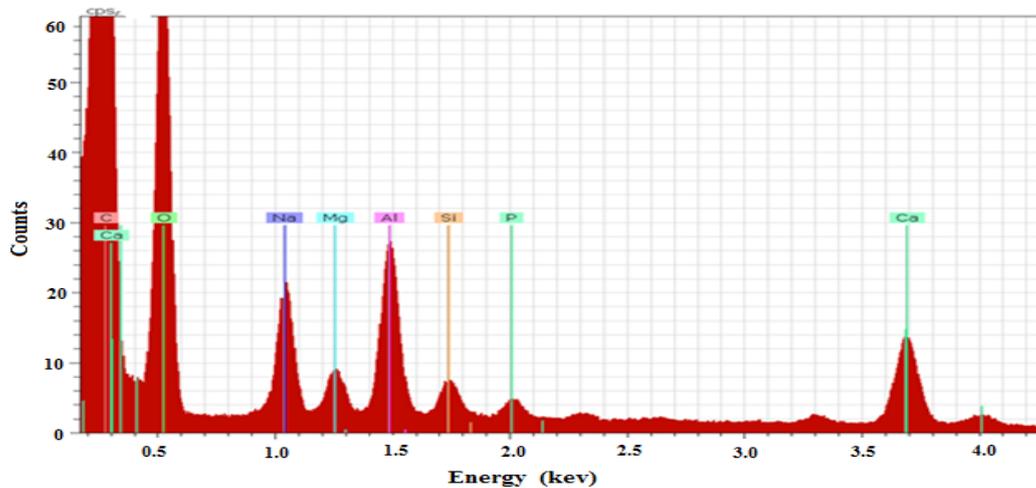


Figure 1a. EDX of Okra leaves before copper(II), cadmium(II), nickel(II) and lead(II) retention

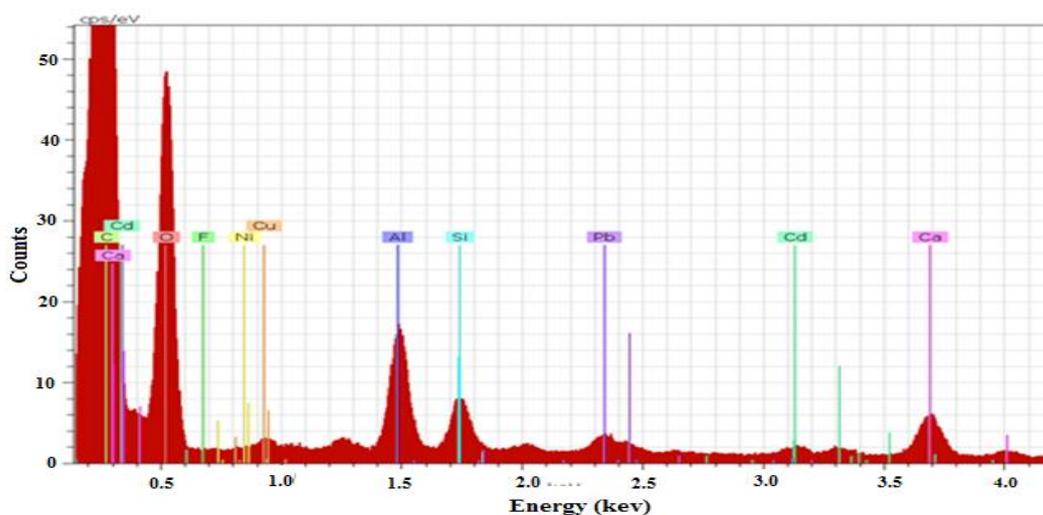


Figure 1b. EDX of Okra leaves after copper(II), cadmium(II), nickel(II) and lead(II) retention

3.1.1. Fourier Transform infrared spectroscopy (FT-IR) analysis

In order to understand the mechanism of interaction between functional groups present in the okra leaves sorbent and metal ions, the FT-IR analysis technique was

employed (Silverstein and Webster, 1998). The spectra of the unloaded and metal ions loaded sorbents were taken in the range of 500-4000 cm^{-1} wave number. The spectra of okra leaves sorbent before and after the metal ions sorption are shown in Fig. 2. The bands at 2847-2921 cm^{-1} , 1589-1634 cm^{-1} , 1409-1421 cm^{-1} 1303-1319 cm^{-1} , 1000-1237 cm^{-1} and 699 cm^{-1} were attributed to H-C-H asymmetric and symmetric stretching (alkane), C=N stretching (oxime), O-H bending (carboxylic acid), N=O bending (nitro group), C-O-C stretching (ethers) and C-H bending (alkenes).

The shift of peaks for copper at (2913 cm^{-1} , 1605 cm^{-1} , 1413 cm^{-1} , 1311 cm^{-1} & 1225 cm^{-1}), cadmium (2913 cm^{-1} , 1413 cm^{-1} & 1225 cm^{-1}), nickel (2847 cm^{-1} , 1605 cm^{-1} , 1413 cm^{-1} , & 1311 cm^{-1}) and lead (2913 cm^{-1} , 2847 cm^{-1} , 1605 cm^{-1} , 1413 cm^{-1} , 1311 cm^{-1} & 1225 cm^{-1}) were observed. The disappearance of peak at 996 cm^{-1} and emergence of new peak at 1000-1012 cm^{-1} in Fig. 2 was also analyzed. These changes in vibrational frequencies and appearance and disappearance of peaks indicate that C-H (alkane), N-H (amide), O-H (carboxylic acid), N=O (nitro group), C-O-C (ether) and C-H (alkene) functional groups are involved in the metal ions binding.

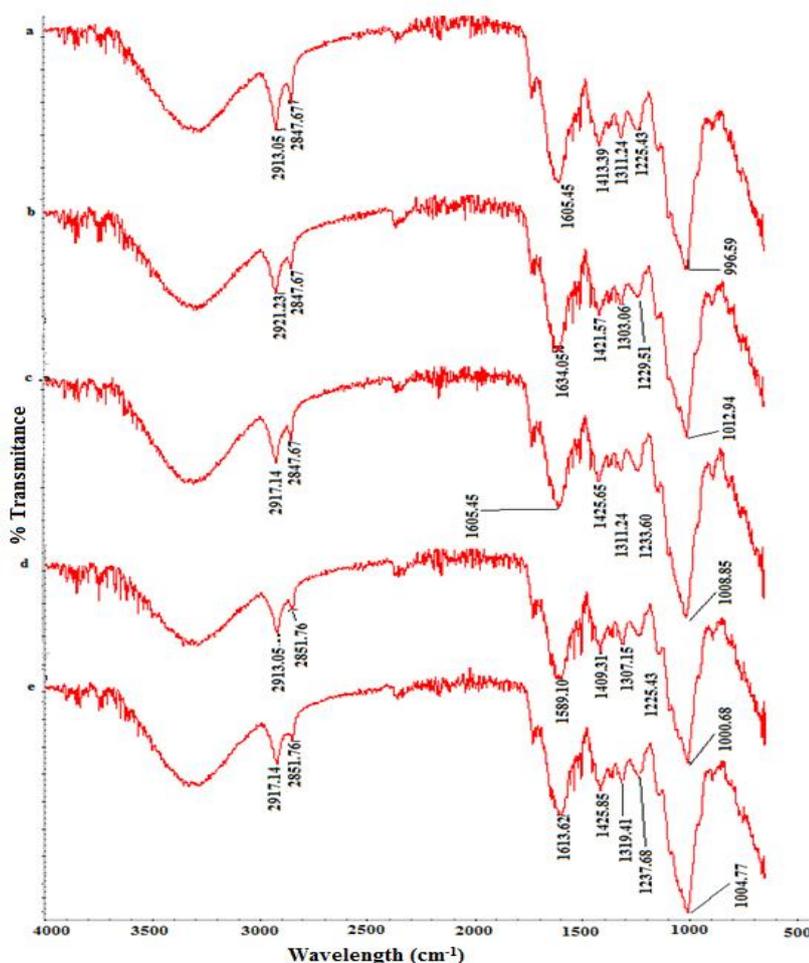


Figure 2. (a) FT-IR spectra of okra leaves (b) Cu(II) (c) Cd(II) (d) Ni(II) and (e) Pb(II) loaded

3.2 Effect of pH

The pH of the metal ion solution can affect the surface charges of the sorbent, degree of ionization of pollutants and dissociation of functional groups at active sites (Bazrafshan *et al.*, 2013). The study of pH identifies binding sites and the type and amount of species sorbed onto the surface okra leave sorbent. The effect of pH (Fig. 3) of Ni(II), Cu(II), Cd(II) and Pb(II) ions solution was optimized with respect to the amount of metal ions loaded onto the sorbent surface.

The initial increase in sorption of all four metal ions was observed with increasing pH up to 3. Copper and lead showed a similar behavior after pH 3 and their sorption remains constant up to pH 6. Both metals showed a little decrease at pH 7 and then increases at pH 8-9. Whereas the sorption of nickel was constant up to pH 7 and then increased drastically at pH 8-9. Cadmium showed completely different behavior than rest of three metals. There was a continuous increase in percent sorption with increasing pH. The different behavior of sorption of metal

ions may be due to the formation of different species at different pH values.

The main specie of Ni(II) at pH 8 is Ni^{2+} and at pH 10 the dominant species of Ni(II) ions would be $Ni(OH)_2$ (60%), Ni^{2+} (18%), $Ni(OH)^+$ (11%) and $Ni(OH)^{3-}$ (10%). At pH 9 the dominant species of Cu(II) would be $Cu_2(OH)_2$ (60%), $Cu(OH)^+$ (~25%), $Cu(OH)_2$ (10%) and Cu^{2+} (~4%) which would change to $Cu(OH)_2$ (40%), $Cu(OH)^{3-}$ (37%), $Cu(OH)^+$ (12%), $Cu(OH)_2^{2+}$ (10%) and $Cu(OH)_4^{2-}$ (5%) at pH 10 (Memon *et al.*, 2007).

Up to pH 7 the main species of Pb(II) is Pb^{2+} (>80%) and at pH 8 the dominant species of Pb(II) ions would be Pb^{2+} (~50%), $Pb(OH)^+$ (~5%), $Pb_3(OH)_2^{+4}$ (~3%), and $Pb(OH)_2$ (~1%) (Memon *et al.*, 2005). Cadmium is the metal having ~100% of Cd as Cd^{2+} (~100) up to pH 8 (Memon *et al.*, 2007) this may explain the reason for its different behavior from all three metal ions. Keeping in view the hydroxyl species of metal ions, pH 6 has been selected as a medium of sorption. Therefore, the hydroxide retention mechanism can be avoided.

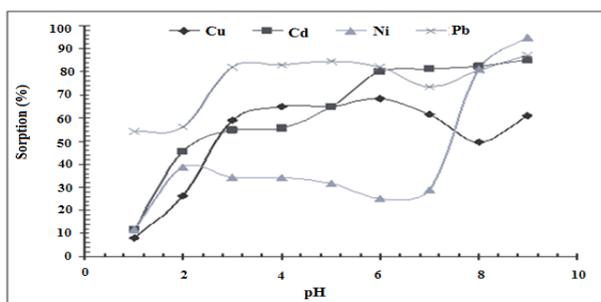


Figure 3. Effect of pH on removal of Cu(II), Cd(II), Ni(II) and Pb(II) on okra leaves

3.3. Amount of sorbent

In sorption process the dosage of sorbent considerably affect the sorption efficiency of the sorbent. The amount of sorbent determines the uptake capacity of okra sorbent for the competitive sorption of various metal ions. The trend of sorption of copper, cadmium, nickel and lead was similar. Initially as amount of sorbent was increased, 30-80% sorption was increased at 0.1mg per 10 mL and then smaller decrease or nearly constant sorption was observed as amount of sorbent was increased. The increase in sorption was due to the availability of the more active sites for the sorption of Cu(II), Cd(II), Ni(II) and Pb(II), while the decrease in sorption may be attributed to the accumulation of sorbent. Accumulation decreases the sorption active sites (Rojas *et al.*, 2005).

3.4. Uptake of Ni(II), Cu(II), Cd(II) and Pb(II) as a function of time

The contact time between sorbate and sorbent is one of the most important design parameters that affect the performance of adsorption process (Bazrafshan *et al.*, 2016). The affect of equilibration time on the amount adsorbed was optimized at pH 6. Results are shown in Fig. 4.

All four metal ions have nearly same trend of equilibration. All four metal ions attained equilibration within 60 minutes and after 60 minutes the sorption remains nearly constant.

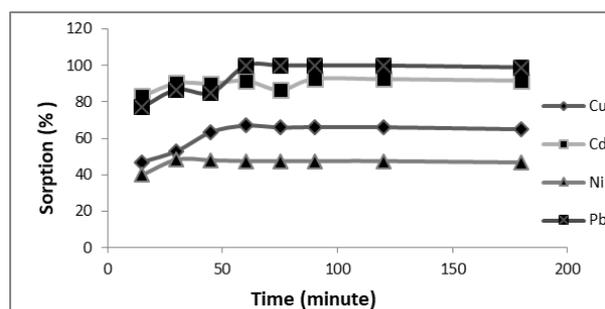


Figure 4. Uptake of Cu(II), Cd(II), Ni(II) and Pb(II) on okra leaves as a function of time

The kinetic data were evaluated by first order, second order rate equations (Khaskheli *et al.*, 2014) as well as Elovich and Morris-Weber equations in order to understand the mechanism of adsorption. Following linearized equations were used:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad \text{Pseudo first order rate equation}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad \text{Pseudo second order rate equation}$$

$$q_t = R_d \sqrt{t} \quad \text{Morris-Weber Equation}$$

$$\frac{1}{q_t} = \ln \frac{\alpha \beta}{\beta} + \frac{\ln t}{\beta} \quad \text{Elovich Equation}$$

Where k_1 is the pseudo first and k_2 second order rate constant, q_e is the amount of metal ions sorbed at equilibrium ($mg\ g^{-1}$), and q_t is amount of metal ions on the okra leaves at specified time ($mg\ g^{-1}$). R_d is the rate constant for intra particle diffusion. α is the initial sorption rate ($mg\ g^{-1}\ min^{-1}$) and β is desorption constant ($mg\ g^{-1}\ min^{-1}$) during any one experiment.

Table 2 shows the kinetic parameters calculated by all four equations. As clear from Table 2 Ni(II) and Cd(II) followed second order rate equation; whereas kinetic data of Pb(II) and Cu(II) followed first order rate equation. From these results it can be concluded that the mechanism of sorption of Ni(II) and Cd(II) is ion-exchange or chemisorption (Kumar *et al.*, 2010) whereas, Pb(II) and Cu(II) follow the physical nature of sorption (Ranjan *et al.*, 2009; Chen *et al.*, 2008; Urik *et al.*, 2009; Ho, 2006).

In case of Morris-Weber equation the straight lines of Ni(II), Cd(II) and Pb(II) did not pass through their origins which demonstrated that intra particle diffusion was not only the rate controlling step but other mechanisms were also involved in the rate determining step.

Elovich equation which was followed by Ni(II) and Cd(II), supported the chemisorption nature of the sorption reaction.

Table 2. Kinetic parameters for the sorption of Ni(II), Cu(II), Cd(II) and Pb(II) on okra leaves

Metal	Elovich			Morris-weber		first order eq.		second order eq.	
	α ($\text{mg g}^{-1} \text{min}^{-1}$)	β (g mg^{-1})	r	R_d ($\mu\text{mol g}^{-1} \text{min}^{-1}$)	r	K (min^{-1})	r	K ($\text{g mg}^{-1} \text{min}^{-1}$)	r
Ni(II)	0.92	0.75	0.94	7.34	0.96	-	-	0.0072	0.98
Cd(II)	35.96	2.07	0.98	1.36	0.97	-	-	0.044	0.99
Pb(II)	-	-	0.97	2.36	0.97	0.0011	0.96	-	-
Cu(II)	-	-	-	-	-	0.0015	0.94	-	-

3.5. Sorption Isotherm studies

Isotherm study demonstrates the relationship between the amounts of metal ions present in solution and adsorbed on the surface of sorbent when equilibrium was established between these two phases. The affect of concentration on the amount of metal sorbed onto the surface was calculated and the data were evaluated using Langmuir, Freundlich (Khaskheli *et al.*, 2016), D-R, Flory-Huggins and Halsey isotherm equations (Basar, 2006; Vijayaraghavan *et al.*, 2006). All equations were analyzed in following linearized form:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{K_L q_{\max}} \quad \text{Langmuir}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{Freundlich}$$

$$\ln q_e = \ln K_{D-R} - \beta \epsilon^2 \quad \text{D-R}$$

$$\log \frac{\theta}{C_i} = \log K_{FH} + n_{FH} \log(1-\theta) \quad \text{Flory-Huggins}$$

$$\theta = 1 - \frac{C_e}{C_i}$$

$$\ln q_e = \frac{\ln K_H}{n_H} - \frac{\ln C_e}{n_H} \quad \text{Halsey}$$

Where C_e is the equilibrium concentration of metal ions in solution (mol L^{-1}), q_e is the amount of metal ions on surface (mol g^{-1}), q_{\max} is the maximum amount of ions sorbed, K_L is the Langmuir constant related to the binding energy of solute, K_F and $1/n$ are Freundlich constants representing sorption capacity and sorption intensity, respectively; ϵ is polanyi potential and equal to $RT \ln(1+1/C_e)$, T is temperature and R is general gas constant; β is related to the mean free energy of sorption per mole of the sorbent when it is transferred from infinite distance in the solution to the surface of the solid by equation:

$$E = \frac{1}{\sqrt{-2\beta}}$$

θ is degree of surface coverage, n_{FH} is the Flory-Huggins model exponent represents the number of metal ions of solute occupy active sites of sorbent, K_{FH} is the Flory-Huggins model equilibrium constant is used to calculate the Gibbs free energy of spontaneity (ΔG°) by following relationship.

$$\Delta G^\circ = -RT \ln K_{FH}$$

K_H is the Halsey constant and n_H is the exponent.

As shown in Table 3 Langmuir adsorption isotherm was nickel and cadmium envisages that all sites on sorbent are equal and uniform, there is no attraction between sorbed molecules and there is no steric hindrance between sorbed molecules and incoming ions and monolayer is formed at the maximum sorption capacity.

Copper and lead experimental data were fitted to Freundlich adsorption isotherm (Table 3). This isotherm describes the heterogeneity of the surface and formation of multilayers sorbed ions on the surface of the sorbent.

D-R sorption isotherm on the basis calculated energy values define the nature of sorption of metal ions. In table 3, energy of sorption range 8-15 for Ni(II) and Cd(II) demonstrates the ion exchange nature of sorption, while energy less than 8 for Pb(II) and Cu(II) shows the physical nature of sorption (Ranjan *et al.*, 2009). The order of maximum metal uptakes calculated by D-R isotherm was $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Cd}^{2+}$ and Ni^{2+} , 453 mg g^{-1} , 81 mg g^{-1} , 13.82 mg g^{-1} and 1 mg g^{-1} respectively.

Flory-Huggins model of isotherm discuss the mature of sorbent. Table 3 shows that there are number of metal ions (n_{FH}) occupying sorption sites [copper (3.19), cadmium (1.87), lead (1.56) and nickel (1.3)] are present on the surface of the sorbent.

In case of Halsey isotherm high value of correlation coefficient ($r = 0.94-0.99$) indicates that data are well fitted to the isotherm and attests the heteroporous (macropores and micropores) nature of the sorbent (Oladoja *et al.*, 2009).

3.6. Thermodynamic Study

The estimation of the feasibility and nature of the sorption process is evaluated by the calculation of thermodynamic parameters (Iftikhar *et al.*, 2009). Thermodynamic parameters (Gibbs free energy, enthalpy change and entropy change) were calculated by using following equations.

$$\Delta G = -RT \ln k_c$$

$$\ln k_c = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$

The graph plotted $\ln k_c$ against $1/T$ gives linear curve. Entropy change (ΔS) and enthalpy change (ΔH) are determined from intercept and slope respectively.

Table 3. Regression parameters for the Langmuir, Freundlich, D-R Florry-Huggins and Halsey sorption isotherms by using okra leaves as sorbent

Isotherm	Cu(II)	Cd(II)	Ni(II)	Pb(II)
Langmuir				
q_{\max} (mg g ⁻¹)	Not obeyed	3.02	7.20	Not obeyed
r	--	0.991	0.972	--
Freundlich				
K_F (mg g ⁻¹)	43.75	Not obeyed	Not obeyed	102.0
r	0.971	--	--	0.970
D-R				
K (mg g ⁻¹)	453.0	18.82	2.155	81.00
E (KJ mole ⁻¹)	7.58	15.4	11.8	7.20
r	0.982	0.987	0.971	0.977
Florry-Huggins				
$K_{FH}(10^4)$	2.7	4.9	0.3	63.8
n_{FH}	3.19	1.87	1.3	1.56
ΔG (KJ mole ⁻¹)	-25.29	-26.76	-19.99	-33.12
r	0.97	0.98	0.96	0.98
Halsey				
n_H	0.63	0.52	0.45	0.44
K_H (L g ⁻¹)	34.81	230.44	129.02	3011
r	0.99	0.98	0.99	0.94

Table 4 shows that Gibbs free energy (ΔG) values of all metals are negative, means sorption reaction of metal ions on okra leaves sorbent was spontaneous (i.e sorption forces are quite strong to overcome the potential barrier). Increase of negative value with the increase of temperature favour the sorption process (Khaskheli *et al.*, 2016). In other words it can be said that the degree of spontaneity increases with increasing the temperature (Thajeel, 2013). Positive values of entropy (ΔS) for Ni(II), Cd(II), Pb(II) and Cu(II) show that there was randomness of metal ions on the surface of sorbent during the process.

These values also reflect the affinity of sorbent for particular metal ions. Positive values of enthalpy change ΔH for all metals indicate that sorption process was an endothermic. These results support that sorption capacity of the adsorbent increases with the increasing of temperature (Surchi, 2011).

Similar trend of Gibbs free energy, entropy change and enthalpy change was observed with heavy metal adsorption on oak sawdust (Argun *et al.*, 2007) and local activated carbon (Thajeel, 2013).

Table 4. Thermodynamic constants for the sorption of Ni(II), Cd(II), Pb(II) and Cu(II) on okra leaves at various temperatures

Heavy metals	Temp. (K)	Inkc (mg g ⁻¹)	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)	R (kJ mol ⁻¹ K ⁻¹)
Ni(II)	293	1.21	-2.94	17.09	0.07	8.3143 x 10 ⁻³
	303	1.37	-3.46			
	313	1.65	-4.32			
Cd(II)	293	1.58	-3.86	8.77	0.04	
	303	1.72	-4.33			
	313	1.82	-4.72			
Pb(II)	293	1.73	-4.22	22.04	0.09	
	303	1.99	-5.02			
	313	2.31	-6.02			
Cu(II)	293	1.99	-4.85	40.43	0.15	
	303	2.44	-6.15			
	313	3.06	-7.95			

3.7. Column sorption studies of Cu(II), Cd(II), Ni(II) and Pb(II) ions

For the evaluation of sorbent efficiency of okra leaves for the sorption of Cu(II), Cd(II), Ni(II) and Pb(II) ions was analyzed by employing the flow method containing column experiments.

3.7.1. Effect of flow rate of sample

At optimum pH, the effect of flow rate in the range 1-3 mL min⁻¹ for the sorption of Cu(II), Cd(II), Ni(II) and Pb(II) ions was analyzed. Fig. 5 shows that maximum sorption was obtained at 2 mL min⁻¹ and then decreased. The decrease in sorption at higher flow rate may be attributed to the short contact time between sample ions and sorbent present in the column. As a result, equilibrium did not properly establish at high flow rate.

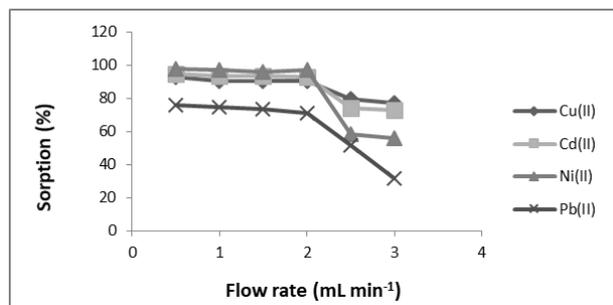


Figure 5. Effect of flow rate on the sorption of Cu(II), Cd(II), Ni(II) and Pb(II) ions on the okra leave sorbent

3.7.2. Regeneration/Desorption Study

To make sorption method more economical, it is necessary to desorb the adsorbed metals ions. Desorption process yields metals in concerted form; facilitate their disposal and restore sorbent for effective reuse (Ladeira and Ciminelli, 2004). For the regeneration of sorbent and recovery of metal ions, different mineral acids and bases were employed. The efficiency of leaching agents was evaluated with different concentrations (0.1-1M) and volumes (1-5 mL). The results indicated that 5 mL of 1M H₂SO₄ recovered 95-99% of metal ions.

3.7.3. Limit of preconcentration and preconcentration factor

The determination of preconcentration limit was based on the principle that the amount of metal ions was maintained constant (10 µg) and volume of solution increased. Cu(II), Cd(II), Ni(II) and Pb(II) ions were quantitatively collected from the solutions having concentrations in the range of 0.04-0.1 µg mL⁻¹. The calculations revealed that preconcentration factor for Cu(II), Cd(II), Ni(II) and Pb(II) ions were 40, 20, 50 and 40 respectively.

3.7.4. Breakthrough study (Total sorption capacity)

Breakthrough study is related to the concentration of the effluent of column. Generally, when the effluent concentration reaches to 3-5% of influent is treated as breakthrough point. Solutions of Cu(II) 7.9×10^{-5} mol L⁻¹, Cd(II) 4.4×10^{-5} mol L⁻¹, Ni(II) 8.5×10^{-5} mol L⁻¹ and Pb(II)

Table 5. Actual concentrations of Ni(II), Cu(II), Cd(II) and Pb(II) in different water samples

Metal	Conc: present in *(S1) mg L ⁻¹	Conc: present in *(S2) mg L ⁻¹	Conc: present in *(S3) mg L ⁻¹	Conc: present in *(S4) mg L ⁻¹
Cu(II)	0.26	0.29	0.300	0.25
Cd(II)	0.29	0.01	0.007	0.00
Ni(II)	0.25	0.08	0.360	0.10
Pb(II)	2.58	2.74	1.100	2.39

*S1:- Hand pump water (Choudhary Mohammad Sadiq Chak 147, Taluka Sadiqabad, Distt: Rahimyar Khan), *S2:- Hand pump water (Basic Health Unit Manthar, Taluka Sadiqabad, Distt: Rahimyar Khan), *S3:- Tap water (Institute For Advanced Research Studies in Chemical Sciences, University Of Sindh, Jamshoro), *S4:- Hand Pump (Madarssa Dar-ul-uloom Manthar Taluka Sadiqabad Distt: Rahimyar Khan)

2.4×10^{-5} mol L⁻¹ were passed through columns. Fig. 6 shows that breakthrough curve is obtained at 75 mL for Cu(II), 110 mL for Cd(II), 130 mL for Ni(II) and 220 mL for Pb(II). Sharp jump in the percent sorption nearly in all metal ions favors the equilibrium.

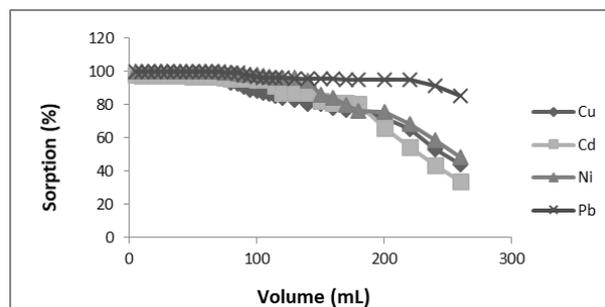


Figure 6. Breakthrough curve for the sorption of Cu(II), Cd(II), Ni(II) and Pb(II) ions on okra leaves sorbent

4. BOD and COD of treated water samples

Water is the main component for the regulating of the normal living system. Generally, the concentration of BOD (biochemical oxygen demand) is lower than the COD (chemical oxygen demand) in drinking water samples. EU (old EEC) recommended the 20-35 mg L⁻¹ of COD in drinking water. After the treatment of contaminated water samples, BOD and COD were measured. The observed results showed that Cu(II), Cd(II), Ni(II) and Pb(II) treated water samples had BOD 0.77 mg L⁻¹, 2.44 mg L⁻¹, 1.33 mg L⁻¹ and 1.513 mg L⁻¹ and COD 28 mg L⁻¹, 21 mg L⁻¹, 24 mg L⁻¹ and 37 mg L⁻¹ respectively.

5. Application of the developed method

The proposed sorbent was applied for the removal of Ni(II), Cu(II), Cd(II) and Pb(II) from drinking water samples. Table 5 shows the actual concentration of all four metal ions in drinking water before removal. Table 5 shows the efficiency of okra leaves for the removal of all four metal ions from real water systems at different concentration of these metal ions. It can be seen from Table 6 that okra leaves have good capacity to remove all four metal ions.

Table 6. Removal of Ni(II), Cu(II) Cd(II) and Pb(II) from drinking water samples

Sample	Amount added (mg L ⁻¹)	Total concentration (mg L ⁻¹)				% Removal				Residual Concentration (mg L ⁻¹)			
		Cu	Cd	Ni	Pb	Cu	Cd	Ni	Pb	Cu	Cd	Ni	Pb
S1	2.5	2.76	2.79	2.75	5.08	50.8	85.3	47.71	48.25	1.36	0.41	1.44	2.63
S1	5	5.26	5.29	5.25	7.58	64.29	96.03	57.94	65.44	1.88	0.21	2.21	2.62
S1	10	10.3	10.29	10.25	12.58	74.28	97.08	69.48	77.98	2.64	0.3	3.13	2.77
S2	2.5	2.79	2.507	2.585	5.244	42.29	88.03	50.1	32.88	1.61	0.3	1.29	3.52
S2	5	5.29	5.007	5.085	7.744	61.44	88.22	53.39	56.35	2.04	0.59	2.37	3.38
S2	10	10.3	10.01	10.09	12.74	65.4	89.71	57.46	72.06	3.56	1.03	4.29	3.56
S3	2.5	2.8	5.3	8.1	13.4	42.86	88.43	72.42	57.78	1.6	0.29	0.79	1.52
S3	5	5.3	10.3	15.6	25.9	57.74	91.21	75.4	69.67	2.24	0.44	1.32	1.85
S3	10	10.3	20.3	30.6	50.9	68.45	93.1	79.45	83.51	3.25	0.69	2.13	1.83
S4	2.5	2.75	2.5	5.251	7.751	53.47	90.4	53.1	43.73	1.28	0.24	1.22	2.75
S4	5	5.25	5	10.25	15.25	58.86	92	57.65	61.82	2.16	0.4	2.16	2.82
S4	10	10.3	10	20.25	30.25	64.59	92.2	60.59	74.65	3.63	0.78	3.98	3.14

6. Conclusion

Present work explores the competitive sorption of Ni(II), Cu(II), Cd(II) and Pb(II) from aqueous solutions. It has been found that the okra leaves can efficiently be used for the removal of all four metal ions simultaneously. Kinetic, equilibrium and thermodynamic studies favour the adsorption of all four metal ions on okra leaves sorbent. EDX analysis confirms the presence of four metal ions on the surface of metal sorbed okra leaves. At the flow rate of 2 mL min⁻¹, about 75-220 mL of metal ions having concentration 0.04-0.1 µg mL⁻¹ can be passed through the column. Further, low values of COD and BOD of treated contaminated water encourage the application of the method. It can be concluded that okra leaves can be used as a replacement to existing expensive sorbents.

References

- Ahmedna M., Marshall W.E., Husseiny A.A., Rao R.M. and Goktepe I. (2004), The use of nut shell carbons in drinking water filters for the removal of trace metals, *Water Research*, **38**, 1062-1068.
- Argun M.E., Dursun S., Ozdemir C. and Karatas M. (2007), Heavy metal adsorption by modified oak sawdust: Thermodynamics and Kinetics, *Journal of Hazardous Materials*, **141**, 77-85.
- Ashenef A. (2014), Essential and toxic metals in tea (*Camellia sinensis*) imported and produced in Ethiopia, *Foods Additives & contaminants: Part B*, **7**, 30-36.
- Basar C.A. (2006), Applicability of the various adsorption models of three dyes adsorption onto activated carbon prepared from waste apricot, *Journal of Hazardous Materials*, **B135**, 232-241.
- Bazrafshan E., Mostafapour F.K. and Mahvi A.H. (2012b), Phenol removal from aqueous solutions using pistachio-nut shell ash as a low cost adsorbent, *Fresenius Environmental Bulletin*, **21**(10), 2962-2968.
- Bazrafshan E., Ahmadabadi M. and Mahvi A.H. (2013a), Reactive Red-120 removal by activated carbon obtained from the cumin herb wastes, *Fresenius Environmental Bulletin*, **22**(2a), 484-590.
- Bazrafshan E., Ahmirian P., Mahvi A.H. and Ansari-Moghaddam A. (2016), Application of adsorption process for the phenolic compounds removal from aqueous environments: A systematic review, *Global NEST Journal*, **18**(1), 146-163.
- Bozic D., Stankovic V., Gorgievski M., Bogdanovic G. and Kovacevic R. (2009), Adsorption of heavy metal ions by sawdust of deciduous trees, *Journal of Hazardous Materials*, **171**, 684-692.
- Bulut Y. and Tez Z. (2007), Removal of heavy metals from aqueous solution by sawdust adsorption, *Journal of Environmental Sciences*, **19**, 160-166.
- Bulut Y. and Tez, Z. (2007), Adsorption studies on ground shells of hazelnut and almond, *Journal of Hazardous Materials*, **149**, 35-41.
- Chandio Z.A., Talpur F.N., Afridi H.I., Khan H., Khaskheli G.Q. and Khaskheli M.I. (2013), Online preconcentration of nickel(II) in textile effluent and soil samples by SDS coated alumina modified with dithizone mini-column coupled with FAAS, *Analytical Methods*, **5**, 4425-4429.
- Chandio Z.A., Talpur F.N., Khan H., Khaskheli G.Q. and Afridi H.I. (2013), Online preconcentration using surfactant coated alumina modified with 1, 5-diphenylthiocarbazon and determination of cadmium in environmental samples by flame atomic absorption spectrometry, *Analytical Letters*, **46**, 1562-1572.
- Chatterjee S.K., Bhattacharjee I. and Chandra G. (2010), Biosorption of heavy metals from industrial waste water by *Geobacillus thermodenitrificans*, *Journal of Hazardous Materials*, **175**, 117-125.
- Chen Y.N., Chai L.Y. and Shu Y.D. (2008), Study of arsenic (V) adsorption on bone char from aqueous solution, *Journal of Hazardous Materials*, **160**, 168-172.
- Evangelin C.D., Gunasekaran S.G. and Dharmendirakumar M. (2014), Preparation and characterization of chemically modified silk cotton hull activated carbon and its effects Cd(II) removal from aqueous solutions, *Bioremediation Journal*, **18**, 81-92.
- Farajzadeh M.A. and Monji A.B. (2004), Adsorption characteristics of wheat bran towards heavy metal cations, *Separation and Purification Technology*, **38**, 197-207.
- Feng D. and Aldrich C. (2004), Adsorption of heavy metals by biomaterials derived from the marine alga *Ecklonia maxima*, *Hydrometallurgy*, **73**, 1-10.
- Fiol N., Villaescusa I., Martinez M., Miralles N., Poch J. and Serarols J. (2006), Biosorption of aqueous Pb²⁺, Cd²⁺, and Ni²⁺ from aqueous solution by olive stone waste, *Separation and Purification Technology*, **50**, 132-140.
- Fuller C.C., Bargar J.R., Davis J.A. and Piana M.J. (2002), Mechanisms of uranium interactions with hydroxyapatite:

- implications for ground water remediation, *Environmental Science and Technology*, **36**, 158-165.
- Ho Y.S. (2006), Second-order kinetic model for the sorption of cadmium onto free fern: A comparison of linear and non-linear methods, *Water Research*, **40**, 1191-125.
- Iftikhar A.R., Bhatti H.N., Hanif M.A. and Nadeem R. (2009), Kinetic and thermodynamic aspects of Cu(II) and Cr(III) removal from aqueous solutions using rose waste biomass, *Journal of Hazardous Materials*, **161**, 941-947.
- Jaeyoung C., Ju Y.L. and Jung-Seok Y. (2009), Biosorption of heavy metals and uranium by star fish and *Pseudomonas*, *Journal of Hazardous Materials*, **161**, 1571-162.
- Kefela M.I., Zouboulis A.I. and Matis K.A. (2000), Biosorption of cadmium ions by actinomycetes and separation by floatation, *Environmental Pollution*, **104**, 283-293.
- Kim Y.Y., Dark S.K., Cho S.Y., Kim H.B., Kim Y.K.S.D. and Kim S.J. (2005), Adsorption of heavy metals by brewery biomass, *Korean Journal of Chemical Engineering*, **22**, 91-98.
- Khaskheli M.I., Memon S.Q., Siyal A.N. and Khuhawar M.Y. (2011), Use of orange peel waste for arsenic remediation of drinking water, *Waste Biomass Valorization*, **2**, 423-433.
- Khaskheli M.I., Memon S.Q., Parveen S. and Khuhawar M.Y. (2014), Citrus paradise: An effective bio-adsorbent for arsenic (V) remediation, *Pakistan Journal of Analytical and Environmental Chemistry*, **15**, 35-41.
- Khaskheli M.I., Memon S.Q., Chandio Z.A., Jatoi W.B., Mahar M.T. and Khokhar F.M. (2016), Okra leaves-Agricultural waste for the removal of Cr(III) and Cr(VI) from contaminated water, *American Journal of Analytical Chemistry*, **7**, 395-409.
- Kumar P.S., Vincent C., Kirthika K. and Kumar K.S. (2010), Kinetics and equilibrium studies of Pb²⁺ ion on removal from aqueous solution by use of nano-silversol-coated activated carbon, *Brazilian Journal of Chemical Engineering*, **27**, 339-346.
- Ladeira A.C.Q. and Ciminelli V.S.T. (2004), Adsorption and desorption of arsenic on an oxisol and its constituents, *Water Research*, **38**, 2087-2094.
- Li X., Tang Y., Cao X., Lu D., Luo F. and Shao W. (2008), Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **317**, 512-521.
- Lu W.B., Shi J.J., Wang C.H. and Chang J.S. (2006), Biosorption of lead, copper and cadmium by an indigenous isolate *Enterobacter* sp. J1 possessing high heavy-metal resistance, *Journal of Hazardous Materials*, **B13**, 80-86.
- Malakahmad A., Tan S. and Yavari S. (2016), Valorization of waste black tea as a low-cost adsorbent for nickel and zinc removal from aqueous solution, *Journal of Chemistry*, <http://dx.doi.org/10.1155/2016/5680983>.
- Martinez M., Miralles N., Hidalgo S., Fiol N., Villaescusa I. and Poch J. (2006), Removal of lead(II), and cadmium(II) from aqueous solutions using grape stalk waste, *Journal of Hazardous Materials*, **B133**, 203-211.
- Memon S.Q., Bhangar M.I., Hasany S.M. and Khuhawar M.Y. (2007), The efficacy of nitrosonaphthol functionalized XAD-16 resin for the preconcentration/sorption of Ni (II) and Cu(II) ions, *Talanta*, **72**, 1738-1745.
- Memon S.Q., Hasany S.M., Bhangar M.I. and Khuhawar M.Y. (2005), Enrichment of Pb(II) ions using phthalic acid functionalized XAD-16 resin as a sorbent, *Journal of Colloid and Interface Science*, **291**, 84-91.
- Memon S.Q., Memon N, Shah S.W., Khuhawar M.Y. and Bhangar M.I. (2007), A green and economical sorbent for the removal of cadmium(II) ion, *Journal of Hazardous Materials*, **B139**, 116-121.
- Oladoja N.A., Oladoja I.A., Idiaghe J.A. and Egbon E.E. (2009), Equilibrium isotherm analysis of sorption of congo red by palm kernel coat, *Central European Journal of Chemistry*, **7**, 760-768.
- Olajide S. (2009), Effect of pre-treatment on dyeing characteristics and kinetics of okra (*Abelmoschus esculentus* L. Moench) slices, *International Journal of Food Engineering*, **5**, 1-11.
- Oliveira W.E., Franca A.S., Oliveira L.S. and Rocha S.D. (2008), Untreated coffee husks as biosorbents for the removal of heavy metals from aqueous solutions, *Journal of Hazardous Materials*, **152**, 1073-1081.
- Panda G.C., Das S.K. and Guha A.K. (2008), Biosorption of cadmium and Nickel by functionalized husk of *Lathyrus Sativus*, *Colloids and Surfaces B: Biointerfaces*, **62**, 173-179.
- Parsad M.N.V. and Freltas H. (2000), Removal of toxic metals from solution by leaf, stem and root phytomass of *Quercus ilex* (holly Oak), *Environmental Pollution*, **110**, 277-283.
- Pehlivan E., Altun T. and Parlayici S. (2009), Utilization of barley straws as biosorbents for Cu(II) and Pb(II) ions, *Journal of Hazardous Materials*, **164**, 982-986.
- Ranjan D., Talat M. and Hasan S.H. (2009), Biosorption of arsenic from aqueous solution by using agricultural residue 'rice polish', *Journal of Hazardous Materials*, **166**, 1050-1059.
- Rao M.M., Ramana D.K., Seshiah K., Wang M.C. and Chien C.S.W. (2009), Removal of some metal ions by activated carbon prepared from *Phaseolus aureus* hulls, *Journal of Hazardous Materials*, **166**, 1006-113.
- Rojas G., Silva J. and Flores J.A. (2005), Adsorption of chromium on cross linked chitosan, *Separation and Purification Technology*, **44**, 31-36.
- Sassi M., Bestani B., Said A.H., Bendorouche N. and Guibal E. (2010), Removal of heavy metal ions from aqueous solutions by a local sludge as a biosorbent, *Desalination*, **262**, 243-250.
- Silverstein R.M. and Webster F.X. (1998), *Spectrometric identification of Organic Compounds*. 6th ed. John Wiley & Sons.
- Sobecka E. (2001), Changes in the iron level in the organs and tissues of wells catfish, *slurus glanis* L. caused by nickel, *Acta Ichthyologica Piscatoria*, **31**, 127-143.
- Southichak B., Nakano K., Munehiro Chiba N. and Nisbimura O. (2006), *Phragmites australis*: A novel biosorbent for the removal of heavy metals from aqueous solution, *Water Research*, **40**, 2295-2302.
- Suman V.B., Melo J.S., Chaugule B.B. and D'Souza S.F. (2008), Biosorption characteristics of uranium (VI) from aqueous medium onto *Catenellarepens*, a red algae, *Journal of Hazardous Materials*, **158**, 628-635.
- Surchi M.M.S. (2011), Agricultural wastes as low cost adsorbents for Pb removal: kinetics, equilibrium and thermodynamics, *International Journal of Chemistry*, **3**, 53-77.
- Thajeel A.S. (2013), Isotherm, kinetic and thermodynamic of adsorption of heavy metal ions onto local activated carbon, *Aquatic Science and Technology*, **1**, 53-77.
- Urik M.P., Littera S.J., Kolencik M. and Cernasky S. (2009), Removal of arsenic (V) from aqueous solutions using modified sawdust of spruce (*Picea abies*): kinetics and isotherm studies,

International Journal of Environmental Science and Technology, **6**, 451-456.

Vijayaraghavan K., Padmesh T.V.N., Palanivelu K. and Velan M. (2006), Biosorption of nickel(II) ions onto *Sargassum wightii*. Application of two-parameter and three-parameter isotherm models, *Journal of Hazardous Materials*, **B133**, 304-308.

Wong K.K., Lee C.K., Low K.S. and Haron M.J. (2003), Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions, *Chemosphere*, **50**, 23-28.

W.H.O, (2011), *Guidelines for drinking water-quality*, 4th Ed, Geneva 27, Switzerland