Competitive Removal of Lead Copper and Cadmium from Aqueous Solution onto Tea Waste

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Abstract:-

Experiments were carried out to use tea waste to remove lead, copper and cadmium ions from aqueous solutions in single, binary and ternary systems. Batch biosorption studies were carried out to examine the biosorption capacity, pH value, agitation speed, and metal ions concentration. The biosorption process showed that the tea waste was an effective biosorbent for metal ions removal with the initial concentrations of 50 mg/l. The residual concentration of Pb (II), Cu (II) and Cd (II) were determined using Atomic Absorption Spectrophotometer. The optimum pH found for removal Pb (II) and Cd (II) ion occurred at pH 5 while for Cu (II) ion occurred at pH of 6 respectively. Zeta potential measurements for tea wastes indicated that the negative sites of tea waste gave the greatest zeta-potential value at pH 5. The effect of functional groups of tea waste was found by Fourier transformation infrared spectroscopy analysis. The results showed that the biosorption was a complex process and depended on the number and type of active groups. Carboxyl, amino, aromatic, hydroxyl and sulfonic groups were involved in this process. Pb(II) made a greater change in the functional groups of tea waste due to high affinity to this metal. The removal efficiencies for metal ions decreased in binary and ternary systems as compared with single system. The sequence for metal ions removal in single system was Pb > Cd > Cu; while in binary and ternary was Pb > Cu > Cd. In addition, the experimental data indicated that the biosorption of Pb(II), Cu(II) and Cd(II) ions fitted well the Langmuir isotherm for single system and extended Langmuir for binary and ternary system. Kinetic studies showed that a pseudo second order model was more suitable. than the pseudo first order model.

Key words: Tea waste, adsorption, single system, binary system, ternary system.

1. Introduction

Environmental pollution is currently one of the most important issues facing humanity. It was increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures [19]. Between different pollutants, heavy metals have been received more attention by environmental engineers since these substances are a unique class of toxicants that cannot be broken down into non-toxic forms [4]. Heavy metals are often derived from heavy industry such as electroplating, battery factories, metal finishing, and chemical manufacturing [14]. Heavy metals are generally considered to be those whose density exceeds 5 g/cm^3[16]. According to World Health Organization (WHO) the metals of most immediate concern are nickel, cadmium, chromium, copper, zinc, iron, mercury and lead [27].From these heavy metals, Pb(II), Cu(II) and Cd(II) are investigated in the present study.

Many methods of remediation have been designed which includes chemical precipitation, solvent extraction, electro-dialysis, electro-flotation, ion exchange, reverse osmosis and membrane filtration. Most of these methods are costly, inadequate efficiencies mostly at low metal ion concentration especially in the range of 1-100 mg/l [10]. Among these treatment processes, adsorption is highly efficient, inexpensive and easy to adapt. Adsorption of metal ions from wastewater is now shifting from the use of conventional adsorbents to the use of biosorbents [1]. Low cost agricultural waste by-products such as sugarcane bagasse, rice husk, sawdust, coconut husk, neem bark, etc., for the elimination of heavy metals from wastewater have been investigated by various researchers [8].Tea is one of the most popular beverages and about 3.5 million tons of tea was consumed annually in the world [23]. The amount of dry tea produced from 100kg green tea leaves is 22 kg on average and approximately 18 kg tea is packed for the market. The other 4kg of dry tea material is wasted. Furthermore, additional amount of tea leaves enters the environment by defoliation and pruning annually. These tea wastes could cause environmental hygiene problems during their degradation process and contaminate water environment by releasing organic matter [24].

The fact cannot be ignored that single toxic metallic species rarely exist in wastewaters. In fact, the presence of multiple metal ions often causes an interactive effect while insufficient attention seems to have been given to this problem. Relatively few studies on multi metal systems have been reported, though multi metal competitive interactions in solution with the sorbent material are amongst the basic factors affecting the degree of metal removal by biosorption [22].

For instance, Putra et al. [18] investigated the use of coconut tree sawdust (CTS), eggshell (ES) and sugarcane bagasse (SB) as alternative low-cost biosorbents for the removal of Cu(II), Pb(II) and Zn(II) ions from aqueous solutions using batch technique. The optimum biosorption condition was found at pH 6.0; 0.1 g biomass dosage and at 90 min equilibrium time. The adsorption data were fitted to the Freundlich and Langmuir isotherm models. They estimated maximum adsorption capacities from the Langmuir model for Cu(II), Pb(II) and Zn(II) as follows: 3.89, 25.00 and 23.81 mg/g for CTS, 34.48, 90.90 and 35.71 mg/g for ES, and 3.65, 21.28 and 40.00 mg/g for SB, respectively. Shahmohammadi-Kalalagh et al. [20] investigated the feasibility of kaolinite as a low-cost adsorbent for the removal of Pb(II), Zn(II) and Cu(II) from aqueous solutions using batch technique then analyzed the data by Langmuir, Freundlich, Temkin and Redlich-Peterson isotherm ,then correlation coefficients showed that the Redlich Peterson isotherm described the data appropriable than others. The effectiveness of kaolinite in the sorption of the three metals from aqueous system was Pb(II) > Zn(II) > Cu(II). Kinetic studies showed that a pseudo second order model was more suiTable. than the pseudo first order model.

This study aim to investigate the ability of tea waste as a low-cost adsorbent for the removal of Pb(II), Cu(II) and Cd(II) from aqueous solution. The sorption was investigated considering the effects of pH, contact time, and initial metal concentration. The isotherms and kinetics of tea waste biosorption were studied to understand the sorption mechanism of metals.

2. Materials and Methods

2.1. Biosorbent and Chemicals

Tea wastes have been collected from solid wastes at home. It was washed with hot water from 3 to 6 times until the filtrate was virtually colorless and then dried under sun for 2 days. The dried leaves were ground and sieved to obtain grain sizes of 500μm in diameter and then stored in polyethylene bags until use. The physical properties of tea waste are measured at the laboratories of Ministry of Oil (Petroleum Research and Development Center) as showed in Table. (1).

All the chemicals used in this study were of analytical grade. Synthetic wastewater used in this experiment containing the required concentration of metal was prepared by dissolving the calculated amount Pb $(NO_3)_2$, $CuSO_4.5H_2O$ and $Cd(NO_3)_2.4H_2O$ in distilled water. Table. (2) shows the main physicochemical properties of the metals tested. The concentration of the metal was subsequently determined using flame atomic absorption spectrophotometer (AAS; SHIMADZU, Model: 7200, Japan). The initial pH of the working solutions was adjusted by addition of 1 mol/l NaOH or HCl using a pH meter(WTW,inoLab 720, Germany).

Table. 1: Physical characteristics of tea wastes

Property	Tea wastes	Test method
Surface area (m^2 /g)	9.9569	ISO-9277-2010
Real density (g/ cm^3)	2.0835	ASTM D-4892
Bulk density (g/ cm^3)	0.2626	ASTM D-4164

Table. 2: Main physicochemical properties of the metals tested

Property	Lead nitrate	Copper sulfate	Cadmium nitrate tetrahydrate
Appearance	white crystals	Blue crystals	White colorless crystals
Chemical formula	$Pb(NO_3)_2$	$CuSO_4.5H_2O$	$Cd(NO_3)_2.4H_2O$

Molecular weight (g/mole)	331.2	249.70	308.7
Atomic weight (g/mole)	207.2	63.546	112.7
Density (g/cm^3)	4.53	2.284	2.45
Solubility in water g/100 ml at 20 °C	54.3	32	136
Hydrated ionic radius, Å	4.01	4.19	4.26
Company	BDH England	RIEDEL DE HAEN Germany	BDH England

2.2 Experimental Work

Batch adsorption experiments have been carried out to find the best pH, agitation speed, contact time, sorbent dosage and initial metal concentration on removal efficiency of lead, copper and cadmium ions from aqueous solutions. Conical flasks of 250 ml volume were filled with 100 ml of known concentration of heavy metals solutions. PH of aqueous solutions in each flask was adjusted to a desired value. A known weight of sorbent material was added into each flask, and then the flasks were placed on a shaker incubator and agitated continuously for desired time and at room temperature ~ 30 ºC. The removal of heavy metal ions using tea wastes was studied in single component system, the effect of parameter with range of 3-8 pH, 125-250 rpm agitation speed and 0-180 minute contact time, while the effect sorbent dosage range of 0. 5- 8 g/l and concentration of heavy metal ions 30-200 ppm were tested in single binary and ternary component systems. After each experiment, the sorbent was separated from aqueous solution by using filter paper (WHATMAN, diameter 7 cm) and then the samples were analyzed by (AAS) for remaining heavy metal content.

The percentage adsorption of Pb(II), Cu(II) and Cd(II) from the solution was calculated from the relationship:

$$\%\text{Adsorption}=\frac{C_o-C_f}{C_o}\times 100\% \quad \ldots.\ (1)$$

Where: C_o corresponds to the initial concentration of metals and C_f is the residual concentration after adsorption.

2.3Isotherm Experiment and Models

Biosorption isotherm of Pb (II), Cu(II) and Cd(II) onto tea wastes was investigated in single , binary and ternary systems. The experiments were carried out in 250 ml stoppered conical flasks containing 100 ml of metal aqueous solution with initial concentration of 50 mg/l of each metal was used in conjunction with sorbent dosage (0.5-8 g/l) under constant shaking (175 rpm) for 120 minutes. The pH solution was adjusted to the best value based on the pH study. After that the adsorbed amount is then calculated by using Eq. (2):

$$q_e=\frac{V_L(C_O-C_e)}{m} \quad \ldots.\ (2)$$

Where V_L is volume of wastewater sample in flask (L); m is the mass of sorbent materials (g). For binary and ternary system, the same procedure of single system experimentation was followed. The sorption isotherm for single, binary and ternary solutions were obtained by plotting the weight of solute adsorbed per unit weight of sorbent (q_e mg/g) against the equilibrium concentration of solute in the solution (C_e mg/l) [5].The experimental isotherm data were fitted with the following sorption isotherm models as shown in Table. (3).

Table. 3 Sorption Isotherms models

<table>
<tr><th colspan="5">Single component system</th></tr>
<tr><th>Model</th><th>Non linear form</th><th>Linear form</th><th>Plot</th><th>Reference</th></tr>
<tr><td rowspan="2">Langmuir</td><td>$q_e = \frac{q_m b C_e}{(1 + bC_e)}$</td><td>$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{b\,q_m} * \frac{1}{C_e}$</td><td>$\frac{1}{q_e}$ vs $\frac{1}{C_e}$</td><td rowspan="2">[21]</td></tr>
<tr><td colspan="3">q_m is the maximum sorption capacity for monolayer coverage, (mg/g);
b is the constant related to the affinity of the binding site, (L/mg).</td></tr>
<tr><td rowspan="2">Freundlich</td><td>$q_e = KC_e^{1/n}$</td><td>$\ln q_e = \ln K + \frac{1}{n} \ln C_e$</td><td>Ln q_e vs ln C_e</td><td rowspan="2">[25]</td></tr>
<tr><td colspan="3">K is constant indicative of the relative adsorption capacity of the adsorbent, $(mg/g)(L/mg)^{1/n}$; 1/n is constant indicative of the intensity of the adsorption.</td></tr>
<tr><td rowspan="2">Temkin</td><td>$q_e = \frac{RT}{c} \ln(k_T\, c_e)$</td><td>$q_e = B * \ln(k_T) + B * \ln(c_e)$</td><td>qe vs ln Ce</td><td rowspan="2">[25]</td></tr>
<tr><td colspan="3">k_T = equilibrium binding constant (L/mg) corresponding to maximum binding energy , B = constant related to the heat of adsorption</td></tr>
<tr><th colspan="5">Multi- component isotherm models</th></tr>
<tr><th>Models</th><th>Non linear form</th><th colspan="2">Plots</th><th>Reference</th></tr>
<tr><td rowspan="2">Extended Langmuir</td><td>$q_{e,i} = \frac{b_i q_{m,i} C_{e,i}}{\left(1 + \sum_{j=1}^{n} b_j C_{e,j}\right)}$</td><td colspan="2">$\frac{1}{q_e}$ vs $\frac{1}{C_e}$</td><td rowspan="2">[26]</td></tr>
<tr><td colspan="3">$q_{m,i}$ and b_i are the single component Langmuir parameters for component i.</td></tr>
<tr><td rowspan="2">Extended Freundlich</td><td>$q_{e,i} = \frac{K_i C_{e,i}^{ni+n1}}{C_{e,i}^{n1} + \sum_{j=1}^{N} K_j C_{e,j}^{nj}}$</td><td colspan="2">Ln q_e vs ln C_e</td><td rowspan="2">[17]</td></tr>
<tr><td colspan="3">K_i and n_i are derived from the corresponding individual Freundlich isotherm equation for the component i.</td></tr>
</table>

The essential characteristics of a Langmuir isotherm equation could be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_s which is defined by the following equation [24]:

$$R_s = \frac{1}{1+bC_o} \quad \text{….. (3)}$$

The separation factor as described above was calculated using the Langmuir model constants. This separation factor yields the type of isotherm as shown in Table. (4).

Table. 4 Values of separation factor and type of isotherm [24]

Value of R_s	Type of isotherm
$R_s > 1$	Unfavorable
$R_s = 0$	Linear
$0 < R_s < 1$	Favorable
$R_s < 0$	Irreversible

The parameters for each sorption isotherm models were determined by fitting of the equations to the experimental data using Microsoft Excel.

2.4 Kinetic Experiment and Models

The biosorption kinetic experiments were conducted for each heavy metal in single system by using 8 volumetric flasks filled with 100 ml of metal solution at initial concentration of 50 mg/l. The contents of volumetric flask were adjusted to the best value of pH based on the pH study. Then, 0.2 g of tea waste adsorbate was added for metal solution in each flask and then shaking at agitation speed of 175 rpm. For a regular time intervals (10, 15, 30, 60, 90, 120, 150 and180 minute), the samples were taken and analyzed to determine the heavy metal content. The biosorption capacity (q_t mg/g) for each time interval was calculated using Eq. (2). Kinetic models can be helpful for understanding the mechanism of sorption and evaluating the performance of an adsorbent [14]. In this study, the sorption kinetics was modeled using the pseudo-first-order and pseudo-second-order kinetic models. The equations of the kinetic models are presented in Table. (5).The parameters for each kinetic model was determined by fitting the equations to the experimental data by using Microsoft Excel.

Table. 5 Kinetic Models

Model	Linear expression	Reference
Pseudo-First Order Kinetic	$\ln(q_{eq} - q_t) = \ln q_e - k_1 t$	[11]
	q_{eq} is the amount of metal sorbed at equilibrium, (mg/g); k_1 is the equilibrium rate constant, (1/min).	
Pseudo Second Order Kinetic	$\frac{t}{q_t} = \left(\frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}\right)$	[9]
	q_{eq} is the amount of metal ion sorbed at equilibrium, (mg/g); k_2 is the rate constant of sorption, (g/mg min).	

2.5 FTIR analysis

The main effective binding sites and the functional groups(carbonyl, carboxylic, hydroxyl and others) present on the biomass of tea wastes can be identified by Fourier-Transform Infrared Analysis (FTIR) spectral comparison of the biosorbent, Pb(II) ions- loaded biosorbent, Cu(II) ions- loaded biosorbent, and Cd(II) ions- loaded biosorbent.

Tea wastes of 0.4g was contacted with 100 ml of 50 mg/l for each Pb(II), Cu(II) and Cd(II) solutions, respectively. The contents of volumetric flask were adjusted to pH value of 5. The samples were shaking in shaker at agitation speed of 175 rpm for 120 minutes.

The adsorbent samples were filtered and left to dry. Dried samples were collected and analysis by using Fourier transform infrared spectroscope (SHIMADZO FTIR, 800 series spectra- photometer) at the laboratories of University of Baghdad (Iben Sena Center).

3. Results and Discussion

3.1 Effect of pH

The pH plays an important role in controlling the sorption process. It affects the solution chemistry of the metal and the network of charges on the surface of the sorbent as well as physico-chemistry and hydrolysis of the metal [8]. In order to evaluate the influence of pH on sorption of the metal ions, the experiments were carried out in pH range of 3 - 8 for Pb (II), Cu (II), and Cd (II) at 2g/l tea wastes dosage with initial metals concentration 50 mg/l for 120 minutes in single system. Fig. 1 Indicates that the percentage sorption of Pb (II), Cu (II), and Cd (II) increases with increasing of pH to attain a maximum between 5 and 6 pH and thereafter it decreases with further increase in pH.

The minimum sorption was observed at lower pH values which may be due to the hydrogen(H^+)ions compete with M(II) for the surface active sites of tea wastes, and the complex between M(II) and the acidic functional groups is expected to be destabilized with the adsorbed M(II) released into the solution. Further increase in pH i.e., above 7 causes precipitation of metal ions on the adsorbent; this due to the insoluble metal hydroxides $M(OH)_2$ start precipitating from the solutions at higher pH values and makes the true sorption studies impossible. The decrease in the removal efficiency at high pH value may be attributed to the fact that the negative species of metals, $M(OH)_3^-$ and $M(OH)_4^{-2}$,are not capable of a combination with the negative surface of sorbents[2, 5 and 23].

To achieve high removal efficiency without metal hydroxide precipitation, pH of 6 for Cu(II) and pH of 5 for Pb (II) and Cd (II) in single component and pH of 5.5 in binary and ternary component were selected for subsequent experiments.

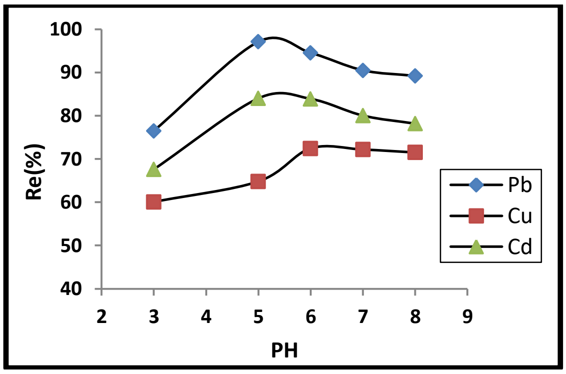


Fig. 1 Effect of pH on the removal of Pb(II), Cu(II), and Cd(II) by tea waste (C_o=50 mg/l; tea dosage=2g/l; rpm=175 ; time=120 min).

3.2 Effect of Agitation Speed

The effect of the agitation speed on the removal efficiency of three metal ions in single system was investigated at three different agitation speed (125, 175, 250 rpm) by using 2 g/L tea wastes, pH 5-6, contact time 120 min and metal concentration 50 mg/l. Fig. 2, it can be noticed that the removal efficiency of metal ions increase with increase of agitation speed from 125 to 175 rpm and further increases has no significant effect (i.e., above 175 rpm). The increase in efficiency is due to the increase in turbulence and as a consequence, decreases the film resistance to mass transfer surrounding the adsorbent particles [13]. Moreover, these results indicate that agitation speed of 175 rpm is sufficient to obtain maximum removal by reducing the boundary layer thickness to a minimum value.

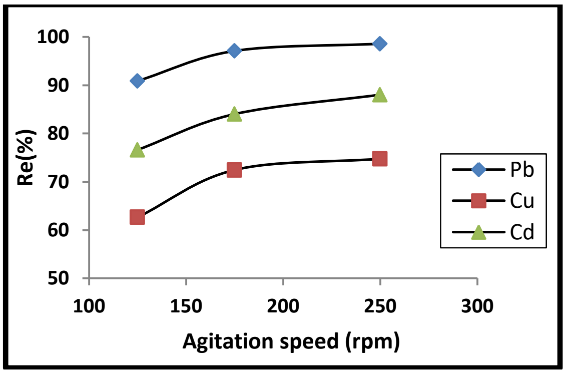


Fig. 2 Effect of agitation speed on removal of Pb(II), Cu(II), and Cd(II) by tea waste in single system (C_o=50 mg/l; pH=5-6; dosage=2g/l; time=120 min.)

3.3 Effect of Contact Time

The removal of Pb(II), Cu(II), and Cd(II) from aqueous solution was studied as function of contact time in the time interval 0-180 minute at 50 mg/l initial metal concentrations, pH 5-6, 2g/l tea wastes dosage and agitation speed 175 rpm for single system. Fig. 3 shows that the percentage of metals ion sorbed increased with increasing time and it reached equilibrium at about 60 minute. Further increases in contact time had no significant effect on metal removal and the sorption rate become practically very slow. It can be concluded that 60 minute contact time is sufficient to reach equilibrium conditions for all metal.

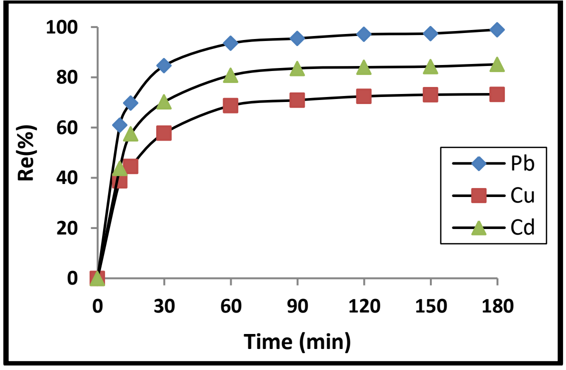


Fig. 3 Effect of contact time on the removal of Pb(II), Cu(II), and Cd(II) by tea waste in single system (C_o=50 mg/l; pH=5-6; rpm=175; tea dosage = 2g/l).

3.4 Effect of Sorbent Dosage

The effect of sorbent dosage on the removal of metal ions was studied using 0.5-8 g/l tea wastes by shaking 175rpm with 50 mg/l of Pb(II), Cu(II), and Cd(II) concentrations for 120 minutes, at pH range between 5-6 for single, binary, and ternary systems. Fig. 4, the results indicated that the retention of metals increased with increasing amount of sorbent up to 4 g/l further increases in sorbent dosage has a small or limited increase in the removal efficiency.

The amount of metal ions removed from the solutions increases by increasing the amount of sorbent. This is an expected result because as the adsorbent concentration increases for a fixed initial metal concentration, the number of sorbent particles surrounding the metal ions or ratio of sorbent particles to metal ions increases, therefore, these particles attach more ions to their surfaces. Increase in sorption with sorbent dose can be attributed to increased sorbent surface area and hence the number of binding sites available to the metal ions [24].

Also Fig. 4 shows that the removal efficiencies of Pb, Cu and Cd at 4 g/l tea wastes were about 98.35%, 89.45% and 92.78% respectively for single system and decreases to 91.4%, 80.6% and 50.93% respectively for ternary system. While for binary system, the efficiency decreased to 93.82% for Pb, 86.33% and for Cu (Pb, Cu system), 97.7% for Pb and 84.59% for Cd (Pb, Cd system), and about 68.24% for Cu and 61.06% for Cd, (Cu,Cd system).

For binary and ternary system, it can be noticed that the removal efficiency of Pb(II) is higher than that of Cu(II) and Cd(II). This can be due to the physical and chemical properties of Pb(II) to be more favorable to be sorbed than Cu(II) and Cd(II). This behavior may be attributed to the hydrated ionic radius Å, which affects the accessibility of the metal ions to the surface of the pores. Thus, due to the competition between metals ions, the ions with hydrated radius smaller than the pore size are able to move easily within the pores. The hydrated ionic radius as given previously in Table. 2 are as follow: Pb(II) (4.01 Å) < Cu(II) (4.19 Å) < Cd(II) (4.26 Å) [15]. Therefore, the sequence of metals removal was Pb > Cu > Cd. But except the case for tea wastes in single system were the removal of Cd(II) is greater than Cu(II) which may related to different affinity of copper and cadmium for the donor atoms (i.e. oxygen) present in the structure of tea waste as noticed by Cay et al. [2]. In addition, the molecular weight of Pb(II), Cd(II), and Cu(II) are 331.2, 308.7 and 249.70 respectively. As the uptake related to the molecular weight of metals and as the molecular weight increases, the uptake rate increases and Pb(II) and Cd(II) having higher molecular weight than Cu(II) [7].

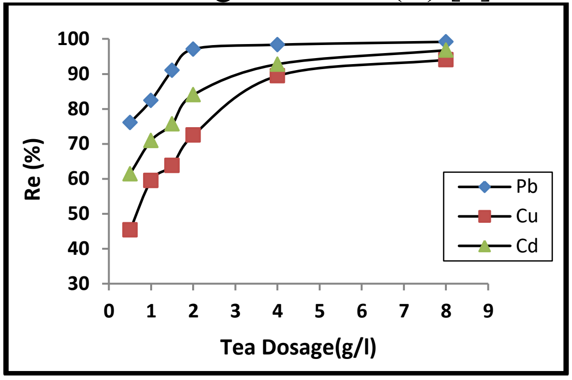
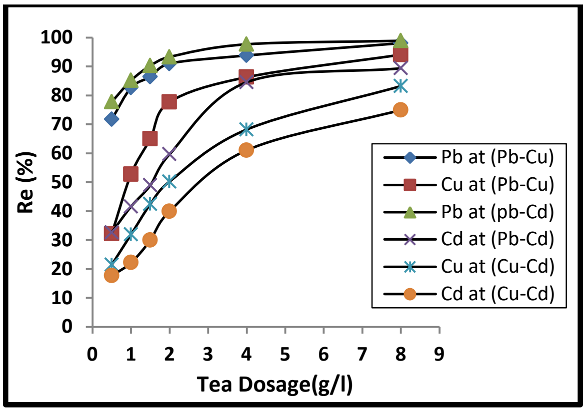
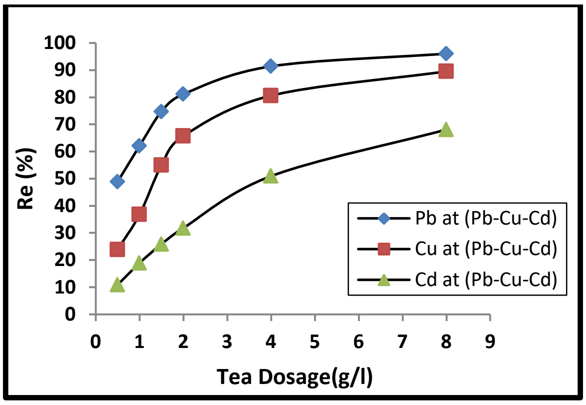


Fig.4 Effect of sorbent dosage on the removal of Pb(II), Cu(II), and Cd(II) by tea waste (Co=50 mg/l; pH=5-6; rpm=175; time=120 min.)

(a)Single system



(b) Binary system



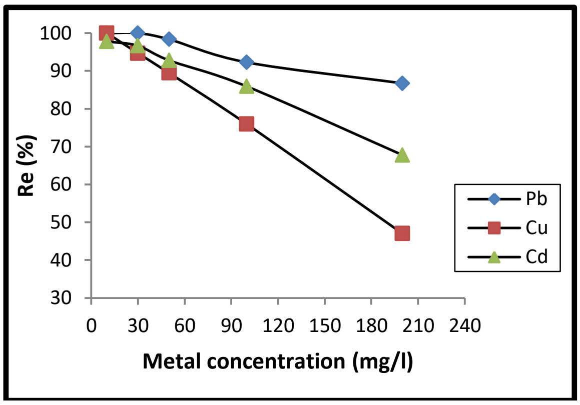
(c) Ternary system

Fig. 4 Continued

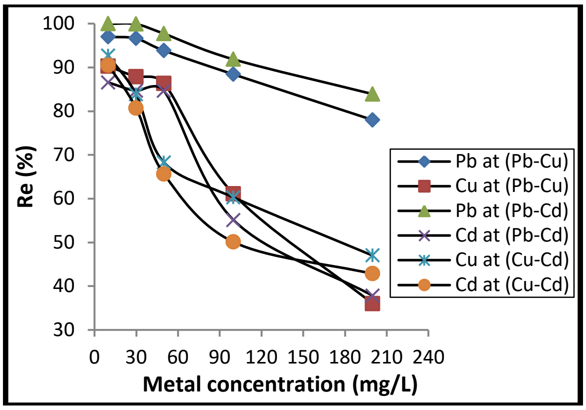
3.5 Effect of Initial Metal Concentration

The experiments were performed at distinct initial Pb(II), Cu(II), and Cd(II) concentrations ranging from 10 to 200 mg/l with 4g/l dosage sorbent in single, binary and ternary system and keeping other parameters constant as shown in Fig. 5.

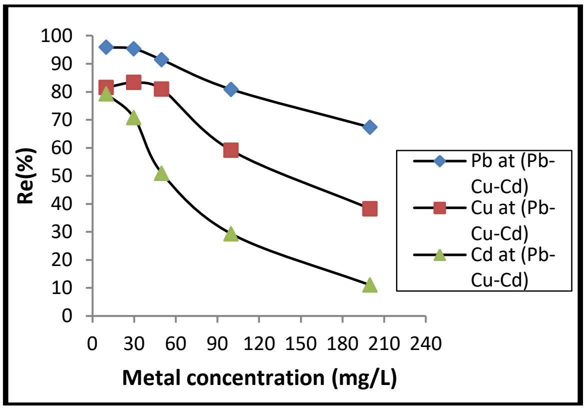
In single system, the results indicated that the percentage removal of metals was slightly decreased with an increase in the initial metals concentration from 10 to 50 mg/l, whereas a rapid decrease in the percentage removal was observed at the initial concentrations between 50 and 200 mg/l. This behavior may be attributed to the decrease in the available sorption sites on the surface area of the sorbent at a metal ion concentration from 50 to 100 mg/l. At higher concentration of metal ions, the ratio of initial number of moles of metal ions to the sorption sites available was higher, resulting in lower sorption percentage. The same behavior had been observed in [5, 14]. From the comparison between the single ,binary and ternary system, it can be seen that the percentage removal decreases with increasing the competing metal ions concentration, and the percentage removal for each metal decreases in binary and ternary system as compared with single system. The difference in percentage removal of different heavy metal ions at the same initial metal ions concentration, adsorbent dose and contact time may be attributed to the competition between metals as a result of the difference in their chemical affinity and exchange capacity with respect to the binding sites and chemical functional group on the surface of the sorbent [23].



(a)Single system



(b)Binary system



(c)Ternary system

Fig. 5 Effect of metal concentration on the removal of Pb(II), Cu(II), and Cd(II) by tea waste (pH =5-6; time=120 min.; rpm=175; dosage= 4 g/l)

3.6 Sorption Isotherm Models

Sorption isotherms are very important tools for the analysis of sorption process and establish the relationship between the equilibrium concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature**.** The Freundlich isotherm is derived by assuming a heterogeneous surface with a non-uniform distribution of heat of adsorption over the surface. Whereas in the Langmuir theory basic assumption is that the sorption takes place at specific homogeneous sites within the adsorbent. Temkin isotherm contains a factor that explicitly takes into the account adsorptive-adsorbent interactions. This isotherm assumes that (i) the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that (ii) the adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [24].

The Langmuir, Freundlich and Temkin sorption constants are evaluated from isotherms and their correlation coefficients in single system are presented in Fig.6 and Table. (6).The obtained data for binary and ternary component system were correlated with Langmuir and Freundlih isotherm models, Fig.7 and Table.7. The parameters for each model were obtained by fitting their equations to the experimental data using Microsoft Excel.

From these Table.s, the Langmuir model described the sorption data slightly better than the other model depending on the value of coefficient of determination (R^2). The equilibrium isotherm for each metal in single component is of favorable type ($0<R_S<1$).

Table. 6. Parameters of single solute isotherm for Pb(II), Cu(II), and Cd(II) ions onto tea wastes

Models	**Parameters**	**Heavy Metals**		
		Pb(II)	**Cu(II)**	**Cd(II)**
Langmuir	b (L/mg)	0.1926	0.0296	0.052
	q_m (mg/g)	86.713	74.096	77.168
	R_s	0.09406	0.4029	0.2777
	R^2	0.9824	0.9771	0.989
Freundlih	K,(mg/g)(L/mg)$^{1/n}$	13.3254	2.4869	3.8145
	n	1.5796	1.228	1.1764
	R^2	0.929	0.9481	0.9602
Temkin	K_t (L/mg)	2.7263	0.4035	0.6031
	B=RT/c	16.6062	14.3856	17.987
	R^2	0.8054	0.7747	0.7331

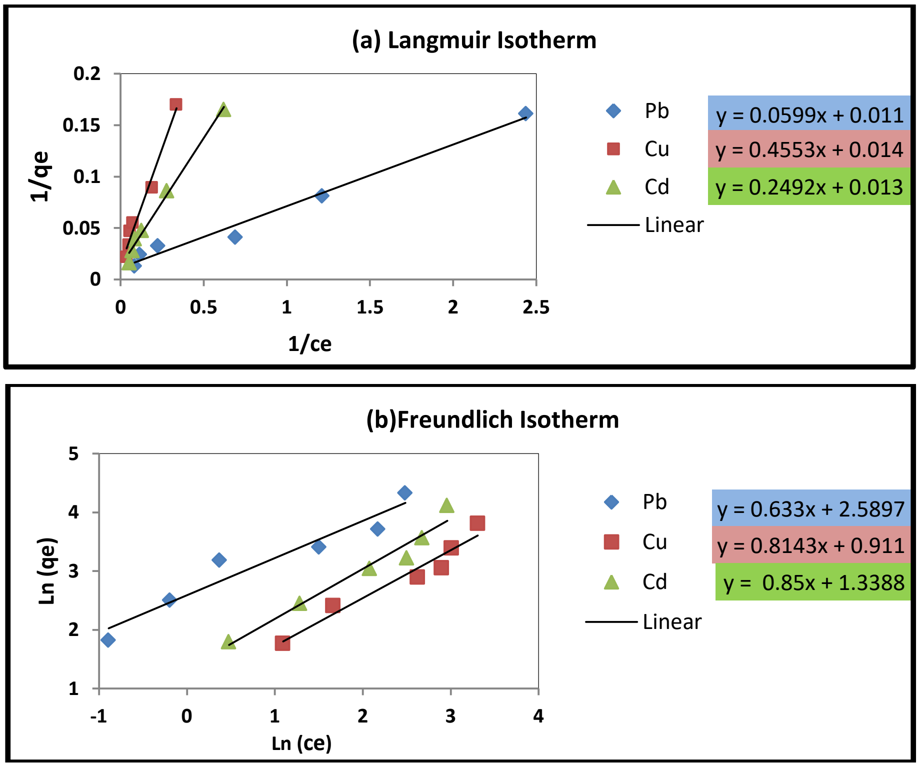


Fig. 6 Sorption isotherm models for Pb(II), Cu(II), and Cd(II) on tea wastes in single system

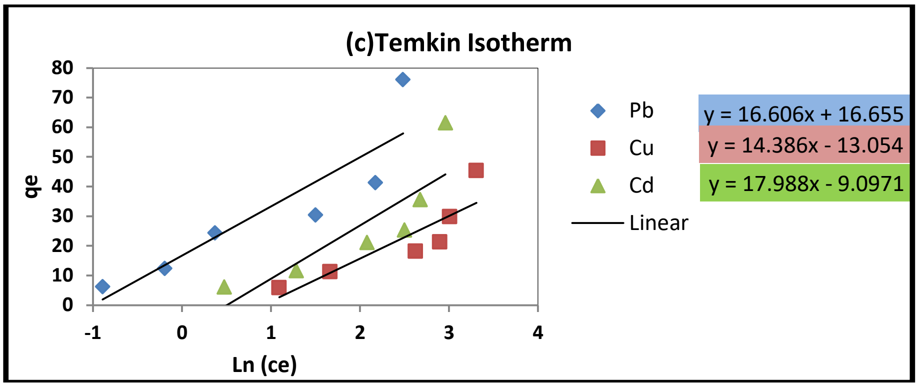


Fig. 6 Continued

Table. 7 Parameters of binary and ternary solute isotherm for Pb(II), Cu(II), and Cd(II) ions onto tea wastes

Models	Parameters	Pb+Cu System		Pb+Cd Cystem		Cu+Cd System		Ternary system		
		Pb	Cu	Pb	Cd	Cu	Cd	Pb	Cu	Cd
Extended Langmuir	b (L/mg)	0.0883	0.0409	0.1533	0.0251	0.0114	0.0074	0.04992	0.0244	0.0061
	q_m (mg/g)	76.225	54.039	79.489	51.446	58.312	56.544	66.723	50.346	48.322
	R^2	0.9572	0.9906	0.9935	0.915	0.9907	0.9441	0.996	0.988	0.9946
Extended Freundlih	K(mg/g)(L/mg)$^{1/n}$	5.467	2.919	9.8778	1.839	0.7912	0.5223	3.578	1.986	0.3837
	n	1.0859	1.4232	1.2834	1.3539	1.1506	1.1426	1.2925	1.449	1.1507
	R^2	0.9661	0.9741	0.9814	0.8813	0.984	0.8672	0.99	0.9512	0.99

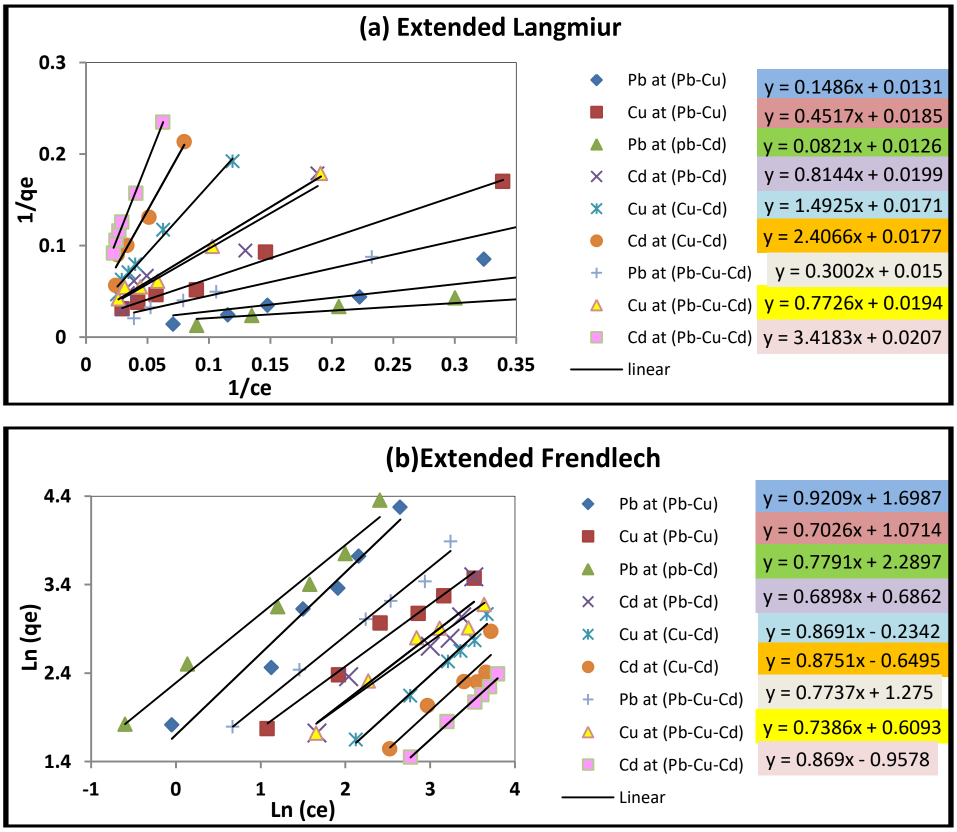


Fig. 7 sorption isotherm models for Pb(II), Cu(II), and Cd(II) on tea wastes in binary and ternary component system.

3.7 Sorption Kinetic Models

The kinetics of lead, copper and cadmium ions sorption onto tea wastes in single system were analyzed using pseudo-first-order, pseudo-second-order as shown in Table. 8 and Fig. 8.it can be seen that the values of correlation coefficient (R^2) indicate a better fit of pseudo- second- order model with the experimental data compared to pseudo- first- order model. The values of q_e calculated from the second order kinetic model agreed very well with the experimental values, and the regression coefficients are over 0.99. Therefore, the second-order model can be applied for Pb (II), Cu (II) and Cd (II) sorption process.

Table. 8 Comparison of sorption rate constants, experimental and calculated q_e values for the pseudo-first- and –second-order reaction kinetics for tea wastes sorbent in single component system.

Metal	q_e experimental mg/g	Pseudo-first-order			Pseudo-second-order		
		k_1 1/min	q_e calculated mg/g	R^2	k_2 g/mg.min	q_e calculated mg/g	R^2
Pb	24.7475	0.02607	11.5455	0.914	0.00665	25.4695	0.999
Cu	18.319	0.03703	13.5551	0.989	0.0614	19.2824	0.991
Cd	21.294	0.03067	11.6072	0.9315	0.00714	22.0723	0.9995

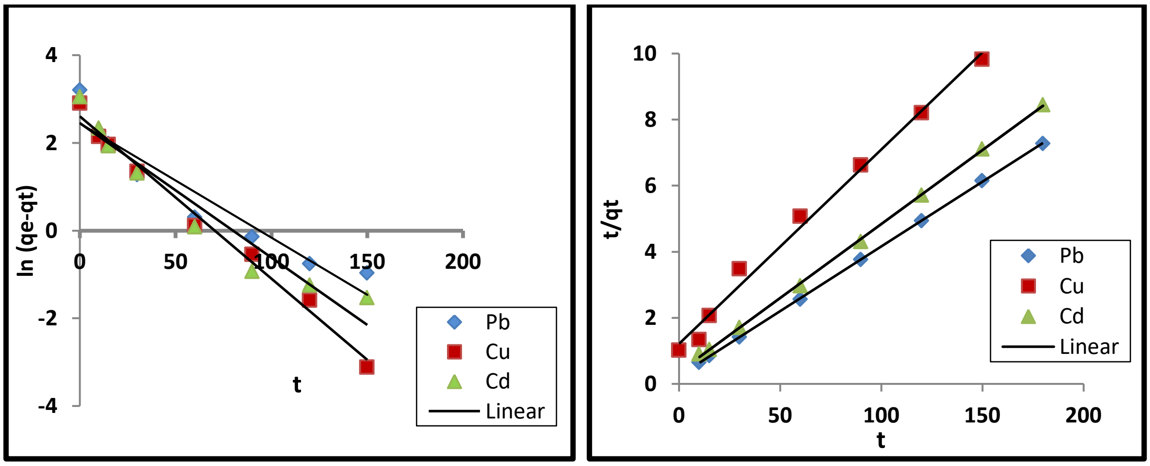


Fig. 8 kinetic models for sorption of Pb(II), Cu(II), and Cd(II) on tea wastes in single system.

3.8 Zeta Potential Measurements for Tea Wastes

The electrical potential at the surface of a particle is zeta potential. Zeta potential for tea waste particles can be determined by the measurement of the particles velocity in the electric field [13]. Fig. 9 shows that all samples indicated negative charge values at pH of 3, 5, 6, 7 and

8 which favorable to the attraction between active sites and positive charges of metal ions, resulting in electrostatic interaction. Tea wastes sorbent at pH 5.0 gave the greatest zeta-potential value.

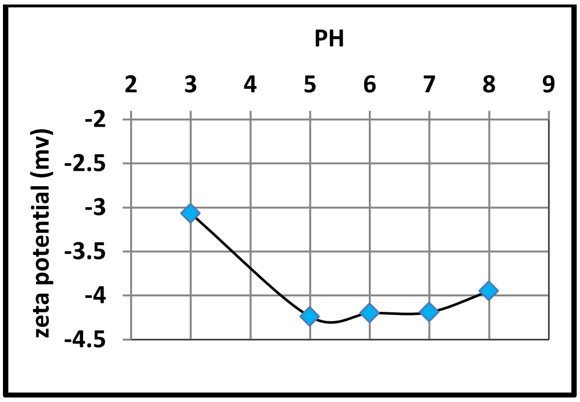


Fig. 9 Zeta-potential of tea waste in different solution pH (Tea dosage =2 g/l, rpm=175, time = 120 min)

3.9 FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out in order to identify the functional groups present in tea wastes. The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wave numbers. Fig. 10 shows the FTIR spectrum of tea wastes before and after adsorption of heavy metals. Table. 9 summarized the observed peaks and its descriptions. Among the functional groups, amine, aromatic, carboxylic acid and hydroxyl have been proposed to be responsible for the adsorption heavy metal ions on the cell surfaces of adsorbent [12]. Adsorption can also happen as plant materials were mainly contained cellulose materials that can adsorb heavy metal cations in aqueous medium. Their importance for metal uptake depends on factors such as the quantity of sites, its accessibility and chemical state, or affinity between site and metal [3].

Based on FTIR spectra results, tea waste has the characteristics to be used as potential biosorbent and Pb(II) ions have greatest changes in the peak values of bands than Cd(II) and Cu(II), while Cu(II) was the lowest one. It can be concluded that functional groups of tea biomass prefers Pb(II) than other metals.

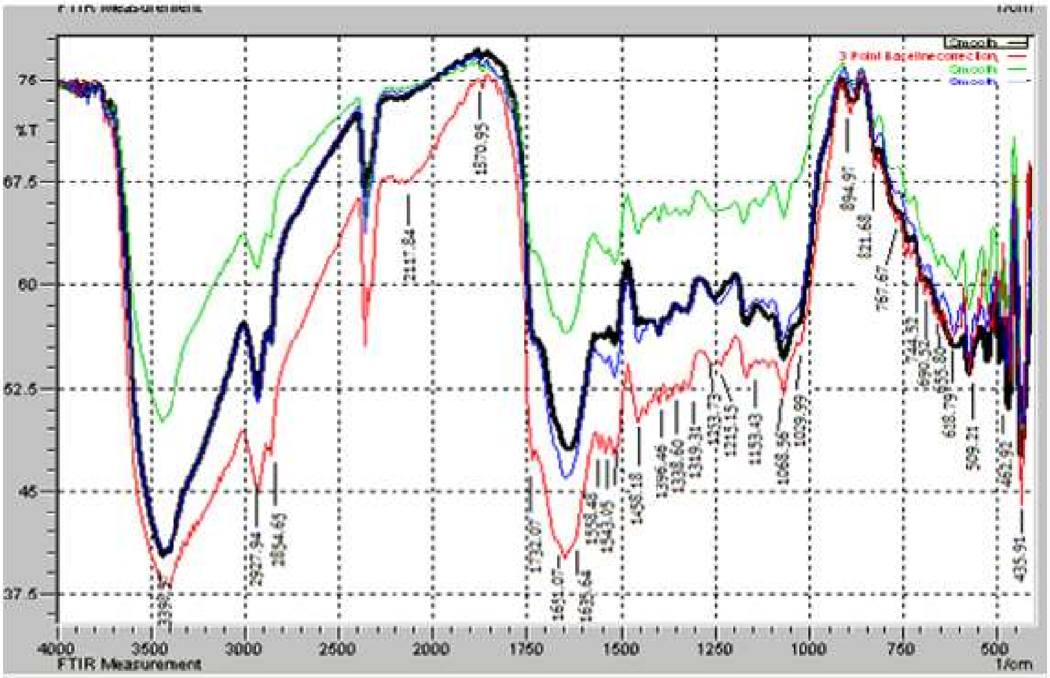


Fig. 10 FTIR spectrums of tea wastes (red line) raw tea, (green line) Pb(II) loaded tea, (black line) Cd(II) loaded tea and (blue line) Cu(II) loaded tea.

Table. 9 The summary of function groups before and after tea wastes biomass loaded with Pb(II), Cu (II) and Cd(II) ions

Assignment Functional Groups	Wave number (cm^{-1})			
	Before adsorption	After adsorption of Pb(II) cm^{-1}	After adsorption of Cu(II) cm^{-1}	After adsorption of Cd(II) cm^{-1}
Hydroxyl group (-OH), Amides(N-H stretch)	3398.57	3437.15	3398.57	3429.43
Carboxyl (C-H aldehyde stretch)	2927.94	2927.94	2924.09	2924.09
Amides (C=O stretch)	1635.64	1629.21	1647.21	1631.78
Nitro aliphatic group (-NO2)	1365.60	1369.46	1373.32	1377.17
Carboxyl(C-C ketone stretch), Alcohol (C-O stretch)	1253.73	1234.44	1246.02	1249.87
Alcohol (C-O stretch), carboxyl (C-C ketone stretch)	1153.43	1172.72	1168.86	1168.86
Aromatic (C-H bend), sulfonate (S-O stretch)	894.97	883.40	887.26	879.54
Aromatic (C-H bend) , sulfonate (S-O stretch)	821.68	829.39	825.35	825.53
Aromatic(C-H bend), Alkyl halides(C-Cl stretch)	767.67	779.24	767.67	763.81
Alkyl halides(C-I)	509.21	524.64	528.50	524.64

4. Conclusion

This study assessed the feasibility of tea waste as a low-cost adsorbent for the removal of Pb(II), Cu(II) and Cd(II) from aqueous solution. Batch experiments showed that TW was a good efficient sorbent to remove these metal ions from wastewater at best condition; initial concentration 50 mg/L, pH 5-6, contact time 60 minute and biosorbent dosage 0.4 gm per 100 mL of solution. The maximum percentage removal obtained under best conditions in the batch system was 98.35%, 89.45% and 92.78% for Pb(II), Cu(II) and Cd(II) respectively by tea waste for single system and it decreases to 91.4%, 80.6% and 50.93% respectively for ternary system. While for binary system, the efficiency decreased to 93.82% for Pb, 86.33% for Cu (Pb, Cu system), 97.7% for Pb and 84.59% for Cd (Pb, Cd system), and about 68.24% for Cu and 61.06% for Cd, (Cu,Cd system). The experimental results were analyzed using three adsorption isotherm models. Langmuir isotherm model gives the best fit model for heavy metals than the other models with the adsorption capacity in single system was (86.713, 74.096 and 77.1685 mg/g) for Pb(II), Cu(II) and Cd(II), respectively while in binary and ternary systems extended Langmuir model appears to give the best fit for the experimental data with the adsorption capacity for the three heavy metal ions in ternary system were (66.724, 50.346 and 48.322 mg/g), for binary system the adsorption capacity was decreased to 76.225 mg/g for Pb and 54.039 mg/g for Cu (Pb, Cu system);); 79.489 mg/g for Pb and 51.446 mg/g for Cd (Pb, Cd system); and about 58.312 mg/g for Cu and 56.544 mg/g for Cd, (Cu, Cd system).The sequence for metal ions removal in single system was Pb > Cd > Cu; while in binary, ternary was Pb > Cu > Cd. The modeling of kinetics data showed that the biosorption profile can be described by the pseudo-second- order model with metal uptake capacity at equilibrium about (25.4695, 19.2824 and 22.0723 mg/g) for Pb(II), Cu(II) and Cd(II), respectively . FTIR analysis showed that the biosorption was a complex process and depended on the number and type of active groups, and carboxyl, amino, and sulfonic groups were involved in this process, also it show that functional groups of tea biomass prefers Pb(II)than other metals .

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الازالة التنافسية لايونات الرصاص والنحاس والكادميوم من محلول مائي باستخدام مخلفات الشاي

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الخلاصة

يهتم البحث بدراسة قدرة مخلفات الشاي لإزالة ايونات الرصاص والنحاس والكادميوم من المحاليل المائية الحالة المفردة والثنائية والثلاثية. تم القيام بسلسلة من تجارب الدفعات لدراسة الظروف التشغيلية: الدالة الحامضية وسرعة الاهتزاز وتركيز أيونات المعادن.

ولقد اثبتت التجارب كفاءة مخلفات الشاي كمادة ممتزه للعناصر الثقيلة عندما يكون تركيزها الاولي حوالي 50 ملغم\ لتر وباستخدام مقياس الطيف الضوئي تم تحديد التراكيز المتبقية من الرصاص والنحاس والكادميوم كما وجد ان الدالة الحامضية المثلى لإزالة الرصاص والكادميوم كانت 5 أما بالنسبة للنحاس فقد كانت 6. بينت نتائج حساب ل(Zeta potential) لمخلفات الشاي الى إن مواقع الشحنات السالبة اعطت اعلى قيمة عند الدالة الحامضية (5). كما تم اجراء فحص التحليل الكيفي لمخلفات الشاي باستخدام جهاز الأشعة تحت الحمراء لغرض دراسة المركبات الكيميائية و المركبات المؤكسدة و معرفة المجموعات الفعالة للمركبات العضوية مثل المجموعات الكربوكسيلية، الأمينية، الاروماتية, الهيدروكسيل و السلفونيك وتبين ان الرصاص احدث تغييرا كبيرا في المجموعات الغاعلة في مخلفات الشاي. كانت نسبة ازالة ايونات المعادن في حالة المزج الثنائي والثلاثي اقل مما عليه في الحالة المفردة حيث ان تسلسل نسبة الازالة في حالة المعادن المفردة الرصاص > الكادميوم > النحاس بينما في حالة مزج المعادن الثنائي والثلاثي فكانت الرصاص > النحاس> الكادميوم كما تم التوصل الى ان الموديل (Langmuir) كان أفضل موديل رياضي يمثل النتائج العملية للمعادن المنفردة وموديل (extended Langmuir) للمعادن الثنائية والثلاثية وكان موديل التفاعل الحركي من الدرجة الثانية (pseudo second order kinetic) أفضل من موديل التفاعل الحركي من الدرجة الاولى(pseudo first order kinetic) لتمثيل النتائج العملية.

الكلمات الرئيسة : نفايات الشاي، الامتزاز، نظام واحد، نظام ثنائي، نظام الثلاثي.