Removal of heavy metal ions from aqueous solutions using tobacco leaves as a sorbent

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ABSTRACT

The effective removal of heavy metals from aqueous solutions is the most important issues for many countries. Removal of lead(II), zinc(II) and cadmium(II) from aqueous solutions were studied using Tobacco leaves. Batch sorption experiments were performed as a function of pH, contact time, solute concentration, temperature, particle size and sorbent dose. The maximum contact time for the equilibrium condition was 120min at the sorbent dose rate of 0.5g. The results were well fitted by both Langmuir and Freundlich isotherm models.

Key word: Tobacco leaves, sorption, heavy metal ions.
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INTRODUCTION

Removal of heavy metals from wastewater is of primary importance because they are not only causing contamination of water bodies and are also toxic to many life forms. Heavy metals in human bodies tend to bioaccumulate, which may result in damaged or reduced mental and central nervous function, and damage to blood composition, lungs, kidneys and liver. The

regulatory levels of health metals in drinking water are presented in Table (1) [1-3].

Table (1): Drinking water limits of heavy metals [1-3].

Org.	Lead (mg/l)	Copper (mg/l)	Nickel (mg/l)	Zinc (mg/l)	Cadmium (mg/l)
EPA	0.015	1.3	n.a.	5.0	0.005
WHO	0.01	2.0	0.07	n.a.	0.003
EU	0.01	2.0	0.02	n.a.	0.005

n.a.: No regulatory level data available.

Several techniques such as chemical precipitation, oxidation, reduction, coagulation, solvent extraction, electrochemical treatment, and membrane separation have been used. Coagulation – flocculation and chemical precipitation are the most widely used techniques. However, they both have the drawbacks of difficult sludge disposal and the diminished effectiveness when treating water with low heavy metal levels [4]. Membrane filtration and reverse osmosis were also reported [5]. However, these methods usually involve materials and high operation costs. Other methods such as electrodialysis, membrane electrolysis and electrochemical precipitation have also been investigated but their applications have been limited due to the high energy consumption [6]. Sorption is an effective way of separating solute particles. On the other hand, it is a cost– effective method due to the involving of

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low – cost materials and convenient operations. They have been proved to be a very effective technique for removing contaminants from water such as ammonia and heavy metals [6-8]. Moreover, ion exchange is particular effective for treating water with low concentration of heavy metals which is very common in practice [5]. In sorption, positive and negative charge ions from an aqueous solution replace dissimilar ions of the some charge initially in the solid [9]. However, these common techniques are too expensive to treat low levels of heavy metals in wastewater. Sorption techniques (adsorption and ion exchange) have been commonly employed for the removal of heavy metal ions [10]. The advantages of this process are the use of relatively low cost materials, high removal efficiency and having no secondary pollution [11, 12].

MATERIALS AND METHODS

Wastewater used in this experiment consists of heavy metals. The heavy metals used consist of lead, zinc, and cadmium. The desired concentration of heavy metals in water was 40mg/l in preliminary experiments, metal salts were dissolved in wastewater.

To achieve a concentration in water of 40 mg/l, mass of heavy metal salts added to water by assuming complete dissolution was calculated as follows equation:

$$W = V \times C_i \times \frac{M.wt}{At.wt} \qquad \ldots\ldots\ldots\ldots\ldots (1)$$

Where: W: Weight of heavy metal salt (mg), V: Volume of solution (l), C_i: Initial concentration of metal ions in solution (mg/l), M.wt: Molecular weight of metal salt (g/mole), At.wt: Atomic weight of metal ion (g/mole)

1.1. Lead
The metal salt used to produce a water of soluble lead was lead chloride $PbCl_2$ has a molecular weight (M.wt) of 278.10 g/mole. The molecular weight of Pb is 207.2 g/mole. To achieve a concentration in water of 40 mg/l of lead cations (Pb^{2+}) the following equations were used:
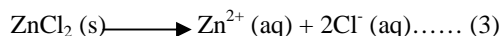
$$PbCl_2 \text{ (s)} \longrightarrow pb^{2+} \text{ (aq)} + 2Cl_2^- \text{ (aq)} \ldots .(2)$$
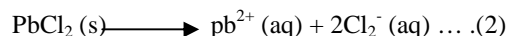
$$W = 1(l) \times 40 \text{ (mg/l)} \times \frac{278.10 \text{ (g/mole)}}{207.2 \text{ (g/mole)}}$$
$$= 53.687mg \ PbCl_2$$

1.2. Zinc
Zinc was added in the form of zinc (II) chloride dehydrate with a formula of $ZnCl_2$ has a molecular weight of 136.29 g/mole. Zinc has a molecular weight of 65.37g/mole. To achieve a concentration of 40 mg/l of zinc cations (Zn^{2+}) the following equations were used:

$$ZnCl_2 \text{ (s)} \longrightarrow Zn^{2+} \text{ (aq)} + 2Cl^- \text{ (aq)} \ldots\ldots (3)$$
$$W = 1(l) \times 40 \text{ (mg/l)} \times \frac{136.29 \text{ (g/mole)}}{65.37 \text{ (g/mole)}}$$
$$= 83.434 \text{ mg } ZnCl_2$$

1.3. Cadmium
Cadmium was added in the form of cadmium chloride has a molecular weight of 228.34g/mol. Cadmium (Cd^{2+}) has a molecular weight of 112.4 g/mole. To determine the amount of $CdCl_2.2\frac{1}{2}H_2O$ necessary for a concentration of 40mg/l of Cd^{+2} the following equations were used:

$$CdCl_2.2\frac{1}{2}H_2O(s) \longrightarrow Cd^{2+} \text{ (aq)} + 2Cl^{-2} \text{ (aq)} + 2\frac{1}{2}H_2O \text{ (l)} \ldots . (4)$$
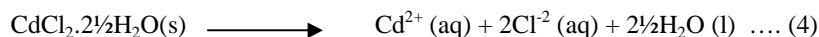
$$W = 1(l) \times 40 \text{ (mg/l)} \times \frac{228.34 \left(\frac{g}{mole}\right)}{112.4 \left(\frac{g}{mole}\right)}$$
$$= 81.26 \text{ mg } CdCl_2.2\frac{1}{2}H_2O$$

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RESULTS AND DISCUSSION

1.4.   Effect of Contact Time:

The sorption capacity of biomass increased with an increase in contact time before equilibrium was reached as shown in Figure (1). Sorption got slowdown in later stages because initially a large number of vacant surface sites may be available for sorption and after sometime, the remaining vacant surface sites may be difficult occupy due to forces between the solute molecules of the solid and bulk phase. The diminishing removal with increasing time may also be due to intraparticle diffusion process dominating over sorption [13].
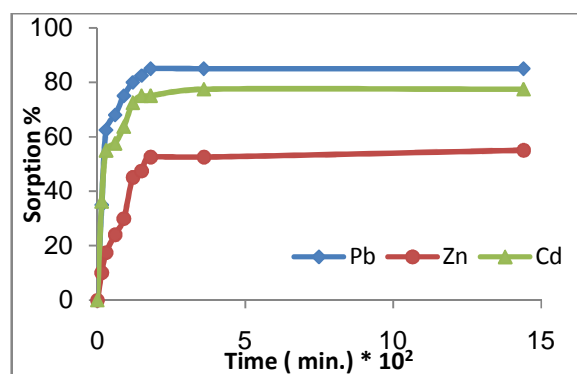

Figure (1): Effect of contact time on removal efficiency of heavy metal ions by Tobacco leaves.
(pH=6; m=0.5 g; T=20±1 °C; C_i=40 mg/L; speed=200 rpm).

The fast uptake capacity obtained at the initial stage may be explained by an increased availability in the number of active binding sites on the sorbent surface. The slow and insignificant sorption observed as time progresses are due to the fact that every sorbent has a limited number of active sites which becomes occupied with time [14].

1.5.   Effect of solution pH:

Most plant materials are made up of complex organic residues such as lignin and cellulose that contain several types of polar functional groups. These groups can be involved in chemical bonding and may be responsible for the typical cation-exchange characteristics of most biomaterials. The pH of the aqueous medium affects the surface charge of the sorbent, the degree of ionization, and the species of the sorbate [15]. The overall trend observed in the pH-dependent sorption behavior suggests that metal uptake occurs through ion-exchange. The binding follows an ion-exchange mechanism that involves electrostatic interaction between the negatively charged groups in the walls of the biomass and the metallic cations. At low pH, the surface of the sorbent would closely be associated with hydroxonium ions (H_3O^+) that hinder the access of the metal ions to the surface functional groups, consequently, the percentage of metal ion removal may decrease at low pH [16]. Figure (2) Show effect of PH.
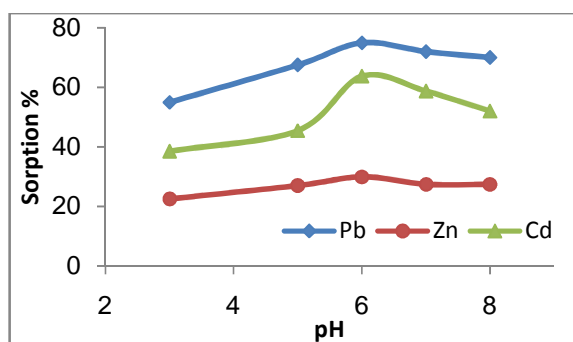

Figure (2): Effect of pH on removal efficiency of heavy metal ions by Tobacco leaves.
(t=90min; m=0.5 g; T=20±1°C; C_i=40 mg/L; speed=200 rpm).

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1.6.   Effect of biosorbent dose:

The sorption of heavy metal ions increases as the sorbent dosage increases due to the limited availability of the number of sorbing species for a relatively larger number of surface sites on the sorbent at higher dosage of sorbent. It is plausible that with higher dosage of sorbent there would be greater availability of exchangeable sites from metals ions. The significant increase in uptake was observed when the dose was increased to reach limited value of dosages, in this value the maximum removal efficiency was keeping same. Any further addition of the sorbent beyond this did not cause any significant change in the sorption show Figure (3). This may be due to overlapping of sorption sites as a result of overcrowding of sorbent particles [17].This suggests that after a certain dose of sorbent, the maximum sorption sets in and hence the amount of ions bound to the sorbent and the amount of free ions remains constant even with further addition of the dose of sorbent. The results can be explained as a consequence of a partial aggregation, which occurs at high biomass concentration giving rise an increase of active sites and hence biosorption [18,19].
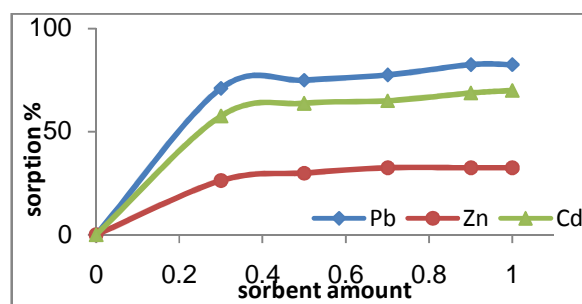

Figure (3): Effect of sorbent amounton removal efficiency of heavy metal ions by Tobacco leaves.
(t=90min; pH=6; T=20±1°C; C_i=40 mg/L; speed=200 rpm).

3.4.   Effect of initial metal concentration:

The amount of initial ions sorbed increased with increase in initial concentration. This is expected because at higher initial concentration more efficient utilization of active sites is envisaged due to a greater driving force by a higher concentration gradient. The increase in concentration leads to increase in collision between the ions and the active sites, which is a major factor in kinetics for increase in the rate of chemical reactions. Also this increase is due to higher availability of ions for sorption. These sorption characteristics indicate that surface saturation is dependent on the initial metal ion concentration, as this determines the amount of metal ions sorbed by the biomass in the presence of available active sites. At low concentrations sorption sites took up the available metal ions more quickly. However, at higher concentration, metal ions need to diffuse to biomass surface by intraparticle diffusion [20].

Some time when the heavy metal ions concentration increased the rate of sorption decreased. In this way metal concentration showed an inverse relation with sorption, i.e. maximum sorption occurs at minimum concentration of metal ions; it may be so because greater number of ions in the solution causes more number of collisions and thus leading to desorption of metal ions from the binding sites of sorbent particles whereas with limited number of ions there are limited number of collision between the metal ions that is why low concentration showed higher rates of sorption [21]. Figure (4) show the effect of initial concentration.
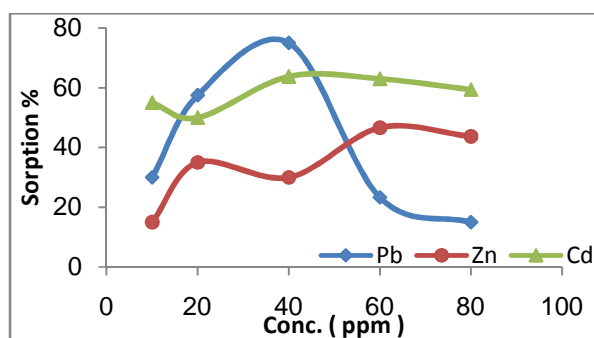

Figure (4): Effect of initial concentration on removal efficiency of heavy metal ions by Tobacco leaves.
(pH=6; m=0.5 g; T=20±1°C;t=90min; speed=200 rpm).

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3.5. Effect of solution temperature:

The sorption of heavy metal ions onto natural sorbents waste biomass increased with increase in temperature suggested that the sorption process is endothermic in nature. The increase in equilibrium biosorption capacity indicates that higher temperature favor the sorption of heavy metal ions from aqueous solution show Figure (5). The magnitude of the increase in amount as temperature is increased continues to decline as temperature is increased [22]. This is because with increasing temperature, the attractive forces between biomass surface and metal ions are weakened and the sorption increases. Also, at high temperature, the thickness, of the boundary layer decreases, due to the increased tendency of the metal ion to escape from the biomass surface to the solution phase, which results in a increase in sorption as temperature increases [23].

3.6. Effect of biosorbent size:

The removal of heavy metal ions at different particle sizes illustrated that removal rate increases as the particle size decreases. The relatively higher sorption rate as the particle size decreases is due to the increase in surface area. Show Figure (6).
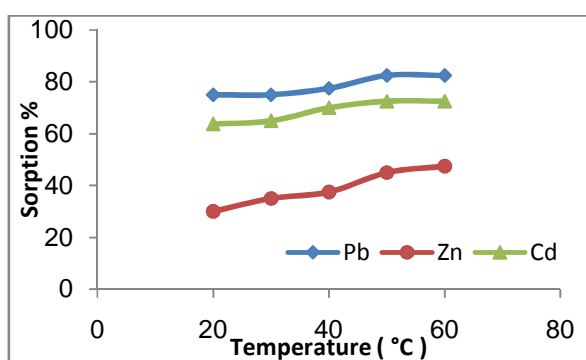

Figure (5): Effect of Temperature on removal of heavy metals by Tobacco leaves.
(pH=6; m=0.5 g; t=90min; C_i=40mg/l; speed=200rpm).

There is a tendency as fine particles exhibit lesser time to equilibriate in shorter time. This was most probably due to increase in the total surface area which provided more sorption sites for metal [24].
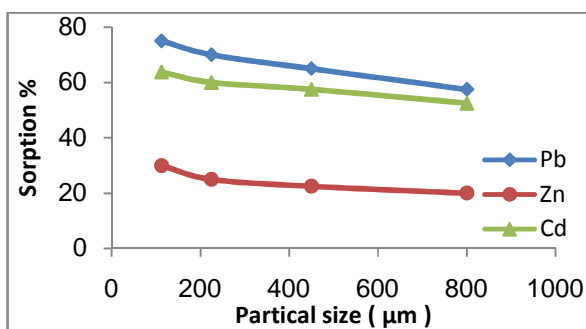

Figure (6): Effect of particles size on removal efficiency of heavy metal ions by Tobacco leaves.
(t=90min; pH=6; T=20±1°C; C_i=40 mg/l; speed=200 rpm).

3.7. Equilibrium Isotherms:

There are several models that express a relation between the amounts of sorption and the residual solute concentration. The most frequent models are the Langmuir, Freundlich, Temkin, and D-R sorption isotherm models. An isotherm describes the relationship of the concentrations of a solute between two separate phases at equilibrium at a constant temperature. A sorption isotherm, then would express the relation between the amount of solute or vapor sorbed as a function of the equilibrium concentration of the solute or vapor in the solution. A sorption isotherm describes the process without reference to the mechanism [25]. The equilibrium sorption isotherm points to how the sorbate molecule or ions are distributed between the solid phase and the liquid phase. To find out the

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suitable isotherm models, analysis of isotherm data by adapting to different isotherm models is an important step that can be used for design purpose. In the present research, the sorption equilibrium data of Pb^{2+}, Zn^{2+}, and Cd^{2+} by Tobacco leaves was analyzed in terms of Langmuir, Freundlich, Temkin, and D-R isotherm models [26].

3.7.1. Langmuir isotherm:

The Langmuir isotherm model is based on ideal assumption of a total monolayer sorption on sorbent surface [27]. Langmuir equation relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature. The isotherm is based on three assumptions, namely, sorption is limited to monolayer coverage, all surface sites are alike and can only accommodate one sorbed atom, and the ability of a molecule to be sorbed on a given site is independent of its neighboring site's occupancy [27,28].

The Langmuir equation was developed in the 1990s to describe the sorption of gas molecules on planer surfaces. This model was later extended to liquid systems, where species in solution are involved. The Langmuir model suggests that sorption occurs on homogenous surfaces by monolayer sorption (sorption onto a surface with a finite number of identical sites), without interaction between sorbed molecules. The equation (5) describes the model:

$$q_e = \frac{q_m \, b \, C_e}{1 + b \, C_e} \qquad \text{......................} \qquad (5)$$

Where: b= is constant related to the affinity of the binding site (L mg^{-1}), q_e = the sorbed metal ions on the biomass (mg g^{-1}), C_e = metal ions concentration in the solution at equilibrium (mg L^{-1}), and $q_{m\,=}$ maximum sorption capacity for a monolayer coverage (mg g^{-1}).

The maximum sorption amount of the metal ion per unit weight of biomass needed to form a complete monolayer on the surface. q_m represents a practical limiting sorption capacity when the surfaces fully covered with metal ions and assists in the comparison of sorption performances. The sorption parameters (q_m, b) can be determined from the linearized plotting 1/q_e vs. 1/C_e as shown in figure (7) according to equation (6) and Table (2) show this parameter.

$$\frac{C_e}{q_e} = \frac{1}{q_m \, b} + \frac{C_e}{q_m} \qquad \text{..........} \qquad (6)$$

Probably the Langmuir isotherm model is the most widely applied model because it allows obtaining the maximum sorption capacity (q_m) for given sorbent/sorbate system, at constant temperature [29].

Figure (7): Langmuir isotherm for sorbent of lead, zinc, and cadmium on Tobacco leaves.
(pH,=7;T=20°C; m=0.5g; t=90min; speed=200 rpm)

3.7.2. The Freundlich isotherm:

The Freundlich isotherm model is based on heterogeneous surface assumption, expressed by equation as [30]:

$$q_e = K_F \; C_e^{1/n} \ldots\ldots\ldots\ldots(7)$$

Where: K_F and n = the Freundlich constants, K_F related to the sorption capacity, (mg g^{-1}).

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Table (2): Parameters of Langmuir isotherm for sorption of metal ions on Tobacco leaves.

Matrix	Metal	$1/q_m\,b$ (g/L)	$b*\,10^{-2}$ (L/g)	R^2
Pb	*Pb*	3.052	4.62	0.933
Zn	*Zn*	1.264	3.188	0.782
Cd	*Cd*	2.124	1.935	0.971
Pb+Zn	*Pb*	3.104	6.798	0.835
	Zn	1.564	3.052	0.88
Pb+Cd	*Pb*	3.598	6.309	0.898
	Cd	2.202	1.435	0.994
Zn+Cd	*Zn*	2.063	3.518	0.675
	Cd	3.178	1.516	0.997
Pb+Zn+Cd	*Pb*	8.604	6.567	0.892
	Zn	3.775	3.091	0.849
	Cd	2.275	1.2	0.994

The Freundlich isotherm describes equilibrium on heterogeneous surfaces and hence doesn't assume monolayer capacity. The larger its value, the higher capacity, n is the sorption intensity or the heterogeneity of the sorbent; the more heterogeneous the surface, the larger its value. If 1/n approaches 1, the equation becomes linear. If 1/n value within 0.1 and 1 there is a favorable sorption of the sorbate on the given sorbent. The Freundlich relation is an exponential equation that assumes that the concentration of sorbate on the sorbent surface increases by increasing the sorbate concentration in the liquid phase. Equation (8) can be linearized in logarithmic form and the Freundlich constants can be determined.

$$\log q_e = \left(\frac{1}{n}\right)\log C_e +\ \log K_F \quad \text{………….. (8)}$$

The values K_F and n can be estimated respectively from the intercept and slope of a linear plot of experimental data of $\log q_e$ versus $\log C_e$ as shown in Figure (8) and Table (3). Freundlich isotherm provides no information on the monolayer sorption capacity in comparison with the Langmuir model. This isotherm is widely recommended due to its accuracy. If gives more accurate results then the Langmuir isotherm for a heterogeneous sorption systems [25,29 and 31].
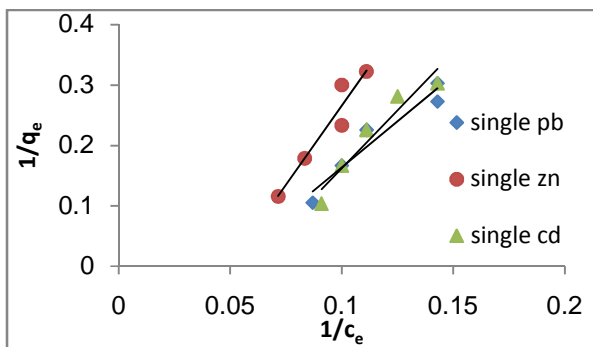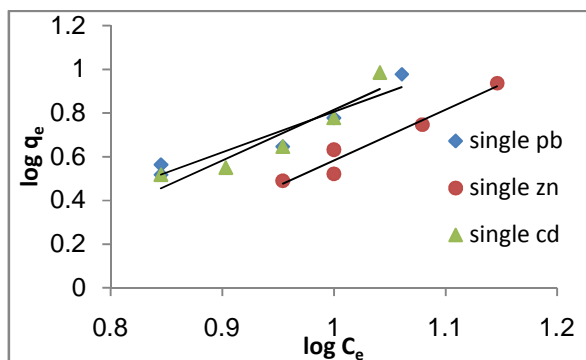

Figure (8): Freundlich isotherm for sorbent of lead, zinc, and cadmium on Tobacco leaves.
(pH=6;T=20°±C; m=0.5g; t=90min; speed=200 rpm)

3.7.3. The Temkin isotherm:
Another empirical equation is the Temkin equation proposed originally by Temkin 1935. Temkin and Pyzhev were considered the effects of indirect sorbate/sorbent interactions on sorption isotherms. The heat of sorption of all molecules in the layer would decrease linearly with coverage due to sorbate/sorbent interactions [32]. The linear form of the Temkin isotherm equations are given as [33]:

$$q_e =\ B_T \ln K_T +\ B_T \ln C_e \text{ ……… (9)}$$

And

$$b_T =\ \frac{RT}{B_T} \text{ …………………… (10)}$$

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Where: K_T is Temkin sorption potential (L/mg), B_T & b_T are Temkin constants.

When q_e was plotted against lnC_e, a straight line with the slope of B_T must be obtained. The height value of correlation coefficient R^2 was indicated that the sorption data was well fitted to the Temkin isotherm. The values K_T and B_T can be estimated respectively from the intercept and slope of a linear plot of experimental data of q_e versus LnC_e as shown in Figure (9) and parameters listed in Table (4).

Table (3): Parameters of Freundlich isotherm for sorption of metal ions on Tobacco leaves.

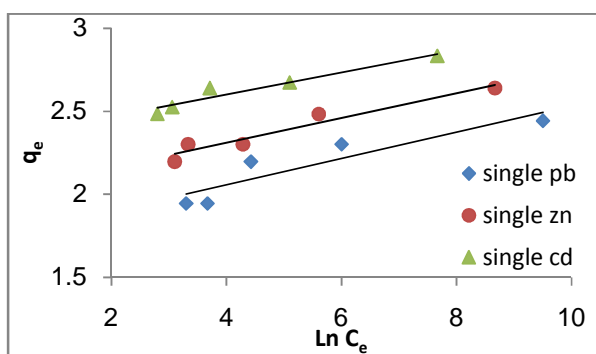| Matrix	Metal	$K_F * 10^{-2}$ (mg/g)	1/n	R^2
Pb	Pb	8.912	1.857	0.913
Zn	Zn	6.229	2.662	0.879
Cd	Cd	3.177	2.948	0.961
Pb+Zn	Pb	5.584	2.249	0.781
	Zn	5.623	1.9	0.875
Pb+Cd	Pb	4.325	2.251	0.827
	Cd	8.37	1.831	0.964
Zn+Cd	Zn	5.754	1.54	0.558
	Cd	4.218	2.533	0.924
Pb+Zn+Cd	Pb	5.333	3.806	0.789
	Zn	7.120	2.28	0.901
	Cd	5.184	3.397	0.964

Figure (9): Temkin isotherm for sorbent of lead, zinc, and cadmium on Tobacco leaves.
(pH=6;T=20±°C; m=0.5g; t=90 min; speed= 200 rpm

3.7.4. The Dubinin-Radushkevich (D-R) isotherm:
Dubinin, Polanyi, and Radushkevich suggested about 1947 a simple but very useful empirical theory allowing one to calculate the amount of gas sorbed in microporous sorbent. The theory was based on a pore filling model [34]. The Dubinin equation (Dubinin, 1966, 1967, 1972, and 1975) has its history in the development of theory for sorption in activated carbon.

Table (4): Parameters of Temkin isotherm for sorption of metal ions on Tobacco leaves.

metal	metal	$B_T *10^{-2}$ (J/mol)	$K_T *10^{-3}$ (L/mg)	$b_T *10^2$	R^2
Pb	Pb	7.9	3.63	3.08	0.835
Zn	Zn	4.2	2.57	5.80	0.946
Cd	Cd	6.6	2.28	3.69	0.935
Pb+Zn	Pb	5.1	1.06	4.77	0.83
	Zn	4.2	6.55	5.80	0.68
Pb+Cd	Pb	5.5	1.86	4.43	0.717
	Cd	3.0	5.48	8.12	0.912
Zn+Cd	Zn	1.1	3.0	2.21	0.438
	Cd	2.2	4.87	1.10	0.873
Pb+Zn +Cd	Pb	3.3	1.37	7.38	0.654
	Zn	2.5	4.26	9.74	0.931
	Cd	3.0	1.39	8.12	0.913

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The best utility of the Dubinin-Radushkevich equation lies in the fact that the temperature dependence of such equation is manifested in the sorption potential [35]. Today it is used for both characterization of porous solids and also for engineering purposes. It has been the sorbate is considered as a fluid phase in the sense of thermodynamics, which is exerted to the external forces of the atoms and molecules located on the surface of a sorbent material [34]. The linear form of the (D-R) isotherm equation is given as [33]:

$$\ln q_e = \ln q_{m,DR} - K_{DR}\varepsilon^2 \ \dots\dots\dots (11)$$

The ε parameter is calculated from

$$\varepsilon = RT \ \ln\left(1 + \frac{1}{c_e}\right) \ \dots\dots\dots\dots (12)$$

Where: K_{DR} is D-R constant (mg^2/J^2), ε is Polanyi potential (J/mg), R is universal gas constant (8.314 J/mol.K) and T is temperature (°K).

When $\ln q_e$ was plotted against ε^2, a straight line with the slope of $-K_{DR}$ must be obtained. The height value of correlation R^2 was indicated that the sorption data was well fitted to the D-R isotherm. The values $q_{m,DR}$ and K_{DR} can be estimated respectively from the intercept and slope of a linear plot of experimental data of $\log q_e$ versus $\log C_e$ as shown in Figure (10) and parameters listed in Table(5).
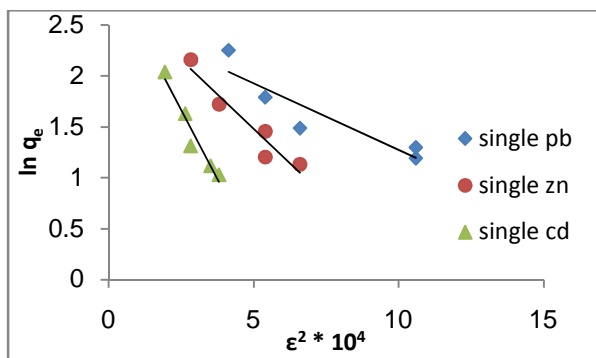

Figure (10): Dubinin-Radushkevich isotherm for sorbent of lead, zinc, and cadmium ions on Tobacco leaves. (pH=6;T=20±°C; m=0.5g;t= 90min).

Table (5):Parameters of Dubinin-Radushkevich isotherm for sorption of metal ions on Tobacco leaves.

matrix	metal	$q_{m, DR}$ (mg/g)	$K_{DR}*10^{-4}$ (mg^2/J^2)	R^2
Pb	Pb	1.322	0.1	0.842
Zn	Zn	3.240	0.2	0.883
Cd	Cd	2.042	0.5	0.937
Pb+Zn	Pb	9.884	0.08	0.856
	Zn	2.809	0.1	0.87
Pb+Cd	Pb	1.756	0.2	0.819
	Cd	1.316	0.2	0.949
Zn+Cd	Zn	2.924	0.1	0.588
	Cd	3.279	0.2	0.914
Pb+Zn+Cd	Pb	3.242	0.4	0.767
	Zn	2.744	0.1	0.884
	Cd	1.635	0.1	0.951

3.8. Sorption kinetics:
Kinetics of sorption describing the solute uptake rate, which is turn governs the residence time of sorption reaction, is one of the important characteristics defining the efficiency of sorption. Several researchers have used different kinetic models to predict the mechanism involved in the sorption process. These include pseudo-first-order model, pseudo-second-order model, Webber and Morris sorption kinetic model, first-order reversible reaction model, external mass transfer model, first-order equation of Bhattacharya and Venkobachar, Elovich's model and Ritchies's

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equation. Pseudo first-order and pseudo second-order kinetic models are widely used [28, 36]. To investigate the reaction-based model, pseudo-first-order and pseudo-second-order models were employed. This model can be expressed by eqs. (11) and (14), respectively [37].

3.8.1. Pseudo first-order kinetic model:

Lagergren (1898)s presented a first-order rate equation to describe the kinetic process of liquid-solid phase sorption of oxalic acid and malonic acid onto charcoal, which is believed to be the earliest model pertaining to the sorption rate based on the sorption capacity. It can be presented as follows [38]:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad \ldots\ldots\ldots\ldots \quad (13)$$

Where: q_e and q_t (mg/g) are the sorption capacities at equilibrium and time t (min), respectively. k_1 (min^{-1})is the pseudo-first-order rate constant for the kinetic model. Integrating eq. (13) with the boundary conditions of $q_t=0$ at t=0 and $q_t=q_t$ at t=t, yields.

$$\ln \left(\frac{q_e}{q_{e-} q_t} \right) = K_1 t \quad \ldots\ldots\ldots\ldots.. \quad (14)$$

Which: can be re-arranged to:

$$log(q_e - q_t) = log \, q_e - \frac{k_1}{2.303} \times t \ldots\ldots.. \quad (15)$$

To distinguish kinetic equations based on sorption capacity from solution concentration, Lagergren's first order rate equation has been called pseudo-first-order [39]. In recent years, it has been widely used to describe the sorption of pollutants from wastewater in different fields, such as the sorption of methylene blue from aqueous solution by broad bean peels and the removal of malachite green from aqueous solutions using oil palm trunk fibre [40-42].
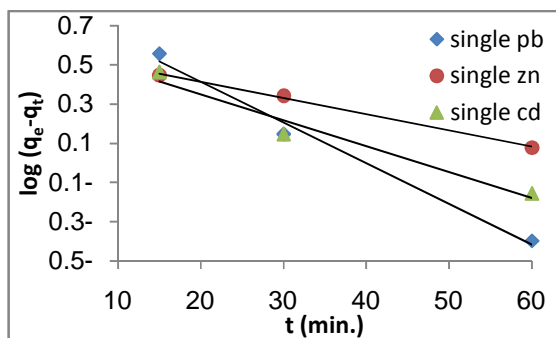

Figure (11): Test of pseudo first order equation for sorption of lead, zinc, and cadmium ions on Tobacco leaves (pH=6; m= 0.5g; speed= 200 rpm; T= 20±1°C, C_i= 40 mg/l).

Table (6): sorption rate constants, estimated q_e and coefficients of correlation associated to the Lagergren first order model for Tobacco leaves.

metal	metal	$q_{e,exp}$ (mg g^{-1})	$K_1 \times 10^{-2}$ (min^{-1})	q_e (mg g^{-1})	R^2
Pb	Pb	6.4	4.606	6.729	0.988
Zn	Zn	3.6	1.842	3.784	0.997
Cd	Cd	5.8	2.993	4.092	0.958
Pb+Zn	Pb	6.4	6.678	11.994	0.984
	Zn	2.8	2.303	3.388	0.998
Pb+Cd	Pb	6	2.763	5.649	0.964
	Cd	5.2	3.454	5.470	0.992
Zn+Cd	Zn	2.8	4.606	3.198	1
	Cd	5	4.375	4.395	0.999
Pb+Zn+ Cd	Pb	6	4.375	5.997	0.999
	Zn	3	3.915	4.666	0.95
	Cd	4.7	3.684	4.139	0.999

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3.8.2. Pseudo-second order kinetic model:

In 1995, Ho described a kinetic process of the sorption of divalent metal ions onto natural sorbents [43], in which the chemical bonding among divalent metal ions and polar functional groups such as aldehydes, ketones, acids, and phenolics are responsible for the cation-exchange capacity. The rate of sorption described by eq.(14) is dependent upon the amount of divalent metal ions on the surface of sorbents at time t and that sorbed at equilibrium. The driving force, (q_e-q_t), is proportional to the available fraction of active sites [44]. Then, it yields

$$\frac{d\,q_t}{dt} = k_2(q_e - q_t)^2 \quad ……………..(16)$$

Eq. (16) can be re-arranged as follows:

$$\frac{d\,q_t}{(q_e-q_t)^2} = k_2dt \quad ………………... (17)$$

Integrating eq.(13) with the boundary conditions of $q_t=0$ at $t=0$ and $q_t=qt$ at $t=t$, yields

$$\frac{1}{(q_e-q_t)} = \frac{1}{q_e} + k_2t \quad ………………. (18)$$

Which can be re-arranged as follows:

$$\frac{1}{q_t} = \frac{1}{h} + \frac{1}{q_e}\,t ……..………..(19)$$

And

$$h = k_2q_e^2 \quad …………………….. \quad (20)$$

Where: h (mg/(g.min)) means the initial sorption rate, and the constants can be determined experimentally by plotting of t/q_t against t. Similarly, Ho's second-order rate equation has been called pseudo-second-order rate equation to distinguish kinetic equations based on sorption capacity from concentration of solution [44]. This equation has been successfully applied to the sorption of metal ions, dyes, herbicides, oils, and organic substances from aqueous solutions [45-50].

Plotting *t/q_t* against *t* at different sorbate concentrations provided second order sorption rate constant (k_2) and q_e values from the slopes and intercepts as showing in Figure (12).

The values of correlation coefficient indicate a good fit of Lagergren second order model with the experimental data. In addition, there is only little difference between the $q_{e,exp}$ and $q_{e,cal}$ (Table 7), reinforcing the applicability of pseudo-second-order. In many cases the first order kinetic process was used for reversible reaction with an equilibrium being established between liquid and solid phases. Whereas, the second order kinetic model assumes that the rate limiting step may be chemical sorption [51].
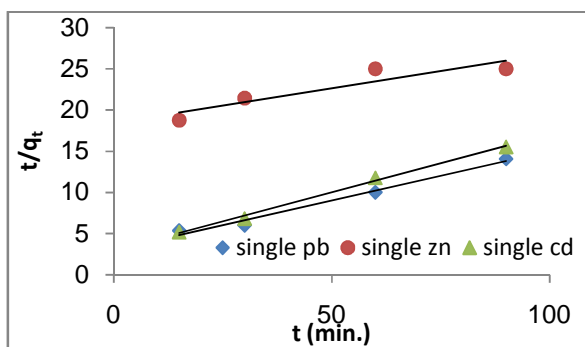

Figure (12): Test of pseudo second order equation for sorption of lead, zinc, and cadmium ions on Tobacco leaves (pH=6; m= 0.5g; speed= 200 rpm; T= 20±1°C, C_i= 40 mg/l).

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Table (7): sorption rate constants, estimated q$_e$ and coefficients of correlation associated to the Lagergren second order model for Tobacco leaves.

metal	metal	q$_{e,exp}$ (mgg^1)	K$_2$ *10^{-2} (g/mg.min)	q$_e$ (mgg^{-1})	R^2
Pb	Pb	6.4	1.957	6.849	0.984
Zn	Zn	3.6	0.806	4.329	0.84
Cd	Cd	5.8	3.834	6.060	0.995
Pb+Zn	Pb	6.4	1.205	6.896	0.98
	Zn	2.8	0.839	3.311	0.971
Pb+Cd	Pb	6	2.192	6.060	0.997
	Cd	5.2	3.930	5.464	0.997
Zn+Cd	Zn	2.8	2.917	3.021	0.992
	Cd	5	3.356	5.025	0.999
Pb+Zn+	Pb	6	4.494	5.952	0.999
Cd	Zn	3	2.972	2.840	0.995
	Cd	4.7	2.336	5.050	1

3.9. Sorption thermodynamics:

The important thermodynamic parameter, Gibbs free energy change for the sorption process is related to equilibrium constant by the classic van Hoff equation as:

$$\Delta G^\circ = -RT \ln K_C \ldots\ldots\ldots\ldots (21)$$

Where: ΔG° is the standard free change   (*J mol^{-1}*), *T* the absolute temperature (°*K*) and *R* gas constant (*Jmol^{-1}K^{-1}*), K_C the equilibrium constant for sorption process is represented as follow equation [52]:

$$K_C = \frac{c_s}{c_e} \ldots\ldots\ldots\ldots\ldots\ldots (22)$$

Where: C_s is the concentration of heavy metals on the sorbent at the equilibrium and C_e is the equilibrium concentration of same metals in the liquid phase.

The Gibbs free energy change is also related to the heat of sorption and entropy change at constant temperature by the Well-known thermodynamic equation:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \ldots\ldots\ldots\ldots (23)$$

Where: ΔH° is enthalpy change (*J mol^{-1}*), ΔS° is entropy change (*J mol^{-1} K^{-1}*). The value of ΔH° and ΔS° can be calculated from the plot of ΔG° vs. *T* [26].

Or: Can be calculated from the slope and intercept of the linear plot of *lnK$_c$* vs. *1/T* from the equation [53]:

$$ln\, K_C = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \ldots\ldots\ldots\ldots\ldots (24)$$
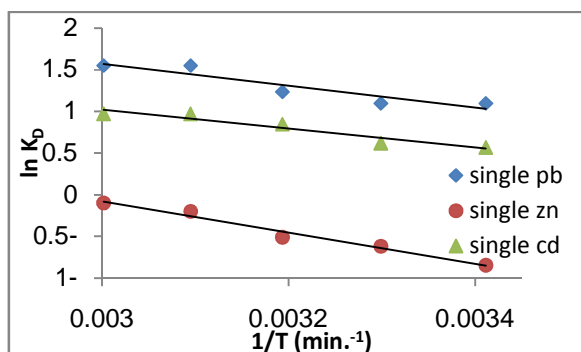

Figure (13): Variation of equilibrium constant (K$_C$) as a function of temperature by Tobacco leaves.

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CONCLUSION

According to the experimental results, the Tobacco leaves sorbent an effective, low cost, and alternative sorbent precursor for the removal of lead, zinc, and cadmium ions from wastewater. The equilibrium conditions were attained equilibrium within 90 min. The sorption capacity first increased with increases in contact time due to the availability of the uncovered surface area of the sorbents, then remains almost constant, which reflects the maximum sorption capacity of the sorbent under operating conditions. It has been found that the sorption increased with increasing in pH until the optimum pH is reached, because the surface of sorbent becomes negative at higher pH values. The amount of heavy metal ions removal was increased with increasing temperature, While the removal percentage of heavy metal ions does not have same behavior with the increasing concentration. The sorption capacity increased with increasing sorbent dosage due to grate surface area. The sorption efficiency of heavy metal ions increased with decreasing particle size due to increasing in surface area which provides greater number of sites for sorption.

The linear Langmuir, Freundlich, Temkin and D-R isotherms were used to represent the experimental data, and the data could by relatively well interpreted by Langmuir isotherm model, and it was found that the sorption of heavy metal ions followed pseudo-second-order kinetics. The sorption thermodynamic study showed that the sorption of heavy metal ions becomes more feasibility and randomness with increasing in temperature due to negative value of ΔG and positive of ΔS, respectively. The sorption process is endothermic due to positive value of ΔH.

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