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Modelling and Simulation for the use of Natural Waste to Purified Contaminated Heavy Metals

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Abstract

The possibility of recovering one of the famous heavy metal ions, divalent copper, from contaminated aqueous solutions (which simulates wastewater) was studied in this study. The removal method was adsorption technique using a laboratory batch-mode unit, while the used tea leaves were the adsorption media. The adsorption process was performed under various operating conditions and ranges that simulate the natural environmental conditions to determine the ideal values that achieve the maximum removal of copper ions. The acquired results demonstrated that the maximum remediation efficiency was 85%, which was achieved at treatment time, shaking speed, initial concentration, temperature, acid function, and adsorption dose of 90 min, 250 rpm, 70 ppm, $25^oC, 4, 4.5g$, respectively. The values of the thermodynamic properties demonstrated that adsorption is spontaneous, exothermic and has negative entropy, while adsorption follows Langmuir's model and the second pseudo-model according to the isotherm and kinetic studies, respectively. To conduct the Zero Residues Level concept, the loaded used tea leaves were prepared to study it effect as a simple type of rodenticide by applying it to Sprague Dawley rats. The results of the test show that the effectiveness of utilizing the residues as rodenticide and the Half lethal dose LD_{50} of the proposed rodenticide were identical to those mentioned in the literature. Based on these results, the current study sheds light on the possibility of converting used tea leaves from harmful solid waste to an environmentally friendly substance using it as an effective adsorbent medium for the treatment of water polluted with heavy metals.

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1. Introduction

The great growth of the world's population, industrial and agricultural progress in the past century led to the pollution of all elements of the environment (water, air, soil and space) and the depletion of natural wealth sources [1]. In addition, the failure to follow appropriate methods in treating the sources of pollution, and the lack of proper planning have. The problems of pollutant accumulation and depletion of natural resources can be considered among the most important major environmental issues at the present time for developed and developing countries alike [2]. Pollution refers the interference of human activities with the resources and energies of the environment, such that this interference endangers human health or natural resources, or puts them in a situation where they are likely to be directly or indirectly exposed to danger [3]. Pollution is defined as the presence of foreign substances in any component of the environment, which renders it unsuitable for use

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or limits its use [4]. Pollutants are defined as substances, microbes or energies that harm humans or living organisms in general and cause diseases or lead to destruction [5]. In the past, natural ecosystems were able to assimilation of the pollutants, whether in the soil, water, or air, because of the small quantities and low concentrations of pollutants, and the absence of difficult or non-degradable foreign substances [6]. Today, natural ecosystems are unable to assimilate these pollutants, and the influence of these contaminants depends on the degree of their concentration in the environment, their chemical, physical and biological characteristics, and the nature of their interaction with each other and with the surrounding environment [4]. Water pollution resulting from industrial and human activities is considered to be one of the main issues in the world, as it is the main cause of 80% of diseases worldwide [7]. The reports issued by WHO show that the safe drinking water does not reach more than 10^9 inhabitants worldwide, and most of them are from poor and developing third-world countries [8, 9]. It should be noted that thousands of chemicals are released into the environment in general and into water sources without any treatment on a daily basis [10]. These chemicals (even drugs, medicines or pharmaceutical products in high concentrations) will be affected the human body [11]. Among these chemicals, heavy metals are among the most dangerous and harmful, even if found in small amounts, because they accumulate inside living tissues [12]. Some heavy metals such as iron, copper and zinc are directly related to the vital activities of living organisms, while others such as lead, cadmium and mercury do not play any role in these activities and are therefore classified as toxic elements [13]. However at high concentrations (exceeding the permissible or recommended limit), all heavy metals are toxic to living organisms, regardless of which they are necessary [14]. There are many ways to recover heavy metals from contaminated water, including membrane separation, electrodialysis, ion exchange, precipitation, liquid extraction and adsorption [15]. Adsorption method is an effective and excellent technique in removing heavy metals and other pollutants. There are many kinds of pollutants remediate by adsorption such as dyes [16], radioactive materials, inorganic toxins and others. The ability may be attributed to the high surface area provided by various adsorption media such as activated carbon [17], alumina [18] and silica [19]. However, the high cost of these media and the loss of some of their mass in each regeneration step prompted researchers to use alternative materials of appropriate efficiency, available, cheap, and at the same time, without toxicity [20]. Among these materials that meet the above conditions are agricultural wastes [21]. Agricultural residues are available in large quantities throughout the year as a result of the human consumption of agricultural crops and can be utilize by different methods, such as producing beneficial chemicals [22], fertilizers [23], and [24], and addition of material to concrete [25] and synthesis of nano-materials [16] because of its unique properties, either naturally or gained after treatment [26]. They are low-cost and not invaluable materials with an appropriate surface area and have proven their efficiency in removing many pollutants from water [27], soil [28] and petroleum [29], and non-toxic substances [30]. In addition, its accumulation (from any source) leads to the pollution of various elements in the environment by raising the vital requirement of water or being a medium for the growth of insects harmful to humans [31]. As a result of the foregoing, researchers studied the ability of this waste to treat polluted water including rice husks [32], banana peels [33], and orange peels [34], pomegranate peels [1], watermelon peels [35], lemon peels [36], egg shells [37], algae [38], water hyacinth [39] among others. Tea leaves are one of the most common types of agricultural waste. Tea is consumed worldwide in large quantities daily. As a result of this consumption, very large quantities of tea leaves are accumulated, which must be disposed of in economical, safe and environmentally friendly ways [40]. This paper studies the adsorption possibility of copper ions (Cu^{+2}) from polluted water by using tea leaves as an available, cheap and non-toxic adsorbent media in a laboratory batch-mode unit. The adsorption procedure was performed using various design parameters to determine the optimum values that gave the highest adsorption efficiency. In addition, we studied a suitable method to dispose the toxic residues using a beneficial route. Thus, this study presents the concept of safe, efficient and economical simultaneous disposal of more than one type of environmental pollutants at the same time.

2. Material and methods

2.1. Adsorbent media preparation

The raw media of adsorption i.e., the used tea leaves were collected from the domestic use as a batch. Each collected batch was washed with two types of water. The first one was performed with excess tap water to remove any dirt or dust that may be stuck. While the second one was conducted by double distilled water to neutralize the adsorption media. The washed leaves were dried for 48 h in a drying oven at 50^oC to avert charred. They were then ground in a domestic mill and sieved to obtain fine powder. Powder that passed through a 35 mesh sieve was selected as the adsorption medium. The prepared powder was stored in opaque glass containers in a cool dry place until use. The used tea leaves were collected, washed and dried in continuous batches. After ending all things, the media was first kept in opaque glass containers (i.e., amber glass jar with tight lid). These jars are put in a dark drawer at room temperature to prevent light and humidity.

2.2. Stock Solution

To avoid competition between copper and other elements may be found in wastewater, adsorption experiments of copper ions were conducted using laboratory prepared solutions with predetermined concentrations. Stock solution of divalent copper ions (1000 ppm) was prepared by dissolving 3.81 g of blue-colored copper (II) nitrate trihydrate salt of $Cu(NO_3)_2.3H_2O$ chemical formula and 241.6 g/mol molar mass. A 99.5% purity salt was purchased from IndiaMART.A stock solution was prepared using a magnetic stirrer under laboratory conditions, which are atmospheric pressure and temperature of $25-28\pm1^{\circ}C$

2.3. Calibration Curve

By Atomic Absorption Spectroscopy (AAS) device, the concentration of Cu^{+2} ions are detecting. The detection was achieved by preparing calibration curve for copper ions at a wavelength of 372.0 nm. The process was carried out by preparing a series of known concentrations of copper ions and accurately determining the absorbance for each concentration. The concentration was plotted against the absorbance so that the calibration curve was ready in its final form. Calibration curve experiments were conducted in triplicate for each concentration and the average between three readings was taken to reduce the error. The calibration curve of Cu^{+2} ions is explained via Figure 1.

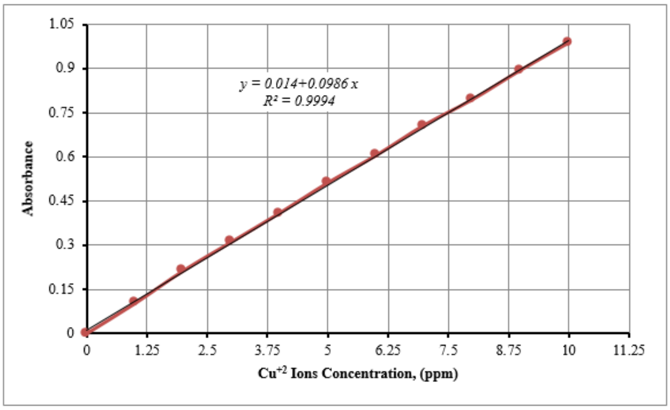

Figure 1. Calibration curve of Cu^{+2} ions using AAS

2.4. Adsorption Experiments

Adsorption experiments of divalent copper ions were conducted using used tea leaves in a batch type adsorption unit consisting of a water bath shaker under various operating parameters. The acidity function, initial concentration of Cu^{+2} ions, shaking speed, adsorbent dose, treatment time and temperature represented the operating conditions of the adsorption process and their values ranged between $1-8$, $1-100$ ppm, $100-350$ rpm, $0.5-5.0$ g, $10-120$ min, $25-50^{o}C$, respectively. The pH was adjusted using a pH meter with 1 M solutions of HCl and NaOH. Glass beakers (100 ml capacity glass) of a specific concentration and pH were placed in a water bath shaker, and the device was turned on after setting the temperature and shaking speed. After the end of the specified time for the experiment, the sample was purified using filter paper and tested using an AAS device. The remaining concentration of unadsorbed Cu was determined from the calibration curve. The percentage of copper ions adsorption and the adsorption capacity are calculated using equations 1 and 2 respectively

$$\%R = 1 - \left(\frac{C_f}{C_i}\right), \tag{1}$$

$$q = \frac{V}{m}\left(C_i - C_f\right), \tag{2}$$

where $\%R$ is the percentage of adsorption, C_f and C_i are the final and initial concentrations of divalent copper ions (ppm), respectively, V is the volume (l), q is the capacity of adsorption (mg/g), m: the adsorbent dose used (g).

2.5. Isothermal Study

The dispersion of copper ions between the solution and the adsorption media can be explained by using theoretical models after the system reaches the equilibrium state. There are many models that explain this relationship, the most important of which are the Langmuir and Freundlich models.

2.6. Langmuir Model

This model was introduced by the American chemist Langmuir at 1916 and it is assumed that the adsorption occurs on one layer only, the energy is distributed in it evenly, and that the number of adsorption sites is specific and identical. When the layer is saturated, the maximum value of adsorption is achieved, in addition to the actuality that the density of the adsorption layer is determined by the same thickness of the particle. Equation 3 symbolizes the general formula of the Langmuir model, Equation 4 symbolizes the linear mathematical formula of this model, and Equation 5 describes the formula for the separation factor R_L by which the type of adsorption is determined.

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \tag{3}$$

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L} \frac{1}{C_e} \frac{1}{q_{max}} \tag{4}$$

Where: q_e: equilibrium adsorption capacity (mg/g) ; K_L: binding sites constant of Langmuir equation, (l/mg); q_{max}: maximum adsorption capacity (mg/g); and C_e: equilibrium adsorbed concentration (mg/l)

$$R_L = \frac{1}{1 + K_L C_e} \tag{5}$$

The value of R_L gives a good indication of the nature and form of adsorption, if the value of the separation factor is higher than 1, the adsorption is not preferred, and linear adsorption if its value is 1. The adsorption is preferred if $0 < R_L < 1$ value, and adsorption is irreversible if $R_L value$ is 0. By plotting the graph between $1/q_e$ and $1/C_e$, a linear relationship is resulted through which the Langmuir constants K_L and q_{max} are calculated.

2.7. Freundlich Model

A model presented by the German scientist Freundlich in 1909 assumes that adsorption gets multiple and heterogeneous layers and adsorption sites can be unsaturated as well as irregular energy levels. Equations 6 and 7 describe the general and linear form of the Freundlich model, respectively

$$q_e = K_F {C_e}^{\frac{1}{n}} \tag{6}$$

$$lnq_e = lnK_F \frac{1}{n} lnC_e \tag{7}$$

Where: K_F: constant of Freundlich equation $[(mg/g).(l/mg)^{1/n}]$, n: adsorption intensity $(-)$.

2.8. *Kinetic Study*

2.8.1. *Pseudo first order model (PFO)*

The assumption of this model represented by the adsorption time rate is of the first order as a result of obtaining adsorption on only one layer. Equations 8 and 9 describe the general and linear form of this model, respectively

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{8}$$

Where: k_1: first order rate constant (s^{-1}); q_e: equilibrium adsorption capacity (mg/g); and q_t amount adsorbed onto adsorbent at any time t (mg/g)

$$ln(q_e - q_t) = lnq_e - k_1 t \tag{9}$$

The relationship shown in Equation 10 can be represented mathematically as a straight line by plotting $ln(q_e - q_t)$ against t its slope equilibrium constant k_1.

2.8.2. *Pseudo second order model (PSO)*

The most important hypothesis of this model is that the adsorption rate time is directly proportional to the number of active sites on the adsorption surface, and it is the model closest to describing adsorption kinetics when physical or chemical interactions occur between the adsorbent and the adsorbent. Equation 10 shows the general form and Equation 11 describes the linear form of this model.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{10}$$

Where: q_e: is the equilibrium adsorption capacity (mg/g), q_t: is the adsorption capacity at any time (mg/g), t : is the time(s) and (k_2): is the second order rate constants ($g.mg^{-1}.s^{-1}$).

$$\frac{1}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{1}{q_e} t \tag{11}$$

The PSO model constants can be found by plotting the relationship between t/q_t with t, which is the equation of a straight line with intercept and slope $1/(k_2 {q_e}^2)$ and $1/q_e$ respectively.

3. Results and discussions

A batch-mode unit was used to study the influence of some design factors, such as pH, shaking speed, temperature, treatment time of the adsorption unit, initial concentration of divalent copper ions, and adsorbent dose (used tea leaves < 700 μm) on the copper ion removal efficiency. The copper ions concentration in the treated simulated aqueous solution after treatment was detected using an AAS device and calibration curve, and then the percentage and the capacity of the adsorption were calculated.

3.1. *Influence of treatment time*

Treatment time is significant design factors that have been studied in experiments to remediate heavy metals from polluted media, owing to the importance of this factor in the unit accessing the state of equilibrium, in which the time affects the adsorption process, and any subsequent period does not affect the adsorption of pollutants. The effect of treatment time was studied in the current study within a range of 10 − 120 minutes, based on similar literature [18].The results of studying of this operating factor indicated that the maximum recovering efficiency of copper ions was achieved at 90 minutes, and this is obviously from Figure 2. At the beginning of the adsorption, the ability of used tea leaves (the adsorption media) to adsorb pollutant ions is high because they are virgin and do not contain any kind of competition for the active sites; therefore, adsorption is the maximum possible. Over time, the heavy metal ions begin to accumulate on the adsorbent surface and are linked to functional groups with diverse bonds, which restricts the arrival of new ions to the active sites; thus the adsorption decreases gradually until the system reaches the equilibrium state. After equilibrium is achieved, any increase in the treatment time on the adsorption efficiency is not beneficial, and the adsorption capacity is fixed while other variables remain constant at the optimum values. These results have been indicated by [40] in their conclusions.

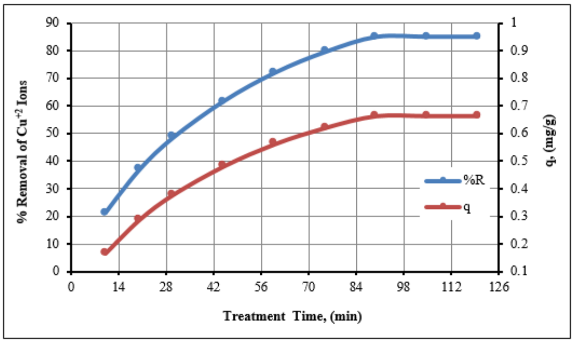

Figure 2. Influence of treatment time on removal of Cu^{+2} ions

3.2. *Influence of initial concentration*

The effect of varying the concentration of Cu^{+2} ions on the removal capacity is shown in Figure 3. It is reported -from the figure- that the highest adsorption efficiency was at the lowest initial concentration. At the same time, the adsorption concentration increased until its maximum value was reached and then remained constant. Studying the influence of the initial concentration of Cu^{+2} ion is significant for its effect on the ability of the material to be adsorbed; the higher the concentration of the initial pollutant, the lower the adsorption ability according to the constant value of the surface area of the adsorption media, and consequently, the limited effective sites of the adsorption media. The initial concentration increase indicates an increase in the mass of a heavy element in the same volume unit, and this means an increase in competition between a large number of molecules for the same number of active sites that are filled with a specified number of molecules. The higher the initial concentration, the greater the number of unadsorbed molecules in the solution that remain free, and thus, the adsorption percentage removal decreases. The results of the current study were confirmed by similar results similar on investigate the adsorption of cadmium by watermelon rinds conducted by [32].

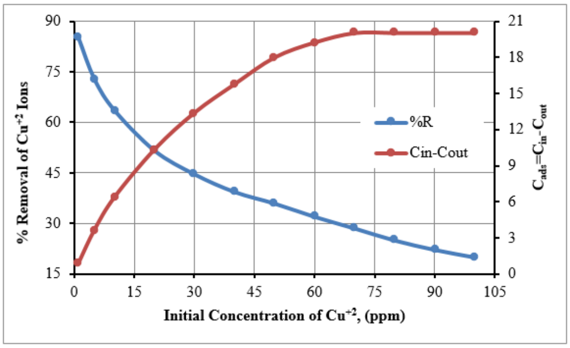

Figure 3. initial concentration influence on Cu^{+2} removal

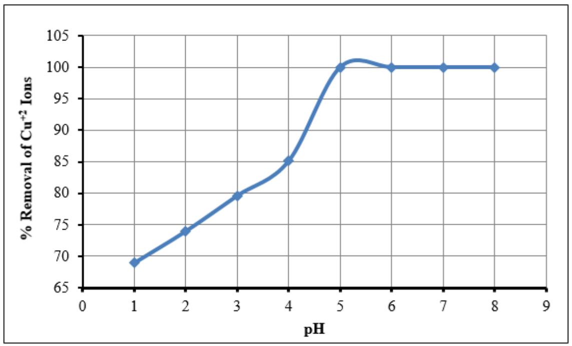

Figure 4. Effect of pH on Cu^{+2} removal

3.3. *Influence of pH*

pH is one of the significant factors affecting the adsorption process of any kind of material in general, and heavy metals in particular, as the positive hydrogen ions (H^+) are considered a competition for the heavy metal ions on the adsorption site owing to the similarity of the charge. On the other hand, hydroxide ions (OH^-) with a negative charge can precipitate positive heavy metal ions in the form of sparingly soluble hydroxide salts if their concentration is high in the solution. The influence of acidity on the efficiency of Cu^{+2} ions adsorption was studied within a range of 1 to 8, while other factors remained constant at their optimum values. The relationship between adsorption efficiency and pH is illustrated in Figure 4. It is noted from the figure that the highest adsorption efficiency for copper ions was achieved at a pH value of 4, which was 85%. At low pH values, the adsorption capacity decreases due to the rivalry of H^+ with Cu^{+2} ions on the adsorption sites, which decreases with increasing pH value. As the value of the acid function increases, the hydroxide ions increase and the hydrogen ions decrease, which reduces competition for active sites. This situation continues until the maximum value of efficiency is reached. Subsequently, the removal efficiency will increase, but due to precipitation in the form of metal hydroxide and not through adsorption on the active sites. This was observed from the precipitation of a bluish-green solid at the bottom of the flask after the acidity function exceeded the value of 4. Although the removal percentage reached its ultimate value, 4 was considered to be the optimal value of the acidity function for the adsorption of copper ions. Both [21, 38] indicated results similar to the acidity function set results obtained in this study.

3.4. *Influence of shaking speed*

The effect of changing the adsorption removal due to varying the shaking speed of the polluted solution by keeping the remaining operational factors at the optimum values is shown in Figure 5. It is noted from the above figure that increasing the shaking speed leads to an increase in the ability of the used tea leaves to steadily remove heavy metal steadily between 100 – 250 rpm. Increasing the shaking speed increases the chance of ions arriving at active sites by increasing the mass transfer rate or destroying the film layer growing on the surface of the used tea leaves, which reduces the resistance that occurs to the transfer of copper ions. After reaching the maximum value at 250 rpm, the adsorption efficiency did not change. This is because the adsorbent reaches the equilibrium state or the rate of collisions between the used tea leaves increases. Thus, the Cu^{+2} ions are adsorbed and then return to the solution after their liberation from the surface of the adsorbent owing to collisions by a process called desorption. In general, the results showed that the best adsorption efficiency for copper ions was recorded at a shaking speed of 250 rpm. These results that we got are compatible with the conclusion of Ghulam et. al. [17].

3.5. *Influence of Adsorbent Dose*

Within a range of 0.5 – 5.0 g, the ability of used tea leaves as an adsorbent media to remove copper ions was investigated, and the effect recorded from practical experiments to study this operating factor was represented in Figure 6. The obtained results indicate that there is a clear direct relationship between the amount of adsorbent material and the adsorption capacity between 0.5 – 4.5 g. The reason for this result is that an increase in the amount of adsorbent means the increase in the surface area and, in turn, provides more active sites. Thus, the chance of adsorption of a larger number of heavy metal molecules will increase and thus reduce their concentration in the solution, thus increasing the adsorption efficiency. The removal continued to increase from 0.5 g of used tea leaves to 4.5 g, and then the removal efficiency remained unchanged. This stability can be explained by the fact that an rising of the amount of material leads to the formation of layers of the material on top of each other, even if there is a sufficient surface area and additional effective sites will remain vacant because there is an obstacle that prevents the arrival of heavy metal ions to the adsorption sites. Therefore, the optimal adsorbent dose for the adsorption of copper is 4.5 g, the rest of the variables remaining constant at the optimum values. Comparable conclusions have been reported by [35].

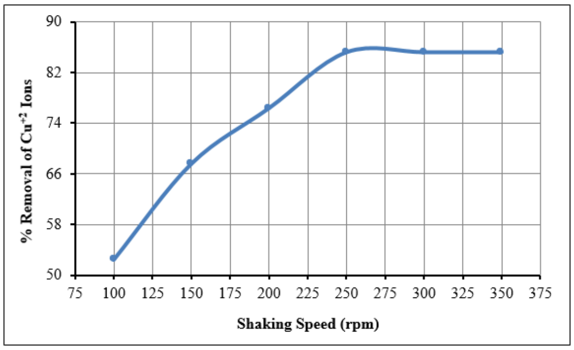

Figure 5. Effect of shaking speed on Cu^{+2} removal

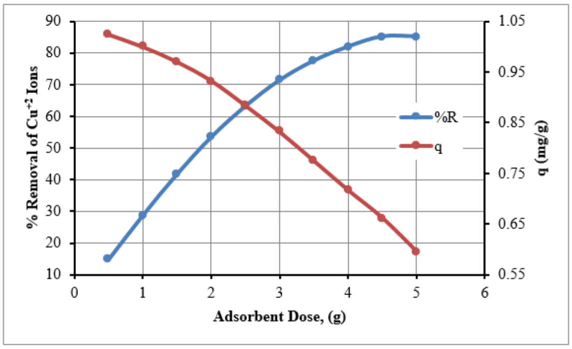

Figure 6. Influence of adsorbent dose on Cu^{+2} removal

3.6. *Influence of Temperature*

It is noted from Figure 7 that the temperature factor owning an adverse influence on the adsorption removal of Cu^{+2} ions using the used tea leaves, and that the highest efficiency was achieved at 25^oC, and then the efficiency begins to decrease with increasing temperature until it reaches its lowest value at 50^oC. Temperature plays a vital role in the results of Cu^{+2} ions adsorption, as its increase leads to raise in the kinetic energy of the Cu^{+2} ions on the surface of used tea leaves, making it able to disengage with it and return to the solution again. Meanwhile, when the temperature arises, the material breaks down into smaller particles after adsorption, which makes the copper ions free to move in the solution again. This is what was observed when adsorption was tested at 45 and 50^OC. Same results are recorded by [15]. The results of isotherm study demonstrated that the adsorption of copper ions utilizing the used tea leaves is subject to the Langmuir model clearly with higher correlation coefficient (0.999), while the results are identical with the Freundlich model with a correlation coefficient of 0.97. This congruence with the Langmuir model can be attributed to the small size of the small adsorption particles ($< 700\ \mu m$) which provide approximately one layer for adsorption. Due to this tiny size, the energy distribution can be homogeneous and the thickness of the layer is the same as the thickness of the particle. It is also shown that the adsorption is preferred type due to the $R_L value$. Figures 8 and 9 and Table 1 show the values of the model constants used in describing the isothermal study.

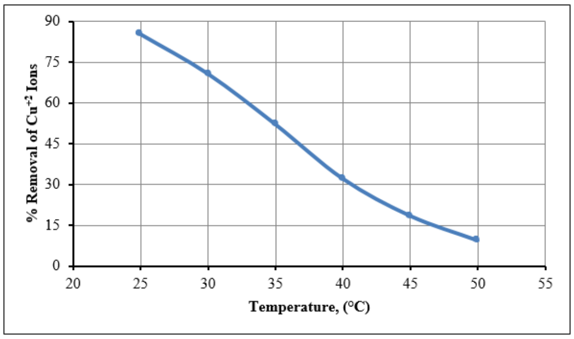

Figure 7. Influence of temperature on Cu^{+2} removal

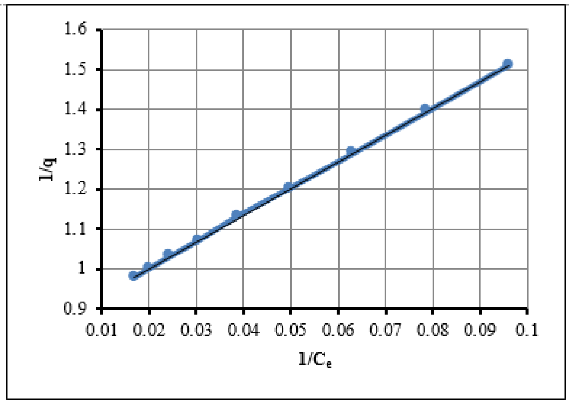

Figure 8. Langmuir

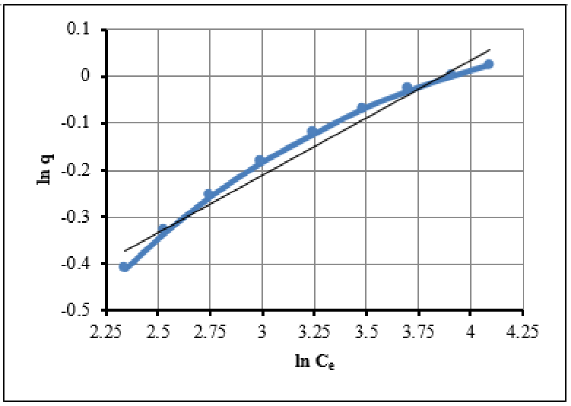

Figure 9. Freundlich

Table 1. The values of the model constants used in describing the isothermal models used in this study

Langmuir			Freundlich	
K_L	q_{max}	R_L	n	K_F
0.1295	1.1537	0.1	4.0733	0.388

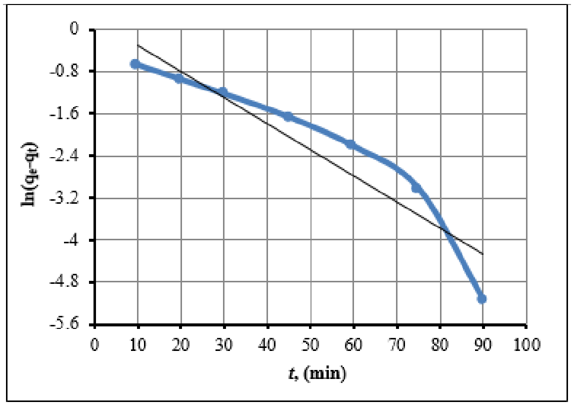

Figure 10. PFO model

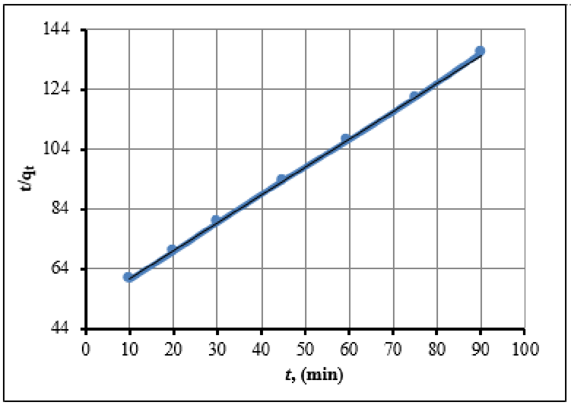

Figure 11. PSO model

Figures 10 and 11 explain the obtained results of the kinetic study. It is noted that the adsorption is subject to the PSO model with a high R^2 that is close to 1, while the other model is far from representing the adsorption results due to the low correlation coefficient. This result can be clarified according the number of active sites that the PSO model takes into account, as the optimum dose of material determines the possibility of reaching the adsorption to the maximum efficiency. It is assumed that adsorption obtains a single homogeneous layer and this is the same hypothesis of the PSO model. The constants values of the kinetic study models used in this study show in Table 2.

Table 2. The values of the model constants used in describing the isothermal models used in this study

PFO model		PSO model	
k_1	q_e	k_2	q_e
0.0496	1.2182	0.01712	1.068

3.7. Thermodynamic Study

In any adsorption process, this study is very important as it detects the thermodynamic functions of the adsorption system through which the spontaneity is combined through the values of the free energy of pressure ($\triangle\ G$) in addition to the values of enthalpy ($\triangle\ H$) and entropy ($\triangle\ S$) changes that show the state of heat emission and the randomness of the adsorption process. These thermodynamic functions can be calculated by finding the equilibrium constant values via Equation 11, and then applying the van't Hoff equation described by

$$k_{ad} = \frac{q_e}{C_e} \tag{12}$$

By plotting the relationship between k_{ad} and $1/T$, it is possible to calculate $\triangle\ H$ from the slope and $\triangle\ S$ from the intercept, from which the compressive energy $\triangle\ G$ of the adsorption system can be determined through Equations 13 and 14 below

$$lnk_{ad} = -\frac{\triangle\ H}{R}\frac{1}{T} + \frac{\triangle S}{R} \tag{13}$$

$$\triangle\ G = \triangle\ H - T\ \triangle\ S \tag{14}$$

Where: k_{ad}: thermodynamic equilibrium coefficient of adsorption (dimensionless); $\triangle H$: enthalpy variation (J/mol) ; R: universal gas constant $(8.3144 J/mol.K)$ and $\triangle\ S$: entropy variation $(J/mol.K)$; T: absolute temperature (K).
Figure 12 and Table 3 show the numbers of thermodynamic functions for adsorption of copper ions on the surface of the adsorbed tea leaves that were studied in this study. It is cleared from the Figure 12 that the values of the equilibrium constant decrease with increasing temperature and the reason for this is that the adsorption efficiency decreases with increasing temperature (as shown previously). As a result, the concentration of copper ions will increase in the solution as a result of the ions returning to it again, in addition to adsorption capacity decreasing in the substance It is also noted from the enthalpy values that adsorption is of the chemical type due to the number of enthalpy, which means that the link between the adsorbent material and the surface of the used tea leaves is the result of chemical adsorption that lead to the generation of a new type of bonds that require high energy to break. This also corresponds to the behavior of temperature (referred to above in paragraph *(Influence of Temperature)*. As for the entropy function, it is noted that it is a negative value, which means that the copper ions are more uniform in the solution compared to their presence on the adsorbent media surface. This result is also logical due to the

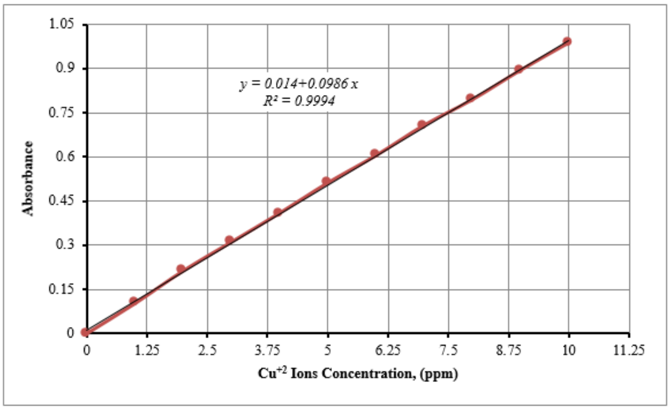

Figure 12. Temperature effect on thermodynamic equilibrium coefficient

Table 3. The values of thermodynamic functions of this study

Temperature, (^{O}C)	Entropy varying $\triangle S$ (J/mol.K)	Enthalpy varying $\triangle H$ (J/mol)	Gibbs Free Energy $\triangle G$ (kJ/mol)
25	-364.2898652	-127726.775	-19.11375145
30			-17.29230212
35			-15.47085279
40			-13.64940347
45			-11.82795414
50			-10.00650482

actuality that rising the temperature leads to lower the adsorption efficiency, which means that the greater number of ions will be in the solution the higher the temperature. The obtained results indicate that the adsorption is spontaneous under the studied operational conditions, due to the negative sign of the values of the free energy of compression, which decreases as the temperature of the adsorption system increases. This proves that the adsorption process is self-occurring and does not need any external energy to complete and that low temperature is better to achieve maximum efficiency.

3.8. *Zero Residues Level (ZRL) Concept Application*

After the process of treating the contaminated aqueous solutions at different design conditions, the used tea leaves loaded with the adsorbed divalent copper ions were collected and classified according to the amount of the adsorbed heavy metal and an attempt was made to dispose of them in a safe, useful, low-cost and eco-friendly method. The use of contaminated leaves residue as a rodenticide was tested by feeding it to white Sprague Dawley rats of the scientific name *Rattus norvegicus domestica*. Use the same procedure used by [35] in preparing and preamble the animal cages, as well as the same feeding method. After the end of the laboratory experiments, the half lethal dose (LD_{50}) was calculated and compared with the dose mentioned in the literature and it was within the known range. Table 4 shows the half lethal dose (LD_{50}) for rats feeding normal and contaminated used tea leaves. Although copper is one of the moderate toxic heavy metals compared to other elements such as lead, chromium, mercury, antimony and others, however, treating laboratory rats with used tea leaves loaded with this metal showed that it has effects that range in severity with increasing dose, leading to the death of rats [24]. The descent of albumin and protein materials with urine, diarrhea, and gradual turbulent skin infections were the corporeal changes that occurred in rats during the period of treatment with pomegranate peels loaded with bismuth metal [14]. As for the anatomical study of laboratory rat's samples that died due to feeding the used tea leaves loaded with copper, it was found that they suffered from kidney atrophy and that the degree of this atrophy was increasing with increasing the treated dose [11].

Table 4. LD_{50} Dose of proposed rodenticide

Group	Type of Feeding	LD_{50} (mg/kg)		
		Male	Female	Standard
Control group	Provender of Rats (Ordinary)	No-mortality	No-mortality	-
G_1	Provender of Rats +used tea leaves	No-mortality	No-mortality	-
G_2	Provender of Rats + Cu^{+2}-used tea leaves	41.7301	38.0689	37-42 (ATSDR, [41]

4. Conclusion

In this research, the efficiency of natural adsorbent ı.e. used tea leaves was tested to remove divalent copper ions from contaminated simulated solutions in a unit of batch-mode and at various design parameters. This available and low-cost substance has proven highly efficient in treating polluted water with different concentrations ranging from $1 - 100$ parts per million, with an adsorption rate of 85%. The study showed that the adsorption efficiency rising with rising pH, adsorbent quantity, shaking speed and treatment time, while it decreases with rising initial concentration and temperature. The obtained results showed that the optimal conditions to achieve the highest removal percentage were pH of 4, adsorbent dose of $4.5g$, treatment time of 90 minutes, shaking speed of $350rpm$, initial concentration of $70ppm$ and temperature of $25^{o}C$. The isothermal study showed that the adsorption follows the Langmuir model with a correlation coefficient very close to 1, while the adsorption was spontaneous and of the PSO model according to the correlation coefficient obtained according to the results of the kinetic and thermodynamic study.

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