Biosorption of Lead, Copper, and Nickel onto Tea Waste: Equilibrium, and Kinetic Studies

Asst. Prof. Dr. Ahmed A. Mohammed
ahmedabedm@yahoo.com
Noor Ali Hameed
noorali19901991@gmail.com

Abstract:

The use of locally abundant agriculture tea waste as natural sorbents for treatment of wastewater polluted by lead, copper, and nickel ions from aqueous solutions was examined. Different parameters that influencing sorption process such as pH, initial metal concentration, biosorbent dosage, contact time, agitation speed were investigated. The adsorption isotherm were described by Langmuir and Freundlich isotherm models for single system. The Langmuir model was found to fit well the equilibrium data. The maximum uptake obtained were 77.155, 59.238, and 52.46 mg/g dry tea waste for Pb(II), Cu(II), and Ni(II) ions respectively. Adsorption kinetic data were tested using pseudo–first order, pseudo–second order, and intra-particle diffusion models. The sorption kinetics followed pseudo –second order kinetic model. The maximum removal efficiency was found to be 93.6%, 71.97%, and 47.3% for Pb(II), Cu(II), and Ni(II) ions respectively. Fourier transformation infrared (FTIR) was carried out for tea waste before and after adsorption to determine the type of functional groups. The results confirm that amino, carboxylic, hydroxyl and carbonyl group on the surface of tea waste were the major groups responsible for adsorption process. From results it can be concluded that tea waste has great potential as an abundant, low cost effective adsorbent material.

Keywords: Biosorption, Heavy metals, Kinetics, Isotherm, Tea Waste

1. Introduction

Increasing industrial activities leads to increase the environmental pollution with organic and inorganic contaminant. Heavy metals are the most inorganic pollutants of water [29, 43]. During the last years, increasing attention has been focused on the separation, pre- concentration and/ or determination of the trace heavy metal ions in the environment. The removal of these hazardous materials may be performed using various techniques, including chemical precipitation, solvent extraction, electro coagulation, ion exchange, membrane filtration, adsorption, and flotation separation processes [26]. However, these methods are expensive, require sensitive operating conditions and produce huge quantity of sludge [12].Therefore, more economic, practical and efficient techniques are needed to meet the requirements of recovery and/or removal of metal ions. Biosorption of metal ions from aqueous solutions is a relatively new technology for wastewater treatment. Biosorption has been defined as the property of certain biomolecules to bind and concentrate selected ions or other molecules from aqueous solution. Biosorbents come under the following categories: bacteria, fungi, algae, industrial wastes, agricultural wastes, and other polysaccharide materials. Among them, agricultural wastes are the potential sources for producing biosorbents as they have no prominent utilization. Agricultural wastes are usually composed of lignin and cellulose as major constituents and may also include alcohols, aldehydes, ketones, carboxylic, phenolic and other groups [17]. A number of studies have been focused on agricultural wastes that are capable of removing metals from wastewater such as apple wastes[28], tea waste and coffee [34], corn corps [14], orange peel [25], rice husk [9], rice straw [10], wood apple shell [8], coconut [6], maize husk [11], adathoda vasica [2], punica granatum (pomegranate) peel waste[5], orange peel and orange peel xanthate[23], peel of citrus sinensis and wood sawdust [18]**,** Sunflower seed shells(SS), mandarin peelings(MS) [35], tobacco steams[22]. Therefore, the present work aims to study the feasibility of using tea waste as an adsorbent for the removal of Pb(II), Cu(II), and Ni(II) ions from aqueous solutions.

2. Materials and Methods

2.1Biosorbent and sorbate preparation

The tea waste used in this study was collected from local coffee shops after cooking. The foreign matter was removed from it and washed with hot water from 3 to 6 times until the filtrate was virtually colorless then washed with distilled water and dried under sun for 2 days. The dried leaves were grinded with house grinder and sieved to particles 125μm which were stored in polyethylene bags until use[31]. The following are the major physical properties of tea waste: surface area (16.449 m^2/g), apparent density (0.4226 g/cm^3), and real density (1.4067 gm /cm^3). The stock solution (1000 ppm) of each Pb(II), Cu(II), and Ni(II) ions were prepared by dissolving appropriate amount of each metal salt in distilled water and then stored in glass containers at room temperature. The three metal salts were obtained from FLUKA company. The desired concentrations were prepared by diluting the stock solution in accurate proportions to different initial concentrations. The concentration of the metal was subsequently determined by using flame atomic absorption spectrophotometer (AAS), type: SHIMADZU, Model: 7200, JAPAN. The initial pH of the working solutions was adjusted to the required value by adding 1 mol/l NaOH or HNO_3 using a pH meter (WTW,Sr.Nr:08490207). The collected samples filtered and analyzed in atomic absorption spectrophotometer (AAS) .

2.2 Experimental work

2.2.1 Operating parameters

The influence of pH on adsorption experiments were carried out at different pH (3, 4, 5, 6, and 7) by adding 0.1M HCl or 0.1M NaOH to get the desired pH by using pH meter type (WTW,Sr.Nr:08490207), The effect of agitation speed on the adsorption of Pb(II), Cu(II) and Ni(II) was investigated by changing the agitation speed in the range of 100, 150, 200, 250, and 300 agitation speed using shaker with optimum pH obtained from previous experiment; initial ions concentration of 50 ppm of each heavy metals was used in conjunction with adsorbent dose (0.5-5 g/l); The optimum dosage that achieved maximum removal efficiency will be used in further experiments; the effect of contact time was investigated from 10 to 120 min at optimum adsorbent dosage, agitation speed and pH; the effect of initial concentration had been studied in the range of concentration (25, 50, 100 and 200 ppm) and temperature 25 ^{o}C and optimum conditions obtained from previous experiments.

2.2.2 Isotherm experiments

Biosorption of each metal onto tea waste was investigated in single system. The experiments were carried out in 250 ml stoppered conical flasks containing 100 ml of 50 ppm and different dosages (0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5, and 5 g/l) of tea waste, under constant shaking at 25±3 °C. The pH solution was adjusted to the best value based on the pH study. For each metal, ten flasks were placed in a shaker (ISO 9001, model: LSI-3016A, NO.B110416002, KOREA) at constant shaking speed (200 agitation speed) for 2 hr. Upon equilibrium, the sorbent was separated from aqueous solution by using filter paper (Whatman 12.5 cm). The residual concentrations of metal were measured by AAS. The biosorption capacity at equilibrium conditions (q_e) was calculated by using the following equation [30]:

$$q_e = \frac{(C_o - C_e)V}{m} \qquad \dots (1)$$

Where q_e is the equilibrium biosorption capacity (mg/g), C_o and C_e are the initial and equilibrium sorbate concentrations in water (ppm), respectively, V is the volume of the used solution (l), and m is the mass of the used adsorbent (g).The percentage of removal (%) was calculated by using the following equation:

$$\% \text{ Removal}=\left(\frac{C_o-C_e}{C_o}\right)\times 100 \qquad \ldots(2)$$

2.2.3: Kinetic experiments

For kinetic experiments, 50 ppm concentration of Pb(II), Cu(II), and Ni(II) ions solutions were used. The sorption time varied between 0 and 120 min. Samples were withdrawn and filtrated then the supernatant solutions were analyzed for the residual metal ion concentration by using AAS. All determinations of each experiment were performed in triplicate and the average was used for this work.

3. Results and Discussion

3.1 FTIR Analysis for Tea Wastes

Fourier Transform Infrared Spectroscopy (FTIR) analysis was carried out in order to identify the functional groups present in tea waste. Functional groups of adsorbents not only affect the adsorption behavior, but also dominate the adsorption mechanism.The peaks appearing in the FTIR spectrum were assigned to various functional groups according to their respective wave numbers. **Fig. 1** shows the FTIR spectrum of tea waste before and after sorption of Pb(II),Cu(II), and Ni(II). **Table. 1** 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 [22]. Adsorption can also happen as plant materials were mainly contained cellulose materials that can adsorb heavy metal cations in aqueous medium [4].

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 Cu (II) and Ni (II), while Ni (II) was the lowest one. It can be concluded that functional groups of tea biomass prefers Pb(II) than other metals.

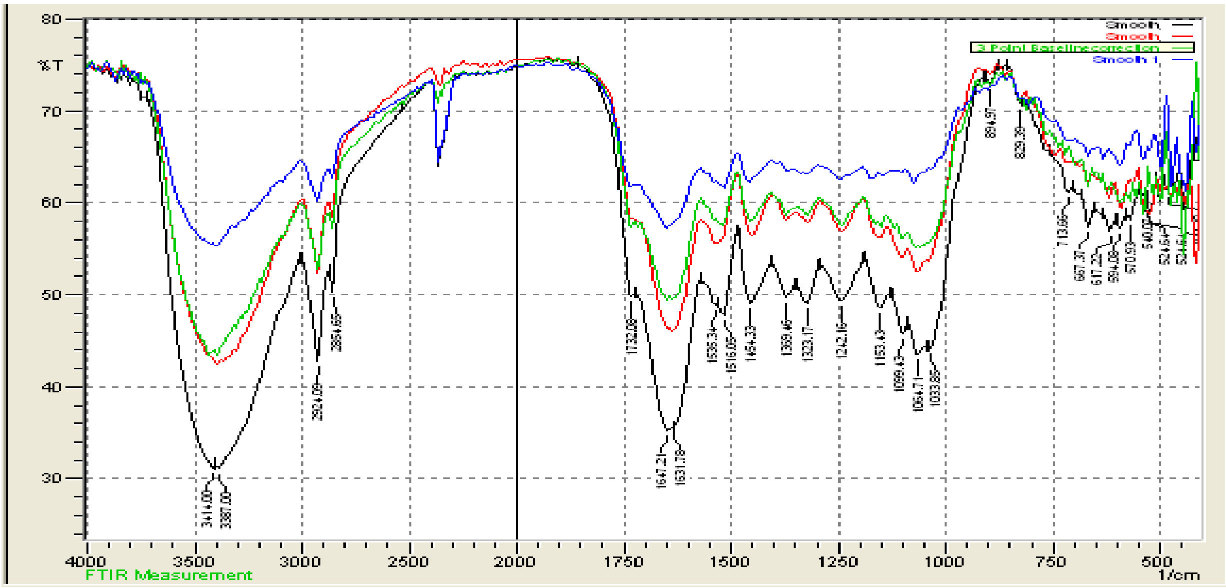

Fig 1. FTIR spectrums of tea wastes (black line) raw tea, (blue line) Pb loaded tea, (green line) Cu loaded tea, and (red line) Ni loaded tea.

Table 1. Functional groups before and after tea waste biomass loaded with Pb (II), Cu (II) and Ni (II) ions in single systems

Assignment Functional Groups	Wave number, (cm^{-1})			
	Before Adsorption	After adsorption of Pb(II)	After adsorption of Cu(II)	After adsorption of Ni(II)
Hydroxyl group (-OH), amides(N-H stretch)	3414.00	3425.58	3421.72	3383.14
Carboxyl (C-H aldehyde stretch)	2924.09	2924.09	2920.23	2920.23
Carboxyl (C-H aldehyde stretch)	2854.65	2854.65	2850.79	2850.79
Amides(C=O Aldehydes stretch	1732.08	1732.08	1732.08	1716.65
Amides (C=O stretch)	1647.21	1651.07	1651.07	1635.64
amides(N-H bend), Nitro aromatic group (-NO2),Aromatic C=C stretch	1516.05	1519.91	1519.91	1519.91
Nitro aliphatic group (-NO2)	1369.46	1369.46	1369.46	1365.60
Nitro aromatic group (-NO2)	1323.17	1323.17	1319.31	1319.31
Carboxyl(C-C ketone stretch), alcohol (C-O stretch), Alkyl halides(C-F stretch)	1242.16	1246.02	1242.16	1246.02
Alcohol (C-O stretch), carboxyl (C-C ketone stretch), Alkyl halides(C-F stretch)	1153.43	1145.72	1149.57	1149.57
Alkyl halides(C-F stretch), Alcohol (C-O stretch)	1033.85	1033.85	1037.70	1037.70
Aromatic (C-H bend), sulfonate (S-O stretch), Phosphines (PH bend)	894.97	898.83	894.97	891.11
Aromatic (C-H bend) , sulfonate (S-O stretch)	829.30	829.39	829.39	825.53
Alkyl halides(C-Cl stretch)	667.37	667.37	667.37	667.37
Alkyl halides [(C-Br) and (C-I)]	540.07	540.07	540.07	540.07
Alkyl halides [(C-Br) and (C-I)]	524.64	524.64	516.62	524.64

3.2 Effect of pH

Several previously reported studies indicated that pH of solution is the most important parameter effecting the biosorption capacity due to the variation in the pH value leading to differences in the surface properties of the sorbent and degree of ionization[30]. In order to evaluate the influence of pH on sorption of the metal ions, the experiments were carried out in the pH range of (3–7) for Pb(II), Cu(II) and Ni(II) ions. The pH ranges were chosen as mentioned ranges in order to avoid precipitation of metal ions in the form of metal hydroxides.

The effect of pH on removal efficiencies is depicted in **Fig 2**. The percentage sorption increases with increase in pH. The minimum sorption was observed at low pH. This behavior may be due to the fact that the presence of higher concentration and higher mobility of H^+ ions favored sorption compared to M (II) [24]. On the other hand in the acidic medium, due to high solubility and ionization of metal ions, the surface of the adsorbent becomes more positively charged at high H^+ concentration such that the attraction between adsorbents and metal cations is reduced. In reverse with increase in pH the negatively charged surface area becomes more thus facilitating greater metal removal and then at very high pH also the percentage removal decreases [33]. The maximum sorption was observed within the pH range 4 to 6 which might be due to partial hydrolysis of metal ions.

Beyond the value of pH 6.0 precipitation will occur to heavy metals, this due to the insoluble metal hydroxides start precipitating from the solutions at higher pH values and make the true sorption studies impossible. This should be avoided during sorption experiments which distinguish between sorption and precipitation metal removal becomes hard [41]. To achieve high extraction efficiency without metal hydroxide precipitation, pH of 5.0 for Pb (II) and pH of 6.0 for Cu(II) and Ni(II) were selected for subsequent experiments.

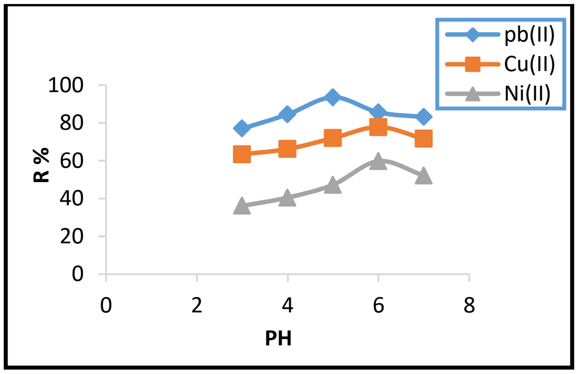

Fig 2. Effect of pH on the removal of Pb(II), Cu(II), and Ni(II) using tea waste (W=2 g/L; T=25°C; C_o = 50 ppm; agitation speed=200 agitation speed, and time=60 min).

3.3 Effect of Biosorbent Dosage

The effect of sorbent dosage on the removal of metal ions was studied using tea waste dosage of 0.5-5 g/l for single system with 50 ppm of Pb (II), Cu (II), and Ni(II) concentrations, at 25°C, pH range between 5-6, and the mixture were agitated on rotary shaker at 200 agitation speed for 60 min. The results are shown in **Fig. 3**, from this figure it can be noticed that the retention of metals increased with increasing amount of sorbent dose up to 4 g/l this values were taken as the optimum amount for other trials. Sorption of metal ions was increased as the sorbent amount increased due to the increased surface area of the sorbent, which in turn increases the number of binding sites, [30], but further increases in sorbent dosage has a small or limited increase in the removal efficiency and this due to that after a certain dose of adsorbent, the maximum adsorption is attained and hence the amount of ions bound to the adsorbent and the amount of free ions remains constant even with further addition of the dose of adsorbent. The results were expected because for a fixed initial metal concentration, increasing adsorbent amount provides greater surface area or sorption site [1].

At dosage 4 g/l, the removal efficiency of Pb(II), Cu(II) and Ni(II) by tea waste were about 93.6%, 77.82%, and 59.8% respectively.

The removal efficiency of Pb(II) is higher than that of Cu(II) and Ni(II). This may be due to the physical and chemical properties of lead to be more favorable to be sorbed than copper and nickel. This could be explained on the basis of ionic radii. Ionic radii of Pb(II), Cu(II), and Ni(II) are 350, 255.6 and 249.2 pm, respectively. Pb(II) having higher ionic radii, therefore, the Pb(II) ions will be removed more efficient. Furthermore, the molecular weight of Pb(II), Cu(II), and Ni(II) are 331.2, 249.70, and 182 $g.mol^{-1}$ respectively. As the uptake related to the molecular weight of metals and as the molecular weight increases the uptake rate increases and Pb(II) having higher molecular weight [13, 32].

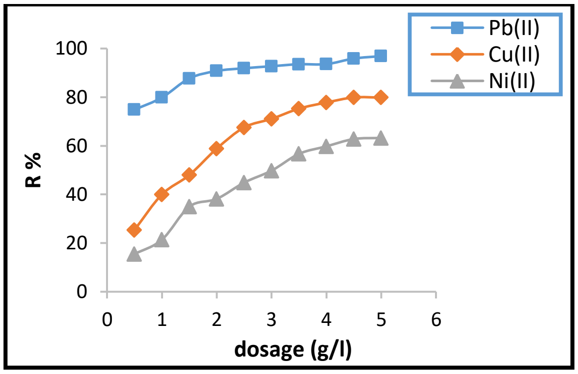

Fig 3. Effect of tea dose on the removal of Pb(II) , Cu(II), and Ni(II) (pH 5-6; T=25°C; C_o = 50 ppm; agitation speed =200; time = 60 min for single component system).

3.4 Effect of Contact Time

The removal of Pb(II), Cu(II), and Ni(II) ions from aqueous solution was studied as function of contact time in the time interval 0-120 min at 50 ppm initial metal ions concentrations, pH 5-6, temperature 25°C, and 4 g/l biosorbent. The effect of contact time on removal of metal ions is shown in **Fig. 4**. From this figure in single system, it was observed that the rate of metal ions removal was higher at the first 60 min and after that, the sorption rate become practically very slow and, after 120 min, it starts decreasing. The difference in the degree of sorption may be due to the existence of greater number of sorbent sites available for the sorption of metal ions. As the remaining vacant surface sites decreasing, the sorption rate slowed down due to the formation of repulsive forces between the metals on the solid surface and in the liquid phase, the same behavior was noticed by [10, 40]. Based on these results 60 min was considered as the optimum time for the rest of the experiments. The results show that the removal of lead is greater than the copper and nickel. The sequence of removal is therefore Pb > Cu > Ni.

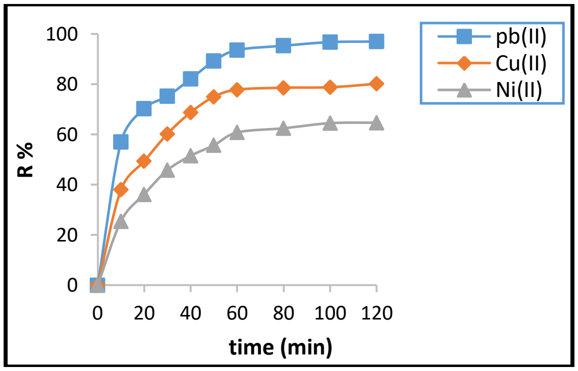

Fig 4. Effect of contact time on the removal of Pb(II), Cu(II), and Ni(II) using tea waste (pH 5-6; T=25°C; C_o= 50 ppm; agitation speed =200; W=4 g/l) for single component system.

3.5 Effect of Initial Metal Concentration

The initial concentration of lead, copper, and nickel provides an important driving force to outweigh all mass transfer resistance of metal between the aqueous and solid phases. Removal of these ions for various initial concentrations (25, 50, 100, and 200 ppm by tea waste dose 4 g/l, contact time 60 min, and at pH (5-6) have depicted in the **Figs. 5 to7**. The percentage removal of lead increased from 72.25% to 95.83%, for copper 47.96% to 82.196%, and 39.74% to 73.34% for nickcl, with decrease in initial concentration from 200 ppm to 25ppm. The results indicated that the percentage removal of metals was slightly decreased with an increase in the initial metals concentration from 25 to 50 ppm, whereas a rapid decrease in the percentage removal was observed at the initial concentrations between 50 and 200 ppm.

According to Kumar et al. [19], at lower metal ions concentration, the percentage uptake was higher due to larger surface area of sorbent being available for sorption. When the concentration of metal ions became higher, the percentage removal decreased since the available sites for sorption became less due to saturation of sorption sites. 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 [40]. The same behavior was noticed by Muhaisn, [31].

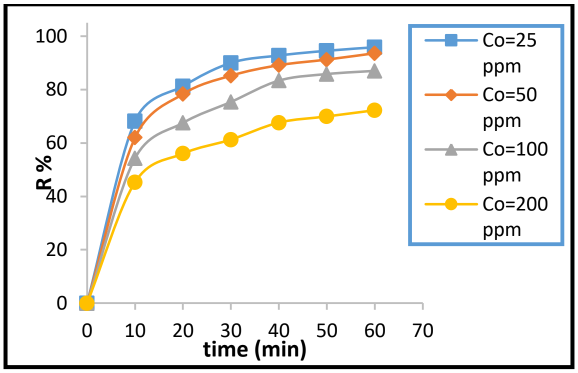

Fig 5. Effect of initial metal concentration on the removal of metal ions Pb(II) using tea waste (pH 5; W= 4 g/l; T=25°C; agitation speed =200) .

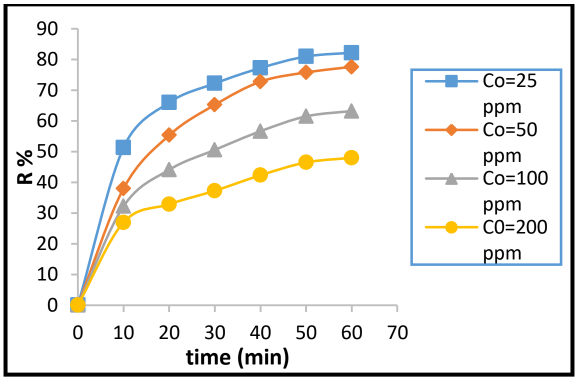

Fig 6. Effect of Initial metal concentration on the removal of metal ions Cu(II) using tea waste (pH = 6; W= 4 g/l; T=25°C; agitation speed =200).

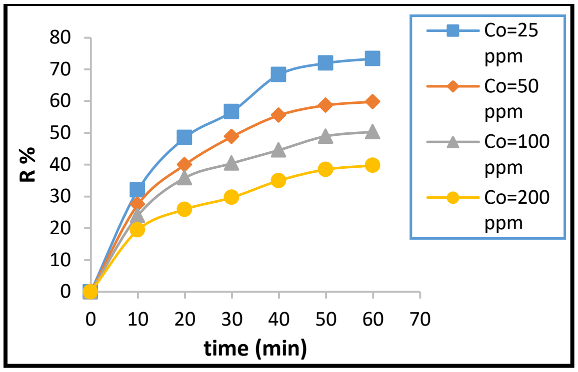

Fig 7. Effect of Initial metal concentration on the removal of metal ions Ni(II) using tea waste (pH = 6; W= 4 g/L; T=25°C; agitation speed =200).

3.6 Effect of agitation speed

The effect of the agitation speed on the removal efficiency of all the metal ions using tea waste is shown in **Fig 8**.The efficiency values increase from 75 to 93.6% for lead, 52.36 to 77.82% for copper and 34.74 to 59.8 for nickel respectively when the agitation speed increased from 100 to 200 agitation speed. It can be clearly seen that mixing speed increases the removal efficiency until it reaches a certain value and further increase is then of no benefit (i.e., above 200 agitation speed). The increase in efficiency is due to the increase in turbulence and as a consequence, the decrease in the external mass transfer resistance thickness around the adsorbent particles with increase in mixing speed [46]. Moreover, these results clearly indicate that a mixing speed of 200 agitation speed is sufficient to obtain maximum removal efficiency by reducing the boundary layer thickness to a minimum value. The same behavior also noticed by Muhaisn, [31].

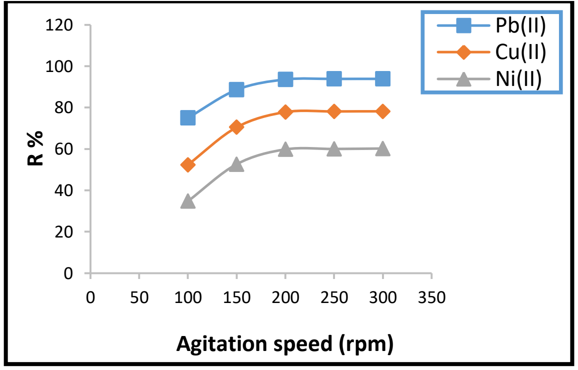

Fig 8 . Effect of agitation speed on the sorption of heavy metal onto tea waste at Co= 50 ppm, pH= 5-6, time = 30 min, W =4 g/l, and temperature = 25°C.

4. Sorption Isotherm models

Adsorption isotherms are very powerful tools for the analysis of adsorption process. Adsorption isotherms establish the relationship between the equilibrium concentration and the amount of adsorbate adsorbed by the unit mass of adsorbent at a constant temperature. The most widely models used are discussed here.

4.1 Langmuir Isotherm Model

The Langmuir adsorption model is valid for single-layer adsorption. It is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface [27]. The Langmuir isotherm equation is:

$$q_e = \frac{q_m b C_e}{(1+bC_e)} \qquad \ldots (3)$$

Where: q_e is the sorbed metal ions on the biomass (mg/g), 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), and C_e is metal ions concentration in the solution at equilibrium (mg /l).

The Langmuir isotherm is used most frequently to describe the adsorption isotherm which is limited by the assumptions of uniform energies of adsorption on the surface of adsorbent. It is based on four assumptions:

- The surface of the adsorbents is uniform, that is, all the adsorption sites are equivalent.
- There is no interaction between molecules adsorbed on neighboring sites.
- All adsorption occurs through the same mechanism.
- Molecules are adsorbed at the define sites on the adsorbent surface.

The results of this model is tabulated in **Table 2**.

Weber and Chakravorti, [45] showed that the essential characteristics of a Langmuir isotherm equation could be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, ‘R_L’ which is defined by the following equation:

$$R_L = \frac{1}{1+bC_o} \quad \text{... (4)}$$

Table 2 . Parameters of Langmuir isotherm for sorption of metal ions in single system.

Parameters	Lead(II)	Copper(II)	Nickel(II)
q_m (mg/g)	77.155	59.238	52.46
b (l/mg)	0.0793	0.017	0.007
R_L	0.2014	0.54	0.74
R^2	0.8695	0.9657	0.8914

4.2 Freundlich Isotherm Model

Freundlich equation is derived to model the multilayer sorption and for the sorption on heterogeneous surfaces. The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations [47]. The equation may be written as:

$$q_e = KC_e^{\ 1/n} \quad \text{...(5)}$$

Where K is a constant indicative of the relative adsorption capacity of the adsorbent (mg/g), 1/n is a constant indicative of the intensity of the adsorption.

Both K and n are constants, being indicative of the extent of adsorption and the degree of non-linearity between solution and concentration, respectively. The linear Freundlich plots are obtained by plotting log q_e versus log C_e from which the adsorption coefficients could be evaluated. The results of this model are tabulated in **Table 3**.

Table 3. Parameters of Freundlich isotherm for sorption metal ions in single system.

Parameters	Lead (II)	Copper(II)	Nickel (II)
K,(mg/g)(L/mg)$^{(1/n)}$	4.9	1.514	0.56
n	1.031	1.314	1.179
R^2	0.931	0.9687	0.8775

5. Sorption Kinetics

The kinetics describes the solute uptake rate which in turn controls the residence time of sorbate uptake at the solid–solution interface. Therefore, it is important to be able to predict the rate at which sorbate is removed from aqueous solutions in order to design appropriate sorption treatment processes [39]. The sorption kinetics, thus, constitute a major principle in the determination of the interest of sorption processes [21].

5.1 Pseudo-First Order Kinetic Model

The Lagergren rate equation [20] was the first rate equation for the adsorption of liquid/solid system based on solid capacity. The Lagergren rate equation is one of the most widely used sorption rate equations for the adsorption of a solute from a liquid solution. It may be represented as:

$$\frac{dq}{dt} = k_1(q_{eq} - q_t) \qquad \dots (6)$$

Integrating equation (7) and applying the boundary conditions $q_t = 0$ at $t= 0$ and $q_t = q_e$ at $t = t$ gives:

$$\ln(q_{eq} - q_t) = \ln q_e - k_1 t \qquad \dots (7)$$

Which is the integrated rate law for a pseudo-first-order reaction, where q_{eq} is the amount of metal sorbed at equilibrium (mg/g); q_t is the amount of metal sorbed at time t (mg/g); and k_1 is the equilibrium rate constant of pseudo first sorption (1/min).

The equation applicable to experimental results generally differs from a true first-order equation in two ways:

- The parameter $k_1 (q_{eq}–q_t)$ does not represent the number of available sites.
- The parameter ln (q_{eq}) is an adjustable parameter. Often it is found not equal to the intercept of a plot of ln $(q_{eq}– q_t)$ against t, whereas in a true first order process, ln (q_{eq}) should be equal to the intercept of a plot of ln $(q_{eq}– q_t)$ against t.

5.2 Pseudo-Second-Order Kinetic Model

There are certain assumptions in description of this kinetic model [16]:

1. There is a monolayer of adsorbate on the surface of adsorbent.

2. The energy of adsorption for each adsorbent is the same and independent of surface coverage.

3. The adsorption occurs only on localized sites and involves no interactions between adsorbed pollutants. The rate of adsorption is almost negligible in comparison with the initial rate of adsorption. The kinetic rate equation can be written as follows:

$$\frac{dq}{dt} = k_2(q_{eq} - q_t)^2 \qquad \dots (8)$$

Where k2 is the rate constant of sorption, (g/mg min), qeq is the amount of divalent metal ion sorbed at equilibrium, (mg/g), qt is amount of divalent metal ion on the surface of the sorbent at any time, t, (mg/g).

For the boundary conditions qt = 0 at t = 0 and qt = qe at t = t; the integrated form of equation (8) becomes (Ho, 2006):

$$\frac{1}{(q_{eq}-q_t)} = \frac{1}{q_{eq}} + k_2 t \qquad \dots (9)$$

Rearrangement the above equation:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}}\right). \qquad \dots (10)$$

5.3 Intraparticle Diffusion Model

The intraparticle diffusion model is expressed as [44] :

$$q_t = k_{id}\, t^{0.5} + C \qquad \dots (11)$$

Where q_t (mg/g) is the amount adsorbed at time t (min), K_{id} (mg /g $min^{0.5}$) is the rate constant of intraparticle diffusion. C is the value of intercept (mg/g) which gives an idea about the boundary layer thickness, i.e. the larger intercept; the greater is the boundary layer effect. According to the intraparticle diffusion model, the plot of q_t vs. $t^{0.5}$ should be a straight line if this model is involved in the sorption process and if the plot passes through the origin then intraparticle diffusion is the sole rate-limiting step [36].

The results are tabulated in **table 4** for Pseudo-first-order, Pseudo-second-order, and Intraparticle diffusion models:

Table 4. Kinetic model parameters for Pb(II),Cu(II), and Ni(II) ions adsorption onto tea waste.

Metal	**q_e experimental** mg/g	**Pseudo-first-order**			**Pseudo-second-order**			**Intraparticle diffusion**		
		k_1 1/min	**q_e calculated** mg/g	**R^2**	**k_2** g/mg. min	**q_e calculated** mg/g	**R^2**	Kid (mg/ g.min$^{0.5}$)	**C**	**R^2**
Lead (II)	32.326	0.053	26.18	0.971	0.0041	34.351	0.9999	2.746	9.543	0.9997
Copper(II)	13.358	0.043	9.843	0.942	0.0061	14.759	0.9979	1.183	2.737	0.996
Nickel (II)	7.1889	0.051	8.751	0.945	0.0072	8.3035	0.9991	0.657	1.079	0.9981

6. Conclusions

- Tea waste seems to be an effective, low cost and alternative adsorbent precursor for the removal of heavy metal ions from aqueous solutions.
- The Langmuir and Freundlich isotherms were used to represent the experimental data and the data could be relatively well interpreted by Freundlich isotherms.

- The experimental data showed that the sorption of three metals well fitted the pseudo-second-order kinetic model.
- An increase in the sorbent dosage (0.5-5 gm/L) resulted in higher metal ions removal efficiency and by increasing the sorbent dosage the contact time that required to reach equilibrium decrease.

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الامتزاز الحيوي لايونات الرصاص و النحاس و النيكل باستخدام مخلفات الشاي: دراسة التوازن و التفاعل الحركي

ا.م.د احمد عبد محمد

نورعلي حميد

الخلاصة:

أجري هذا البحث لدراسة إمكانية استخدام المخلفات الزراعية المتوفرة محليا كمخلفات الشاي كوسط ماز طبيعي لإمتزاز عناصر الرصاص و النحاس و النيكل من من المحاليل المائية. كما تم دراسة العوامل المؤثرة على عملية الأمتزاز مثل قيمة الدالة الحامضية, التركيز الأولي للعناصر الملوثة, كمية المادة المستعملة, زمن التماس بين المادة الممتزة والسطح الماز, وسرعة الاهتزاز. تم تحليل البيانات الناتجة من عملية الأمتزاز بواسطة موديلات لانكمير و فريندلج. أظهرت النتائج أن موديل فريندلج هو المفضل أكثر لامتزاز أيونات الرصاص و النحاس و النيكل على سطح مادة مخلفات الشاي مقارنة بموديل لانكمير تحت نفس الظروف. تم ايجاد السعة القصوى للأمتزاز للنظام المفرد ليكون 77.155 , 59.238, 52.46 ملغم \ غم لكل من الرصاص و النحاس و النيكل على التوالي. وتم اختبار البيانات الحركية من الدرجة الاولى و الثانية , تبين انها ملائمة مع الدرجة الثانية اكثر من ملائمتها مع الدرجة الاولى للنظام المفرد. وجد ان اعلى كفاءة إزالة للرصاص والنحاس والنيكل هي 93.6 , 71.97 و 47.3 ٪ على التوالي. و قد تم اجراء فحص التحليل الكيفي لمادة مخلفات الشاي باستخدام جهاز الأشعة تحت الحمراء لغرض دراسة المركبات الكيميائية و المركبات المؤكسدة و معرفة المجموعات الفعالة للمركبات العضوية مثل المجموعات الأمينية، الكربوكسيلية، الهيدروكسيل و الكربونيل.

الكلمات الرئيسة : امتزاز حيوي, معادن ثقيلة , تفاعل حركي , توازن , مخلفات الشاي.