

Kinetic and Thermodynamic study of Cd (II), Co (II), Zn (II) removal from aqueous solution by Kiwi Tree Leave

Navid Nourbakhsh¹, Hassan Zavvar Mousavi^{2,*}, Eskandar Kolvari³, Aisan Khaligh⁴

¹Guilan Water & Wastewater Co, Rasht, Iran

²Department of Chemistry Faculty of Science, University of Guilan, Rasht, Iran

³Department of Chemistry, Semnan University, Semnan, Iran

⁴Department of Chemistry, Bilkent University, 06800 Ankara

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Abstract

In this study, a perfect adsorbent presented for removal of the heavy metals Co^{2+} , Cd^{2+} and Zn^{2+} from aqueous solution and waste water by using activated carbon prepared from agricultural waste, kiwi tree leaves. Studies agree with, Langmuir adsorption isotherm. The values of constants for the Thermodynamic and kinetic isotherms were obtained. The kinetic isotherm experiment data could be well described with the pseudo-second order kinetic model and, Thermodynamic studies indicated that the adsorption processes were exothermic and spontaneous in nature. The result of experiments showed that Cd^{2+} , Co^{2+} and Zn^{2+} metal ions removal increased with increasing pH, amount of adsorbent and, decreased with increasing the temperature and initial concentration of solutions. It was demonstrated that the developed method based on Kiwi tree leaves is safe, easy, inexpensive, fast and trusty for eliminate of toxic metal ions from wastewater.

Keywords: Heavy metals; low-cost adsorbent; Adsorption Isotherms; Agricultural Waste.

1. Introduction

Environmental contamination can occur through large industrial factories, Pesticides and, chemical fertilizers, Colored wastes, Petroleum industry and leaching of heavy metals, from water resources to soil and ground water[1-4]. Therefore, the maximum acceptable level of discharge into the environments and accordingly controlling the water pollution level have ordered by Word Heath Organization (WHO) and Environmental Protection Agency (EPA).

According to U.S. Environmental Protection Agency (EPA) and World Health Organization (WHO), the max acceptable concentrations recommended for cadmium and zinc in drinking water is 0.005 and 5 $\mu\text{g/L}$, respectively [5,6].Therefore, the elimination of heavy metals from water is serious to protect public health. Treatment operation to remove metals from polluted water include chemical precipitation, ion exchange, membrane filtration, carbon adsorption and coprecipitation/adsorption [7,8]. Today's, adsorption has been shown to be an economically applied another method for elimination metal ions in water [9].

*.Corresponding author: Professor of Analytical Chemistry, Faculty of Chemistry, Gilan University, Rasht, Iran. E-mail address: hzmousavi@guilan.ac.ir

Various common methods are was applied to eliminate toxic metal ions from industrial sewages [10,11]. Some of these techniques have weaknesses such as expensive, slow process, high energy consumption and production of toxic sludge[12]. Recently adsorption technique has been archived as one of the most important and effective methods for water treatment of some contaminants because of somewhat in term of kinetic adsorption reaction are fast, low operation costs and high metal adsorption capability[13].

Agricultural wastes, due to fibrous nature, being spongy and weightless, are non-conventional Inexpensive adsorbents for metal adsorption. Carboxylic and hydroxyl groups on the surface of agricultural wastes have a high capacity to adsorb toxic heavy metal ions. Modifications of agricultural wastes can maximize surface area, type of adsorbing sites and porosity. Therefore modifying sorptive capacity, which may gratify for the cost of additional processing [12,13]. This paper described the adsorption behavior of Cd^{2+} , Co^{2+} , and Zn^{2+} on agricultural waste and activated carbon prepared from orange tree leaves. The adsorption parameters in this study in a batch mode were studied. Various experimental terms such as pH, amount of adsorbent, temperature, and contact time for the optimum adsorb of all the metal ions by Kiwi Tree Leaves (KTL), and Activated Kiwi Tree Leaves (ACKTL) investigated and optimized. In the following, adsorption of metal ions mechanisms are generally explored by isotherm models, kinetic and finally thermodynamic parameters.

2. Experimental procedure

2.1. Materials and method

In Guilan region, North Iran, agricultural wastes are frequently produced, and in most cases these wastes are burnt or added to the soil. Experiments were conducted with kiwi tree leaves collected from guilan province, north of Iran.

Analytical grade (MERCK) Zinc nitrate ($\text{Zn}(\text{NO}_3)_2$), cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$), Cobalt nitrate ($\text{Co}(\text{NO}_3)_2$) were used. The concentrated nitric acid and sodium hydroxide used for pH adjustment were all ACS reagent grade and obtained from MERCK (Darmstadt, Germany).

Deionized water (DI-water) took from a Millipore Continental Water System (Bedford, MA, USA) applied in this research. 1000 mL, 1000 ppm, stock solutions of Co^{2+} , Zn^{2+} , and Cd^{2+} , were prepared from the nitrate salts, in deionized water.

2.2. Apparatus

To heavy metals measurement, atomic absorption spectrophotometer (Agilent, AA-200, USA) given by the manufacturer with air-acetylene flame, the pH parameter were adjusted by a digital pH meter (E-632, Metrohm, Herisau, Switzerland), supplied with a glass combined electrode.

2.3. Adsorbents

The kiwi leaves were cut from the tree. The leaves were then cleaned with deionized water, and dried at 110 °C for 15 h, in a convection oven. For the first type of absorbent, the dried leaves were dried by grinding machine and converted into powder. The activated adsorbent was prepared by burning of the leaf powder prepared as above at 260 °C in a furnace for 1h.

2.4. Batch Studies

At first stock solution with a 1000 mg L⁻¹ concentration of metal cations were prepared. Experiments were carried out with 100 mL with the initial concentration of 100 mg L⁻¹ aqueous solutions of metal, ions (from each one). Desired pH values in solution were adjusted by adding volumes of NaOH or HNO₃ solutions. Then added the proper amount of the adsorbent to samples. The samples were shaken in an orbital shaker in proper time and speed, at a fixed temperature. Then the mixture was separated from each other by filter paper. The residual concentrations of Cd^{2+} , Co^{2+} , and Zn^{2+} ions were defined by atomic absorption spectrophotometer. The removal of metal ions was obtained from Eq.1.

$$\text{Removal, \%} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (\text{Eq. 1})$$

The equilibrium concentration of heavy metals after the sorption process, q_e (mg g⁻¹), determined using the Eq.2.

$$q_e = \frac{(C_0 - C_e)}{m} \times V \quad (\text{Eq. 2})$$

Where C_0 is initial and C_e is the final concentration of Cd^{2+} , Co^{2+} and Zn^{2+} ions ($mg L^{-1}$), V is the volume of the solution (L), and m is the mass of adsorbent (g).

3. Results and discussion

The FT-IR analysis of the samples before and after activation is shown in Figure 1. Also, the better providing about the functional groups are presented by (Figure 1) FT-IR analysis.

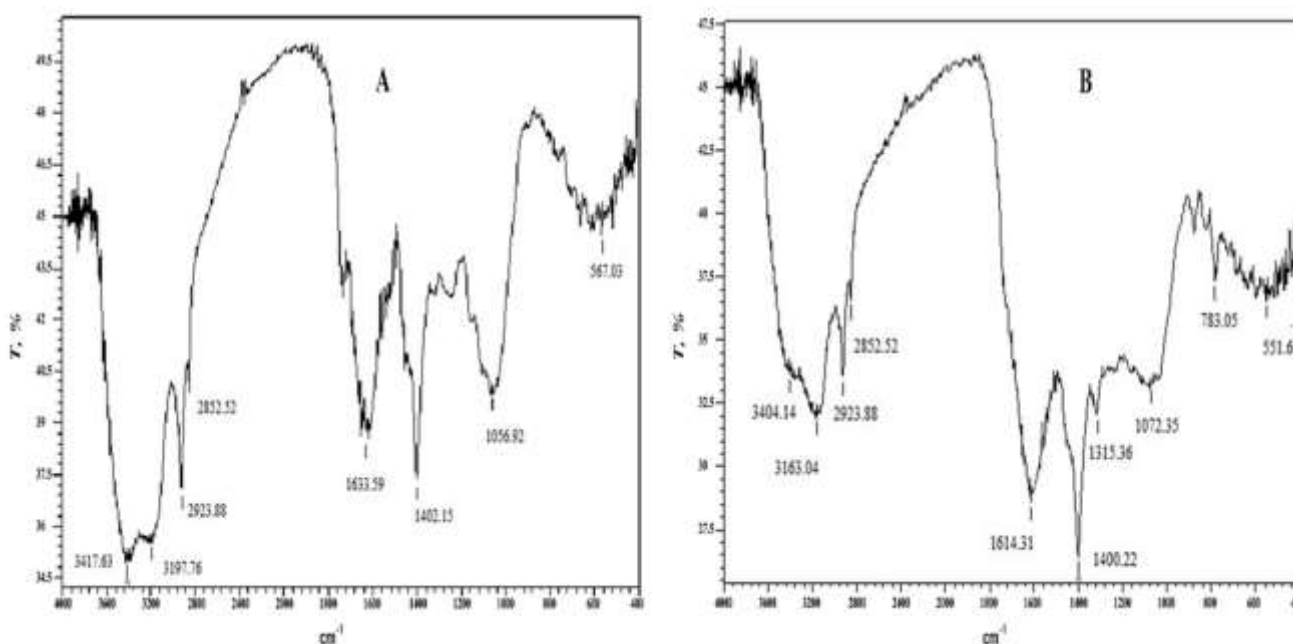


Fig. 1. FT-IR spectrum of adsorbents (A) KTL (B) ACKTL.

In the FT-IR spectrum (Fig. 1), showed that, the absorption bands at 1614 cm^{-1} ($C=C$), characteristic peaks at 3404 cm^{-1} for stretching vibrations of (O-H) and ($C=O$) of the carboxyl groups and 2850 cm^{-1} for Stretching vibration of (C-H), the only difference, in the amplification of in peaks at 551 and 783 cm^{-1} .

3.1. Effect of pH

Adjusting pH of the solution has a significant effect on the number of heavy metals because it determines the

degree of ionization, the surface charge of the adsorbent, and speciation of the adsorbate[14]. The effect of pH on the adsorption of the Cd^{2+} , Zn^{2+} , Co^{2+} by KTL and ACKTL were studied at room temperature by test with different values of the pH of the solution – adsorbent suspension from 2.0 to 7.0. The results are shown in Figure 2.

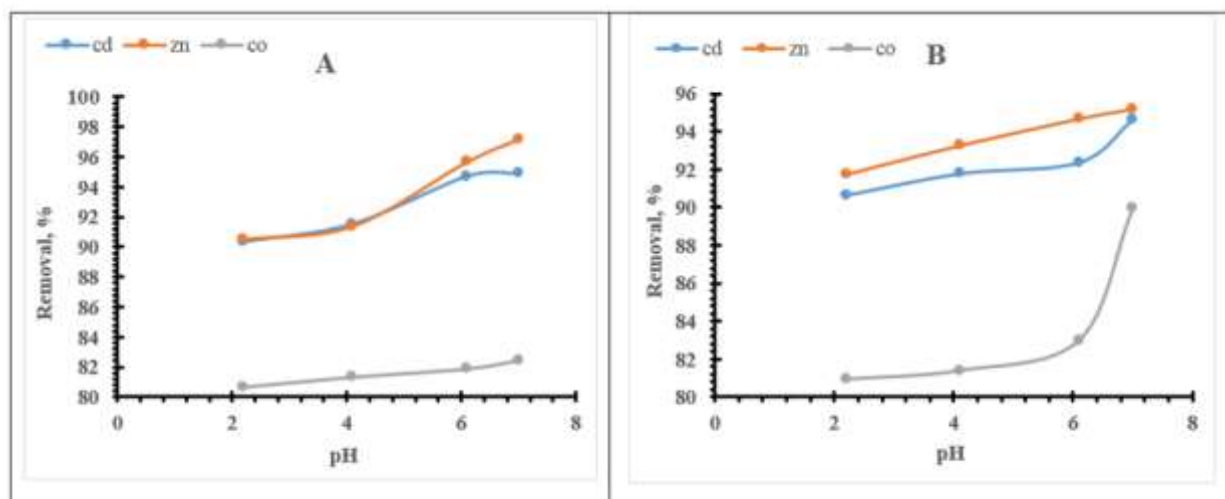


Fig. 2 : The effect of pH on metal removal through (A): KTL adsorption (B) ACKTL adsorption Conditions: adsorbate concn. 100 mg L^{-1} , temp. 298.15 K and adsorbent mass. 0.1 g KTL and 0.07 g ACKTL , contact time. 30 min

Effect of pH was serious because of the pH of solution efficacy the distribution of active sites on the surface of KTL and ACKTL. At the alkali pH, the OH^- on the surface prepares the ability of binding cations. With the decrease of pH to the acidic side, leads to the neutralization of surface charge, and OH^- is dislocated from the surface. As a result, when the surface carries positive charges, it begins to adsorb anions. At $\text{pH} > 7.0$ values, according to KSP value of the metal ions, precipitation is mechanism if removal, and thus the separation may not be due to adsorption. Therefore $\text{pH} = 7.0$ was obtained as optimum status and was applied for another study for the mixture of heavy metals. Similar mechanism has also been presented in the same studies [14-17].

3.2. Effect of contact time

Time of equilibrium in other words, contact time between solution and adsorbent is the serious parameter to the treatment of wastewater from heavy metals. The effect of this parameter on the deletion of ions by 0.1 g KTL and 0.07 g ACKTL was tested in time intervals of 5-120 min, ($\text{pH} = 7.0$), 100 mg/l of metal ions, at $25 \text{ }^\circ\text{C}$. The ratio of eliminating of metal ions by KTL and ACKTL in this condition were indicated in Fig. 3.

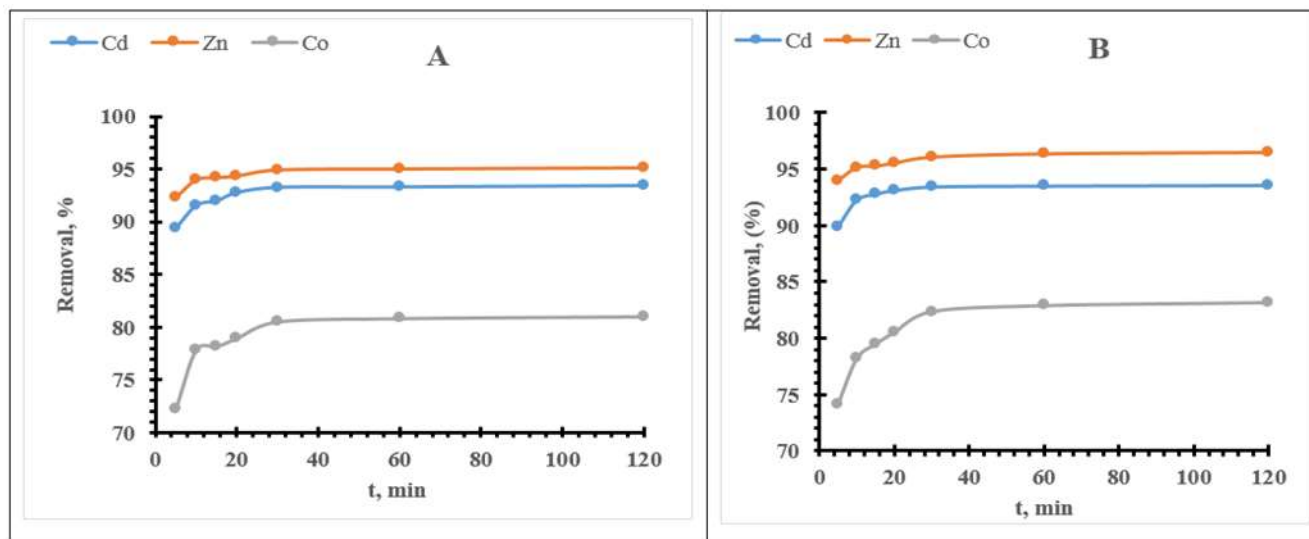


Fig. 3: The effect of contact time of heavy metals on removal through (A): KTL adsorption (B) ACKTL adsorption Conditions: adsorbate concentration. 100 mg L^{-1} , temp. 298.15 K and adsorbent mass. 0.1 g KTL and 0.07 g ACKTL , pH. 7.0 .

Visibly, the adsorption rates of tested metal ions by KTL and ACKTL, demonstrate that many adsorption sites readily available. Then, removal rates decreased, slowly and this process until the time of balance (30 minutes), for KTL and ACKTL, continued. This shown that time to adsorb metal ions in 30 minutes would be to reach saturation. This may be due to that initially; the concentration gradient was high, all adsorbent sites were empty. However, with the time, adsorption will be slower by the saturation of the adsorbent surface by metal cations, because of the repulsive force between adsorbed metal ions on the adsorbent surface and ions existent in solution, more sorption of metal ions is hard. Thus, the sorption rate decreased overtime until it reached equilibrium. Other researchers have reported similar results [16-20]. Accordingly, the optimal condition of contact time was selected as 30 min, for all the further studies with (KTL) and (ACKTL).

3.3. Effect of amount and type of adsorbent

The effect of adsorbent mass on the sorption of metals was investigated at contact by applying the various mass of KTL and ACKTL ($0.02\text{-}0.3 \text{ g}$) at the constant pH and contact time. Results shows that when the adsorbent doses are low, the percentage of removal is low, but is increased by increasing the amount. Concerning the balance, (optimization range) 1.0 g of KTL dose and 0.07

g of ACKTL were determined. This is due to the presence of a high level of vacancies and active sites at the beginning. This, causing increase percentage is eliminated, since the number of free accelerator sites available at a higher volume of KTL and ACKTL with increasing adsorbent mass, it results in better absorption. As the mass of adsorbent increases, the adsorbent sites existing to adsorb of metal ions are increased, and As a result, better adsorption happens [20-22].

3.4. Effect of temperature

The effect of changes of temperature on the adsorption of Cd^{2+} , Zn^{2+} , and Co^{2+} by KTL and ACKTL were studied by varying the temperature from 15.0 to $70.0 \text{ }^\circ\text{C}$ while keeping the other parameters, such as pH and metals concentration at a constant value. Figure 5 shows this effect on metal ions adsorption.

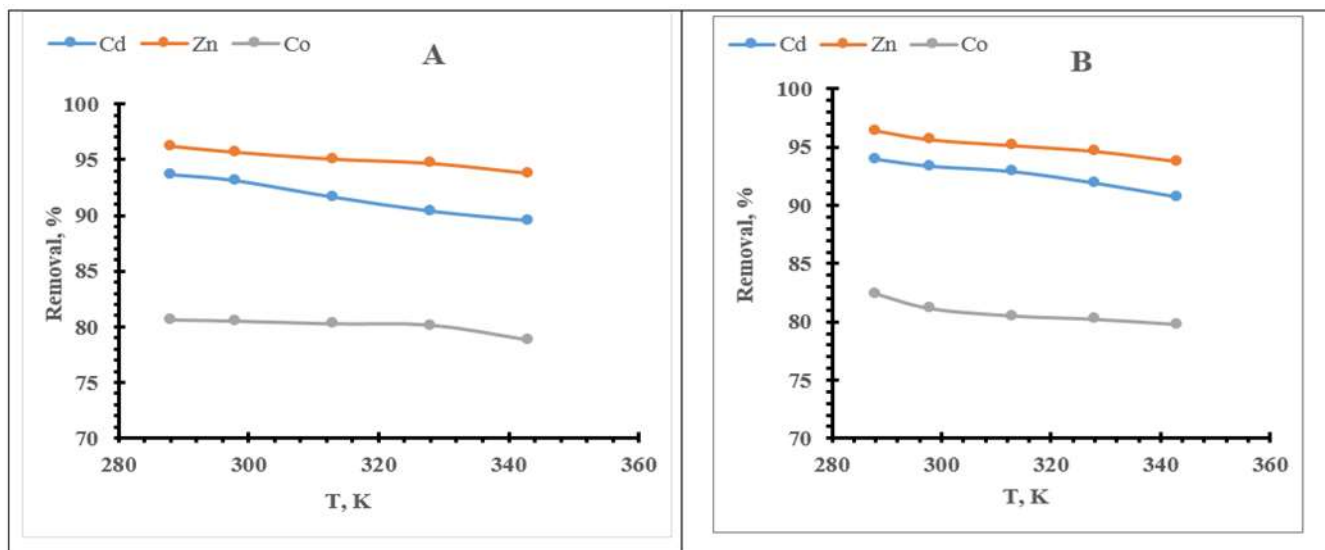


Fig. 4: The effect of temperature of heavy metals on removal through (A): KTL (B) ACKTL adsorption Conditions: pH =7.0, adsorbate concentration 100 mg L⁻¹ and adsorbent mass. 0.1 g KTL and 0.07 g ACKTL, contact time. 30 min.

This is mostly because of the decreased activity of the surface, proposing that the process of adsorption was exothermic. It was also observed that simultaneously with increasing temperature, physical forces (attractive)

Conditions: pH 7.0, temperature. 298.15 K and adsorbent mass. 0.1 g KTL and 0.07 g ACKTL, contact time. 30 min

Fig. 5: The effect of initial concentration of heavy metals on removal through (A): KTL adsorption (B) ACKTL adsorption between the surface of adsorbent and heavy metals, is weakened and thus the ratio of sorption decreases [28,29]. So, the adsorption of heavy metals may include mostly of a type of physical sorption. Other researchers have reported similar results [16,18,22].

3.5. Effect of initial Concentration

The effect of initial concentration on the adsorption of Cd²⁺, Zn²⁺, and Co²⁺ by KTL and ACKTL were studied at room temperature by varying the initial concentration of metal solution – adsorbent suspension from 10.0 to 100.0 ppm in Figure 5.

According to Figure 6, with increasing initial heavy metal ions concentration, the percentage of removal rises and, however then the specified level of initial heavy metal ions, an increase of the amount of removal lowers down. As considered, being a high initial concentration of metal accelerates the driving force and reduces the mass

transfer persistence. Similar results have also been reported [16,18,22].

3.6. Competitive behavior sorption of ions

In this section, the rate of sorption capacities of metals by both KTL and ACKTL in the mixed mode systems were tested, and the results were explained in Fig. 6.

Because of the chemical action and reaction among metal ion types in multi component mixtures, the part that has higher dependence will readily be adsorbed by existing adsorption sites. Electron affiliation of three

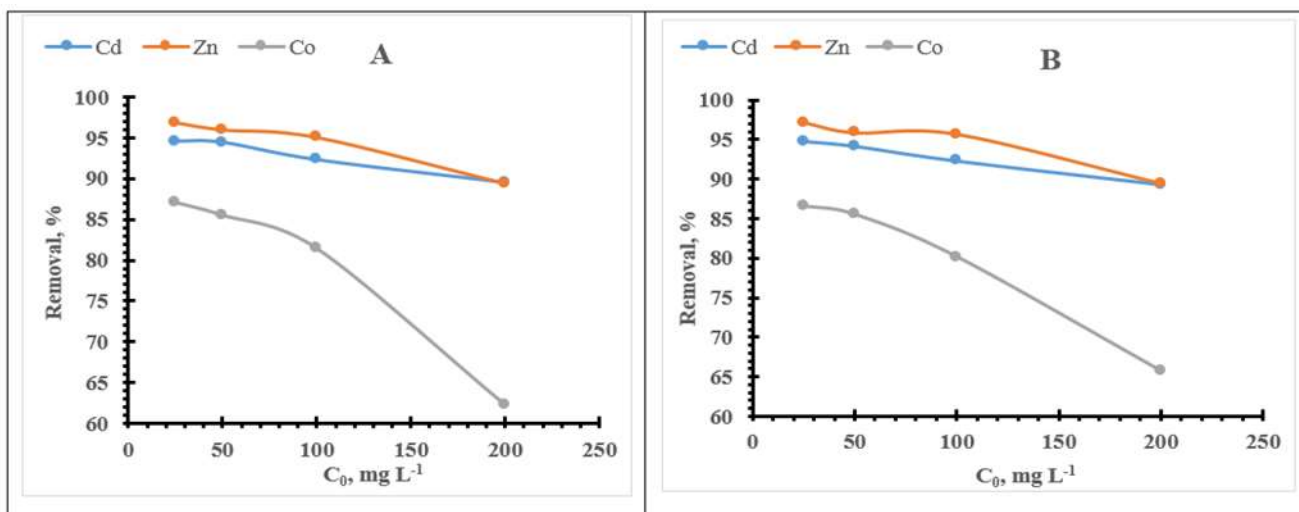


Fig. 5: The effect of initial concentration of heavy metals on removal through (A): KTL adsorption (B) ACKTL adsorption Conditions: pH 7.0, temperature, 298.15 K and adsorbent mass. 0.1 g KTL and 0.07 g ACKTL, contact time. 30 min

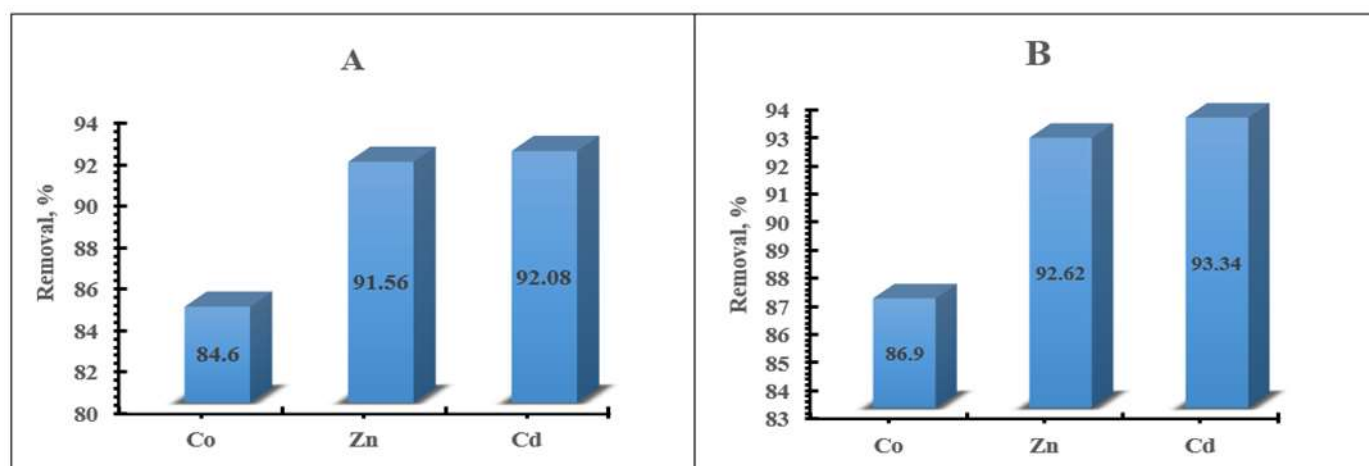


Fig. 6: The mixed mode of heavy metals removal through (A): KTL adsorption (B) ACKTL adsorption Conditions: pH 7.0, adsorbate concn 100 mg L⁻¹, temp. 298.15, and adsorbent mass. 0.1 g KTL and 0.07 g ACKTL, contact time. 30 min.

heavy metal ions that shows in Table. 1 follows the same order of adsorption as their amount of removal. The rate of removal for mixed mode system decreased in the order of Cd²⁺> Zn²⁺> Co²⁺ for KTL and ACKTL. This is maybe because of a various electrostatic attraction between negatively charged that on adsorption sites and metal ions, mostly linked to the hydrated ionic radius of the three studied metals. All these discoveries justify the most adsorption of Cd whereas for Zn and Co, most of these attributes were placed in Table 1.

Table 1. Physicochemical properties of Cd, Zn and Co divalent ions

Physicochemical property	Cd	Zn	Co
Effective ionic radius A ⁰	0.97	0.74	0.70
Electronegativity	1.69	1.65	1.88
Electron affinity	0.33	0.49	0.66
Atomic mass	112.41	65.41	58.93

3.6. Adsorption isotherms

Adsorption isotherm is a good gadget, to understanding the character of a surface parameters, an. However, an accurate choice of adsorption isotherm among the existing equations for different concentration ranges disclose an exact illustration of the surface. At light coating, Freundlich models describe the adsorption process, whereas the model that explains that at high-level concentrations monolayer coating is Langmuir [31]. The Temkin isotherm model obtains that the energy of adsorption with the surface coating because of some indirect adsorbate/adsorbate action and reaction, linearly decreases [31].

In this study, the sorption data to various sorption isotherms have been exposed, namely, Freundlich,

Langmuir, and Temkin models. The linear forms of isotherm models are described as:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{max}} + \frac{C_e}{q_{max}} \quad (\text{Eq. 3})$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (\text{Eq. 4})$$

$$q_e = B_T \ln K_T + B_T \ln C_e \quad (\text{Eq. 5})$$

The Langmuir isotherm is used to describe the observation of sorption phenomena. This isotherm to adsorption on all over homogenous surfaces with little interaction between adsorbed molecules applies. By attention to Langmuir adsorption isotherms and comparison with Langmuir equation, equilibrium constants of Langmuir isotherms can be obtained. The constants are shown in table 2.

The constant q_{max} implicates the capacity of adsorbent to adsorption (mg g^{-1}). This constant represents the monolayer coating of the adsorbent with adsorbate and should vary with temperature. According to the q_{max} (mg g^{-1}) parameter in this study, adsorption on KTL and ACKTL is produced following $\text{Zn}^{2+} > \text{Cd}^{2+} > \text{Co}^{2+}$. Evidently, the (q_{max}) of ACKTL applied in this study is considerable. Further ACKTL was more effective in the removal of Cd(II), Co(II) and Zn(II) ions than KTL. Therefore, ACKTL is selected to be a potential inexpensive adsorbent for eliminating of heavy metals from water and waste water.

3.7. Adsorption kinetics

Study of kinetic behavior of adsorption is one of the greatest parameters to predict the mechanism of the adsorption and to recognize the efficiency of the adsorbents. The removal process of Cd^{2+} , Zn^{2+} and Co^{2+} ions from an aqueous solution by adsorbent can be described by using examining the rate-controlling mechanism of the adsorption process such as chemical reaction, and finally kinetic models. In order to investigate and predict the adsorption rate the kinetic parameters are helpful, and which can be used as important information in designing of the adsorption operation. Different kinetic models involve pseudo-first-

order, pseudo-second-order, and intra particle diffusion model were applied for the experimental data to predict the adsorption kinetics of metal ions onto KTL and ACKTL was tested in this study. The correlation coefficient (R^2) was presented to compare the compatibility of 3 various models. The equations of the three kinetic models mentioned above are as follows: [9,11,22,31]:

$$\ln (q_1 - q_t) = \ln q_1 - k_1 t \quad (\text{Eq. 6})$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_2^2} + \frac{t}{q_2} \quad (\text{Eq. 7})$$

$$q_t = k_i t^{1/2} + C_i \quad (\text{Eq. 8})$$

The results showed a good adoption with the pseudo second-order equation. According to the linear plot, the correlation coefficient, R^2 , proposed a strong connection between the parameters and also illustrates that the adsorption process, follows pseudo-second-order kinetics (Table 3). This model is according to the rate-limiting steps parameter, probably a chemical sorption process such as valence forces by exchange or

Table 2: Langmuir, Freundlich and Temkin constants for equilibrium capacity studies (sorbate concentration 25-200 mg L⁻¹; m_{KTL}= 0.1 g, temp. 298.15 K, m_{ACKTL}= 0.07 g)

Meal ion	Langmuir				Freundlich			Temkin		
	Q _{max} mg g ⁻¹	K _L L mg ⁻¹	R _L * R _L * [*]	R ²	K _F	n	R ²	K _T L mg ⁻¹	B _T KJ mol ⁻¹	R ²
KTL										
Cd (II)	285.7	0.067	0.130	0.992	21.24	1.45	0.987	0.966	53.3	0.9698
Zn (II)	243.9	0.132	0.07	0.9981	30.89	1.65	0.9823	1.72	47.88	0.9762
Co (II)	166.7	0.049	0.169	0.9992	12.84	1.76	0.9583	0.530	33.19	0.9953
ACKTL										
Cd (II)	416.7	0.066	0.132	0.9932	30.36	1.45	0.9929	0.978	75.94	0.9618
Zn (II)	333.3	0.150	0.063	0.9901	45.22	1.69	0.9709	1.88	67.04	0.9713
Co (II)	250	0.043	0.189	0.9997	17.14	1.69	0.9711	0.485	52.481	0.9939

*: C₀=100 mg L⁻¹

sharing of electrons between the adsorbent and the adsorbate ³⁵. Other researchers have reported similar results [6,27-34].

Adsorption thermodynamics

In order to describe the effect of temperature on the thermodynamic parameters, standard free energy ΔG^0 , standard enthalpy ΔH^0 and standard entropy ΔS^0 were determined. The apparent equilibrium constant (K_c) of the adsorption is defined as:

$$K_c = q_e C_e^{-1} \tag{Eq. 9}$$

In this research, the change in the scale of adsorption in relation to temperature has been described according to thermodynamic factors. Thermodynamic factors were measured in the temperatures between 15-70 °C. The thermodynamic factors were deliberated by using the thermodynamic equations described below [26]:

$$\Delta G^0 = -RT \ln K_c \tag{Eq. 10}$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \tag{Eq. 11}$$

According to Eq. 11, parameter R (8.314 J mol⁻¹ K⁻¹), is the ideal gas constant, T (K), is the absolute temperature, and K_c is the constant of thermodynamic equilibrium which explained by q_e C_e⁻¹. ΔH^0 and ΔS^0

values were acquired from the slope and intercept of the plot ln K_c versus T⁻¹.

The thermodynamic parameters values for both the adsorbents were recorded in Table 4. According to the results, Negative values of ΔH^0 at various temperatures proposed that the process of adsorption had exothermic nature, thus expected the adsorption of ions with the increasing temperature, decreases. As well as negative values of ΔG^0 displayed that the adsorption of metal ions, under the conditions applied, was feasible and spontaneous. The positive values of entropy showed an increased randomness during metal ions adsorption similar results reported in case of interpretation kind reaction by some researchers [18,22,28,34].

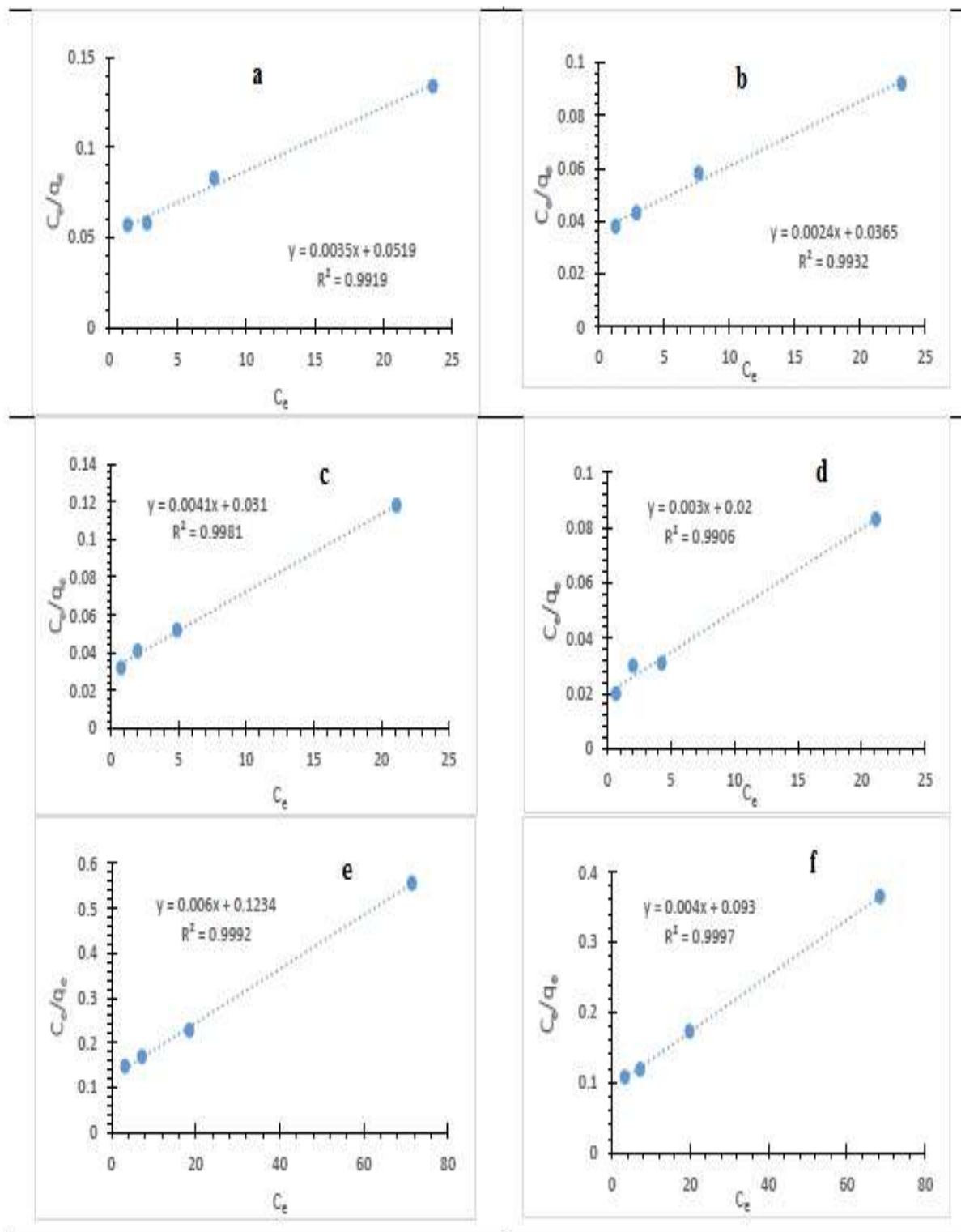


Fig. 7: Langmuir adsorption isotherms (a) Cadmium on KTL (b) Cadmium on ACKTL (c) Zinc on KTL (d) Zinc on ACKTL (e) Cobalt on KTL (f) Cobalt on ACKTL. Conditions: pH 7.0, adsorbate concn 100 mg L⁻¹, temp. 298.15 K, and adsorbent mass. 0.1 g KTL and 0.07 g ACKTL.

4. Conclusion

The experimental results indicate that removal of cadmium, Zinc, and cobalt by kiwi tree leaf and activated kiwi tree leaf adsorption from aqueous solutions are effective. The potential of the kiwi tree leaf and activated

kiwi tree leaf as a modern adsorbent to the elimination of Cd²⁺, Zn²⁺, and Co²⁺, ions from Lab samples were performed. In a series of batch experiments, the effects of sensitive factors on the deletion were reviewed and optimized. In optimal status to eliminate of Cd²⁺, Zn²⁺,

and Co^{2+} , by KTL and ACKTL, contact time and volume of adsorbent were collected (30 min and 0.1 g), and (30 min and 0.07 g), respectively, at pH=7.0 KTL and ACKTL and 25°C. The results obtained from adsorption isotherms were well fitted by the Langmuir isotherm model. In this study, regarding kinetic, pseudo-second-order model explained the adsorptions kinetics, Also in the thermodynamic review, the results showed that this process for 3 metals that was examined was spontaneous and exothermic. According to results, KTL and ACKTL can be presented for treatment and control of sewages from heavy metals.

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