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Adsorption of copper ions from water by different types of natural seed materials

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ABSTRACT

Different plant seeds of okra, pumpkin, grape, and squash available locally were used as adsorbents for the removal of copper ions from their aqueous solutions. Batch sorption experiments were carried out to investigate the seeds' capability to remove copper ions. Grape seeds showed higher uptake compared with other adsorbents. Experimental results for grape seeds showed that an increase in the initial pH, temperature, or initial adsorbate concentration influenced copper uptake positively. However, copper ion uptake decreased with increasing adsorbent concentration. The optimum pH range for metals removal was 3–4. Addition of sodium or potassium salts to the metal solution resulted in greater metal removal. The copper equilibrium was attained after 3 h contact time. The uptake of Cu^{+2} were found to be reliable on both the Freundlich and Langmuir isotherms. The results of work will urge the public to use these tested seeds in their diet for possible removal of heavy metals that contaminate either food or drinking water.

Keywords: Seeds; Copper; Adsorption; Activation

1. Introduction

It is well known that toxic heavy metals discharged into the environment as industrial wastes are considered dangerous because of their potential toxic effects on soil, humans, animals, plants, and aquatic life. The latter effect (their continuous discharge) results in the accumulation of phenol and toxic metals in food structures, which makes their concentrations more appearing in human bodies than in water and air. Accordingly, they can poison humans and animals and can cause various diseases and disorders like kidney damage, miscarriages and

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subtle abortions, disorders of nervous system, and brain damage. Pb^{+2}, Cu^{+2}, Fe^{+3}, and Cr^{+3} are especially common metals that have a tendency to build up in organisms causing different diseases and disorders [1]. Therefore, they must be removed from the polluted water in order to meet increasingly stringent environmental quality standards. The major techniques employed for heavy metal removal from industrial wastewaters include precipitation [2], membrane filtration [3], ion exchange [4], sorptive flotation [5], and adsorption [6–12]. Among these methods, membrane filtration is usually efficient. However, it has moderately high maintenance and operation costs and susceptible to fouling. Due to the availability of different cheap adsorbents such as agricultural wastes, clay materials, zeolite, biomass, and seafood processing wastes, attempts have been made by several researchers to develop alternate low-cost materials as possible sorbents for the elimination of heavy metals. Examples of these adsorbents include solid waste from the olive industry, soils, oil shale [13] decaying leaves, nutshell carbons [14], and bituminous coal. Zeatoun and Yousef [15] have used activated and nonactivated tar sands as adsorbent of copper ion and found that the adsorption process was dependent upon the activation of tar sands. Al-Asheh and Duvnjak [16] used pine bark as adsorbent for cadmium and other heavy metals. Pine bark was found to be a good adsorbent for Cd^{2+} and showed that decreasing the bark concentration or increasing Cd^{2+} ions concentration increases cadmium uptake per unit weight of bark. Pine bark was also able to sorb Pb^{2+}, Cd^{2+}, Cu^{2+}, and Ni^{2+}, and fine pine bark particle can be re-utilized for further adsorption step. Cao et al. [17] studied the adsorption of heavy metals by phosphate rock (PR) and concluded that PR has the highest affinity for Pb^{2+}, followed by Cu^{2+} and then Zn^{2+}. The selection of adsorbents used in this study was motivated by following rationale: plant seeds, an inexpensive and naturally occurring material.

The aim of the present work was to study the possibility of the removal of copper ions from aqueous solution by adsorption using different plant seeds. The removal conditions and the suitable adsorption isotherms with their related constants were determined. Laboratory batch kinetics and isotherm studies were performed to estimate their adsorption capacity. Also, the effects of contact time, temperature, pH, and initial adsorbate and adsorbent concentrations were investigated.

2. Materials and methods

2.1. Adsorbents

The seed materials which were used in this study were grown in Jordan, dried naturally under the sunshine, washed with distilled water, crushed, sieved to obtain different particle size up to 0.71 mm, and then used in the experiments without any further treatment.

2.2. Stock solution

A stock solution of 1000 ppm of Cu^{+2} was prepared by dissolving copper sulfate in deionized water. The stock solution of the adsorbate was diluted to initial concentration of 100 ppm. The residual concentrations of Cu^{+2} after the adsorption process were determined by flame atomic absorption spectrophotometer (SPECTRO AA10).

2.3. Batch sorption experiments

Batch kinetics tests were conducted with good mixing using a shaker. Twenty ml of the stock solution (diluted to initial concentration of 100 ppm) was placed into glass vials containing 0.1 g of the adsorbent (pumpkin or grape seeds). The bottles were placed and agitated using isothermal bath shaker adjusted to the required value. Samples were taken out at different time intervals (5, 10, 15, 30, 60, 120, 180, and 1,440 min). The sorbent was separated from the samples by filtration using a 0.45 μm filter paper and the filtrate was analyzed by flame atomic absorption spectrophotometer (SPECTRO AA10).

The bottle-point technique was used to conduct the adsorption equilibrium test. The mixture was allowed to equilibrate over 24 h in a shaking water bath. Finally, the concentration of copper ions remaining in the solution was measured, and the adsorption capacity of the adsorbent for the copper ions was calculated.

The effect of adsorbent concentration was determined by preparing a standard solution containing copper metal ions with initial metal ion concentration (C_o) of 100 ppm. The pH of the standard solution was adjusted to 4. The following masses: 0.02, 0.01, 0.75, and 1 g of adsorbent were added to 20 ml of the standard in a glass bottles, and the mixtures were shaken using a rotary shaker at about 100 rpm for 24 h. Afterward, the bottles were removed from the shaker for analysis.

All experiments were performed at a temperature of 25˚C (unless stated otherwise). In each experiment, when varying any given parameter, all other parameters were held constant. When one parameter was varied, all the other parameters had the following values (unless stated otherwise): adsorbent concentration, 5 mg/ml; Cu^{2+} ion concentration, 100 ppm; adsorption temperature, 25˚C; pH, 4; nonactivated grape seeds; no salt added; and contact time of 24 h.

Neither metal ions nor precipitate were adsorbed to the wall of the bottles with the tested metals under the experimental conditions. Each experiment was performed in duplicate and the average results are shown in this work.

3. Results and discussion

3.1. Effect of contact time

Batch experiments were used to determine the relation between the adsorption of copper on two different natural materials (grape seeds and pumpkin) of 15 mg/ml, at initial sorbate concentration of 100 ppm and pH = 4.0. Copper adsorption kinetics is shown in Fig. 1. The rate of copper removal was very rapid during the first 60 min, and it proceeds then slowly till it reaches equilibrium. There was no considerable increase in adsorption after about 60 min. The copper uptake reaches equilibrium state after 180 min for both grape seeds and pumpkin (Fig. 1). Also, the uptake of copper is 1.4 mg/g for grape seeds, while only 0.8 mg/g for pumpkin. This indicates that grape seeds have higher removal capacity of Cu^{2+}. Initially, a large amount of copper ions were jumping rapidly onto the adsorbent due to the availability of large number of active binding sites. However, due to the formation of repulsive forces between the copper on the solid surface and the liquid phase, the binding sites shortly became limited and the remaining vacant surface sites were hard to be occupied by copper ions [18,19]. Furthermore, as a result of the saturation of meso-pores with the adsorbed metal ions, the copper ions had to pass through the deeper surface of the pores for binding and face much larger resistance, which slowed down the adsorption during the later phase of adsorption [18].

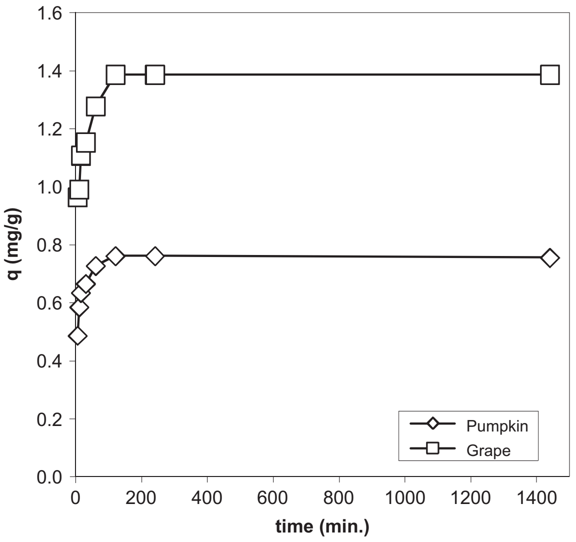

Fig. 1. Adsorption kinetics of copper on two different seed materials (rpm: 100; pH: 4; T: 25˚C, C_o: 100 mg/l; m_s: 5 mg/ml; nonactivated adsorbent).

3.2. Effect of adsorbent concentration and type

The effect of adsorbent concentration and type on the equilibrium concentration of Cu^{2+} ions was investigated using 10 ml of aqueous solution with initial metal ion concentration (C_o) of 100 ppm. The adsorbent amount varied from 5 to 20 mg/ml at a fixed temperature, pH, contact time, and initial adsorbate concentration. Fig. 2 shows that different amounts of Cu^{2+} ions were removed from their solutions by the sorbent depending on both the adsorbent concentration and type. Highest copper uptakes were 3.4 and

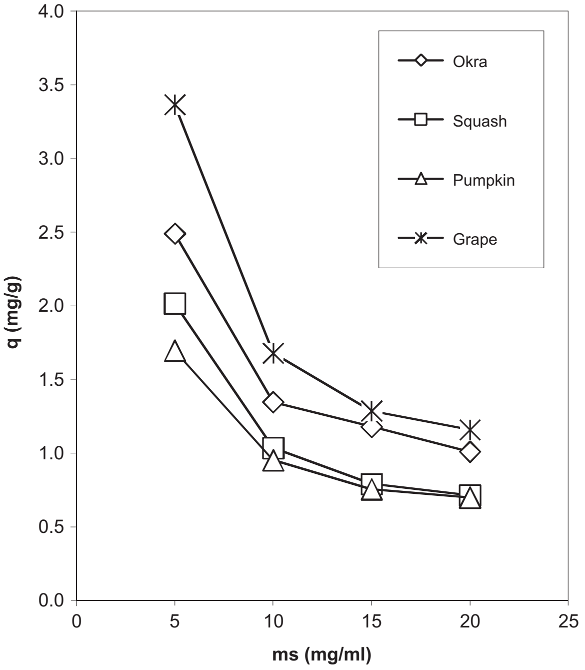

Fig. 2. Effect of adsorbent concentration and type on the uptake of Cu^{2+} ions (rpm: 100; pH: 4; T: 25˚C, C_o: 100 mg/l; nonactivated adsorbent).

2.5 (mg/g) for grape and okra seeds, respectively, at an adsorbent concentration of 5 mg/ml. Thereafter, the copper uptake started to decline with increase in mass of adsorbent for all four types.

> This result is expected due to the fact that, the ratio of sorbent particles to metal ions increases as these particles attach more metal ions to their surfaces, or in words, as the adsorbent concentration increases, the number of adsorbent particles surrounding the metal ions increases. [13]

The sequence of copper uptake (mg/g) from certain concentration of copper sulfate solution (100 ppm.) at constant pH by the different natural materials is in the order: grape > okra > squash > pumpkin seeds. Grape seeds have the highest uptake, so it was decided to carry out the rest of the work using grape seeds.

3.3. *Effect of initial pH*

The effect of the initial pH value on the adsorption of Cu^{2+} ions was studied. This was performed by adjusting the initial pH value of the system using either HCl or NaOH. The copper uptake increases sharply between pH 2 and 3, then remains fixed for pH values larger than 3.0 (Fig. 3). The increase in Cu^{2+} ion uptake with increasing solution pH might be attributed to the drop in H^+ concentration, which hinders the H^+ competition on the vacant sites [20]. When pH is higher than 6.5, Cu^{2+} ions would precipitate (data was not shown). Thus, it is very important to avoid adsorption at this pH.

3.4. *Effect of temperature*

To study the effect of temperature on the uptake of Cu^{2+} ions by grape seeds, experiments were carried out at 25, 35, and 45°C and different initial Cu^{2+} concentrations in the range of 10–100 ppm. It was noticed that metal ion adsorption was increased with temperature, thus suggesting exothermic nature of the process (Fig. 4) [15].

3.5. *Effect of salt addition*

Soft and hard ions are among agents that interfere with the adsorption of heavy metal onto adsorbents. In this study, various concentrations of Na^+ ions in the form of NaCl or K^+ ions in the form of KCl were added to the adsorbent and Cu^{2+} ions suspension. Fig. 5 shows that sodium ions influence the Cu^{2+} removal positively. Higher NaCl concentrations, up to 0.5 M, resulted in more Cu^{+2} removal than at lower NaCl concentrations. In addition, the presence of K^+ ions in the solution would also influence the adsorption process significantly, and the Cu^{+2} uptake was higher than that in the case of Na^+ ions. This may be attributed to the competition between Na^+ and Cu^{2+} ions on the vacant-active

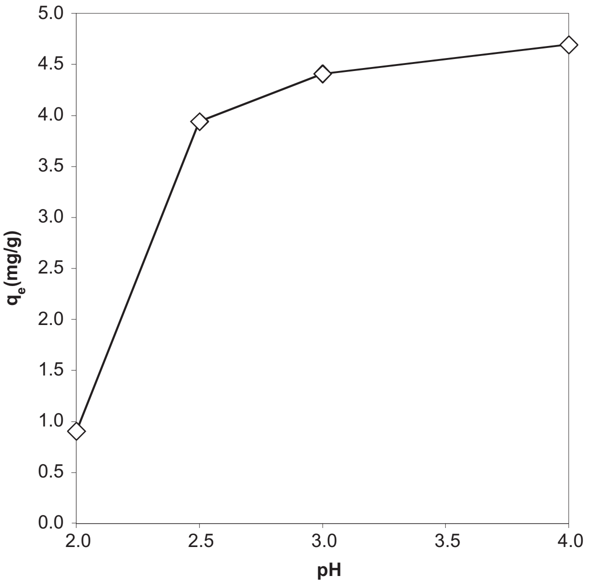

Fig. 3. Effect of initial pH on the uptake of Cu^{2+} ions by grape seeds (rpm: 100; pH: 4; T: 25°C, C_o: 100 mg/l; m_s: 5 mg/ml; nonactivated grape seeds).

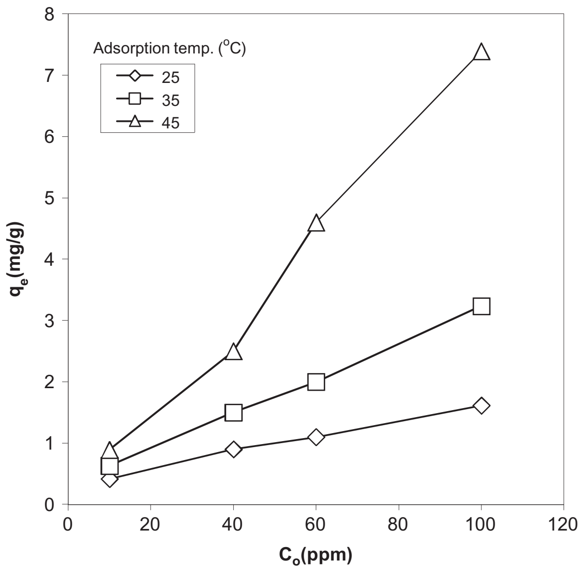

Fig. 4. Effect of solution temperature on the uptake of Cu^{2+} ions by grape seeds (rpm: 100; pH: 4; T: 25°C; m_s: 5 mg/ml; nonactivated grape seeds).

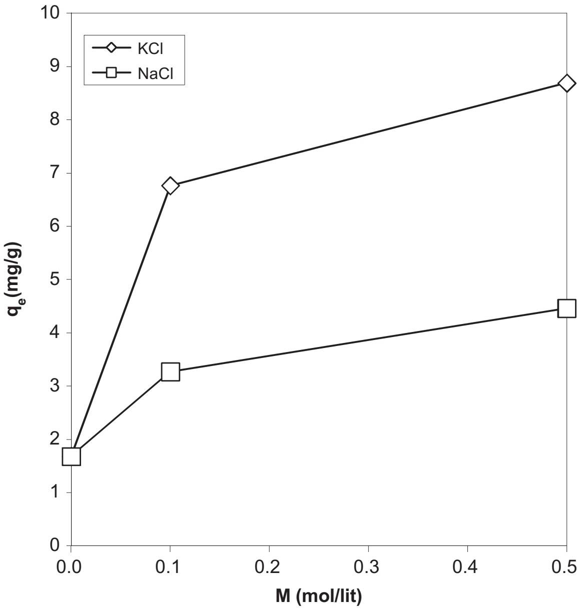

Fig. 5. Effect of salt addition on the uptake of Cu^{2+} ions by grape seeds (rpm: 100; pH: 4; T: 25°C; C_o: 100 mg/l; m_s: 5 mg/ml; nonactivated grape seeds).

sites of the grape seeds. In such a case, due to the repulsive forces between Cu^{2+} and Na^+, Cu^{2+} ions delay Na^+ ions from reaching the sorbent-active sites. The latter finding is in a good agreement with the results of Thiem and others [21], who reported a positive effect of soft and hard ions on the sorption of Hg^{2+} sorption by activated carbon.

3.6. Adsorption isotherms

Adsorption isotherms describe the equilibrium relationships between the liquid phase concentration and surface concentration of adsorbate. The Freundlich and Langmuir linear relations were used to fit the equilibrium data as in Figs. 6 and 7, respectively. This reliability is noticed in the Freundlich linear adsorption isotherm plotted according to Equation:

$$q_e = K_F \times C^{1/n} \tag{1}$$

and linearized form of (1) is:

$$\ln q_e = \ln K_F + n \ln C \tag{2}$$

where q_e is the mass of adsorbate adsorbed per unit mass of adsorbent (adsorbed phase concentration) at equilibrium (mg/g), K_F is the Freundlich constant related to the capacity of adsorption, $1/n$ is the Freundlich constant related to the intensity of adsorption, and C is concentration of adsorbate at equilibrium (mg/l). The constant K_F and exponent (n) can be obtained by plotting of ln q_e vs. ln C (Fig. 6). Experimental results were also applied to the Langmuir adsorption isotherm, and the linear state of the Langmuir adsorption isotherm was obtained. The mathematical form of Langmuir linear adsorption Equation is:

$$\frac{1}{q_e} = \frac{1}{K_L} + \frac{1}{C} \times \frac{1}{b \times K_L} \tag{3}$$

where b and K_L are the model parameters associated with the energy of adsorption and the maximum theoretical adsorption capacity, respectively. The results were presented in the form of a linearized Langmuir isotherm as shown in Fig. 7. The Langmuir and Freundlich's constants were determined from the

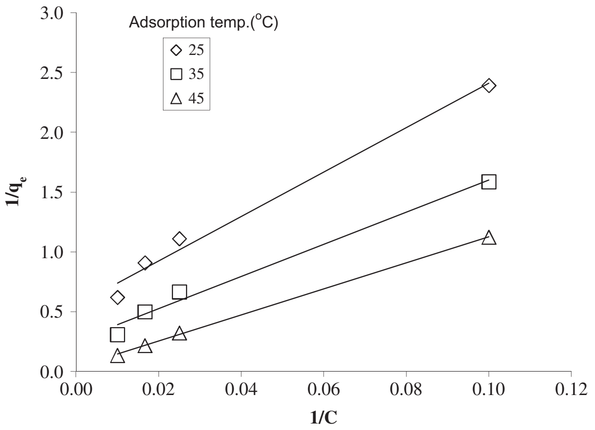

Fig. 6. Langmuir plot for the adsorption of Cu^{2+} on grape seeds (rpm: 100; pH: 4; m_s: 5 mg/ml; nonactivated grape seeds).

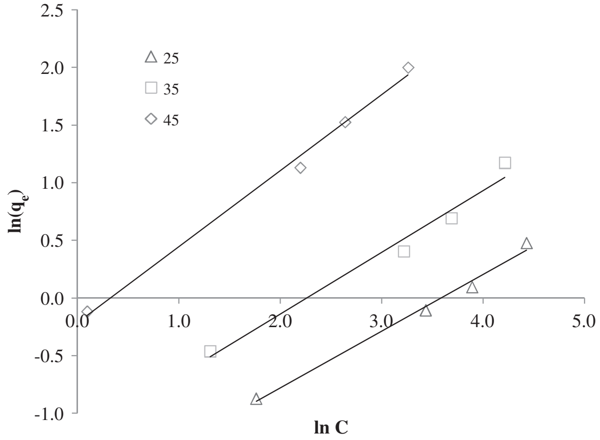

Fig. 7. Freundlich plot for the adsorption of Cu^{2+} on grape seeds (rpm: 100; pH: 4; m_s: 5 mg/ml; nonactivated grape seeds).

Table 1
Langmuir and Freundlich's constants related to adsorption of Cu^{2+} from aqueous solution by grape seeds

Adsorption temp. (°C)	Langmuir isotherm			Freundlich isotherm		
	K_L	b	R^2	K_F	$1/n$	R^2
25	1.805	0.029	0.986	0.808	0.658	0.993
35	3.912	0.018	0.986	0.298	0.536	0.975
45	13.141	0.003	0.999	0.172	0.491	0.991

intercept and slopes of their linear adsorption isotherms (Table 1). It can be seen that as the temperature increased from 25 to 45°C, the value of K_L (the maximum adsorption capacity) increased from 1.8 to 13.14, respectively. The maximum adsorption capacity for grape seeds was found higher than in the previously reported method of copper adsorption by tar sands [15]. From a theoretical point of view, when the adsorption process is exothermic, the adsorption rate decreases with increasing temperature, and consequently the uptake decreases [20]. This discrepancy might be attributed to the fact that the grape seeds samples used to study the effect of temperature were nonactivated, this indicates that the adsorbent has different trace elements from agriculture residue [22] already adsorbed onto its surface. A possible explanation might be that the temperature increase will result in an increase in the desorption rate, and hence more vacant sites will be available for copper ions adsorption. This leads to an increase in both the uptake of Cu^{2+} ions and the number of vacant sites and consequently, the value of K_L is increased. The latter is in a good agreement with the results of Zeatoun and Yuosef [15], who reported a similar effect of adsorption temperature on the K_L value. The K_F constant is concerned with the tendency of the adsorbent to adsorb and the n-constant is concerned with ability of the adsorbate to be adsorbed. As noticed in Table 1, the values of n were between 1 and 10, which means favorable adsorption of Cu^{2+} on grape seeds. In addition, the K_F and n constants of the copper ions adsorbed at different temperature change is in the order of $25 > 35 > 45$°C.

Thermodynamic parameters such as enthalpy, ΔH, for using copper ions adsorption by grape seeds were calculated using the following Equation:

$$\ln b = \ln b' - \frac{\Delta H}{RT} \tag{4}$$

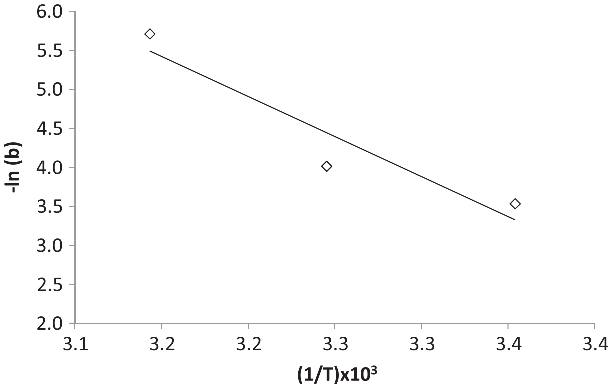

Fig. 8. Variation of ln b with reciprocal of temperature (rpm: 100; pH: 4; m_s: 5 mg/ml; nonactivated grape seeds).

where b' is the adsorption energy constant, T is the absolute temperature (K), and R is the universal gas constant. Linear plot of ln (b) vs. $1/T$ shows the applicability of the above equation for grape seeds as shown in Fig. 8. The ΔH value determined graphically from the slopes of the plot was -85.285 kJ/mol; the negative values of the enthalpy confirm the exothermic nature of the adsorption process. Consequently, in view of the fact that the value of ΔH was found to be greater than an absolute value of -62.7 kJ/mol, it is indicative that chemical adsorption occurs with the agriculture residue [22].

4. Conclusions

This work has shown that low-cost materials like plant seeds may be considered as a potential adsorbent for the removal of Cu^{2+} ions from their aqueous solutions, and grape seeds exhibit maximum copper uptake. The copper ions removal was pH dependent as the uptake was increased with increasing the pH value of the solution. The copper ions showed an exothermic behavior toward adsorption on grape seeds by increasing the adsorption temperature. On the other hand, the presence of ions such as Na^+ or K^+ improved the adsorption of Cu^{2+} on the surface of the grape seeds. The adsorption process was considered fast and equilibrium was reached in a short period of time. Adsorption of copper ions was well presented with both Langmuir and Freundlich isotherms. The experimental studies showed that plant seeds could be used as an alternative, cheap, and efficient material to eliminate appreciated amounts of copper metal ions from contaminated water.

Nomenclature

m_s — initial concentration of adsorbent (mg/ml)
C_o — initial concentration of adsorbate (mg/l)
C — concentration of adsorbate at equilibrium (mg/l)
K_F — Freundlich constant $(l/mg)^{1/n}$
R^2 — correlation coefficient
q_e — mass of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g)
$1/n$ — constant related to the intensity of adsorption
b — constant related to enthalpy (Langmuir model) (l/mg)
K_L — constant related to the maximum theoretical adsorption capacity (mg/g)
ΔH — enthalpy of adsorption (kJ/mol)
b' — the adsorption energy constant
R — the universal gas constant (J/mol K)

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