# REMOVAL OF COPPER IONS FROM INDUSTRIAL WASTEWATER USING WALNUT SHELLS AS A NATURAL ADSORBENT MATERIAL

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*This study aims to remove copper ions from solution of the simulated wastewater using walnut shells as a natural adsorbent material in batch adsorption system. Effects of experimental parameters such as pH, contact time and adsorbent dose at different initial concentrations on the adsorption efficiency have been studied. A set of experiments have been done in order to achieve the best conditions for the highest removal efficiency which was 79.54 %. The experimental data were fitted with Langmuir and Freundlich isotherm models to determine adsorption isotherm parameters. Kinetic adsorption of experimental data was obtained as a function of time by using pseudo-first and the pseudo-second order kinetic models. FTIR analysis of dry walnut shells have been carried out, in order to find out which functions are responsible for adsorption of copper ions.*

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**Keywords:** heavy metals, copper ions, batch adsorption, walnut shells

## 1. Introduction

The high concentration of heavy metals in the environment causing by the development of the industry and it can be detrimental to a variety of living species [1]. Copper is the major available type of heavy metal in the aquatic environment. Copper in the blood system may generate reactive free oxygen species and damage the protein, lipids and DNA [2]. The excess copper compound in the human body may also effects on aging, schizophrenia, mental illness, Indian childhood cirrhosis, Wilson’s and Alzheimer’s diseases [3]. Copper has damaged the marine ecosystem and damaged the gills, liver, kidneys, the nervous system and changing sexual life of fishes. Maximum permissible limit of copper in drinking water is 1.3 mg/L according to the World Health Organization (WHO) and United State Environmental Protection Agency (USEPA) [4].

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Copper is released from batteries industry, metal-finishing, electroplating and electrical industries. A variety of suitable methods can be used for the removal of copper and other metal pollutants from liquid wastes such as: filtration, chemical precipitation, coagulation, solvent extraction, electrolysis, ion exchange, membrane and adsorption. The industrial application of the previous processes is restricted by the inefficiency and operating costs of the technique [5]. Adsorption is the most common and effective processes for the removal of heavy metal ions [6].

In recent years, many low cost adsorbents including agricultural waste have been tested in batch adsorption system by a number of researchers [7]. Several adsorbents have been used for the removal of copper from wastewater. It has been reported that some aquatic plants, waste tea leaves and sawdust have an efficient role [8, 9]

In this work, we use dry walnut shells, which are agriculture waste, as a low-cost adsorbent material to remove copper ions from aqueous solutions. The effect of various parameters such as pH, contact time and adsorbent dose at different initial concentration on adsorption process was studied.

## 2. Experimental part

### Material and Chemicals:

Walnut shells were collected from local market and washed twice in distilled water to remove the dust dried at (105) $^{o}C$ for (24) hrs, then grinded and sieved to obtain (1-3) mm diameter of adsorbent particles.

Copper sulfate hexahydrate ($CuSO_4.6H_2O$), (M.wt= 249.68) g/mol (REACTIVUL® Company, Bucharest, Romania) used to prepare a solution of the simulated wastewater contains (100) mg/L of Cu(II) ions. Lower concentrations were then prepared when required by further dilution of the stock solution with distilled water. Hydrochloric acid [1M] and Sodium hydroxide pellets were used to adjust pH to the desired value.

### Procedure of sorption experiments

Batch adsorption of Cu(II) ions, experiments have been carried out at temperature at 25 $^{o}C$, agitation speed of 200 rpm and adsorbent particles diameter of 1 mm to find the optimum of pH, contact time, adsorbent dose at different initial concentrations. The procedure involved filling the flask with 50 mL of Cu(II) ions solution dumped into a flask 100 ml. Experiments were carried out at initial pH value ranging from 3 to 8, contact time (10-180) min and adsorbent dose (0.125-1) g. All previous experiments occur at initial concentration of heavy metal ions between 10 to 100 mg/L. After equilibrium, samples with (20 mL) were taken from the flask. These samples were filtered and the concentration of heavy metal ions in the solutions was determined by Atomic Absorption

Spectrometry: AAS (GBC 933 plus, Australia). The percent of removal efficiency (R %) was calculated using equation (1).

$$R\% = \frac{C_o - C_e}{C_o} * 100 \quad (1)$$

## 3. Results and discussion

The adsorbent material characteristics [10] were specific natural walnut.

**Factors affecting heavy metals removal:**

**Effect of pH**

The pH of the aqueous solution is an important variable which controls the adsorption and plays an important role in the precipitation and adsorption mechanisms. In order to examine the effects of pH on removal efficiency of Cu(II) ions onto dry walnut shells, the experiments were carried out at various values of pH (from 3 to 8) with different initial concentration for Cu(II) ions (from 10 to 100 mg/ L). The experimental data showed that the maximum removal efficiency of the Cu(II) ions onto dry walnut shells is 79.56%. This value is obtained when the pH value is 6 and at initial concentration is 50 mg/ L; this is in good agreement with previous studies [11]. At pH below 3, the positive charge ($H^+$) density on the sites of biomass surface minimizes metal sorption, and above pH above 6, metal precipitation is favored. Fig. 1 shows the effect of pH on the adsorption efficiency at different initial concentration for Cu(II) ions.

The adsorption capacity of biomass increased with an increase in contact time before equilibrium was reached [12]. Fig. 2 shows that the adsorption by the inactive instant dry walnut shells reached equilibrium after 150 min contact time for different initial concentrations of Cu(II) ions. The removal efficiency increased rapidly and reached maximum after only 150 min due to the availability of binding sites present on the inactive dry walnut shells surface. With the progressive saturation of the sorbent with increasing contact time the sorption process became less efficient. It can be noticed the trend was similar for all initial concentrations. Therefore, considering the aforementioned observations, 150 min was selected as optimum contact time for Cu(II) sorption by the inactive instant dry walnut shells.

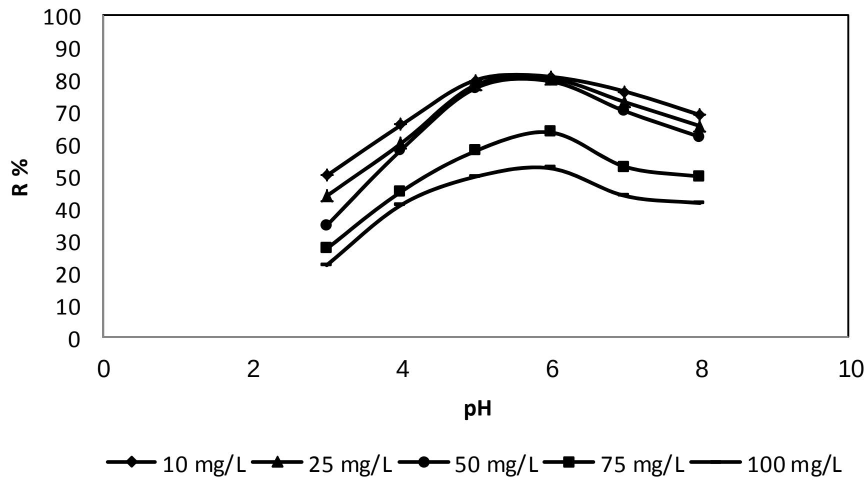


Fig. 1 Effect of pH on the removal efficiency of Cu(II) ions onto dry walnut shells at different initial concentrations (contact time = 150 min and adsorbent dose= 0.5 gm).

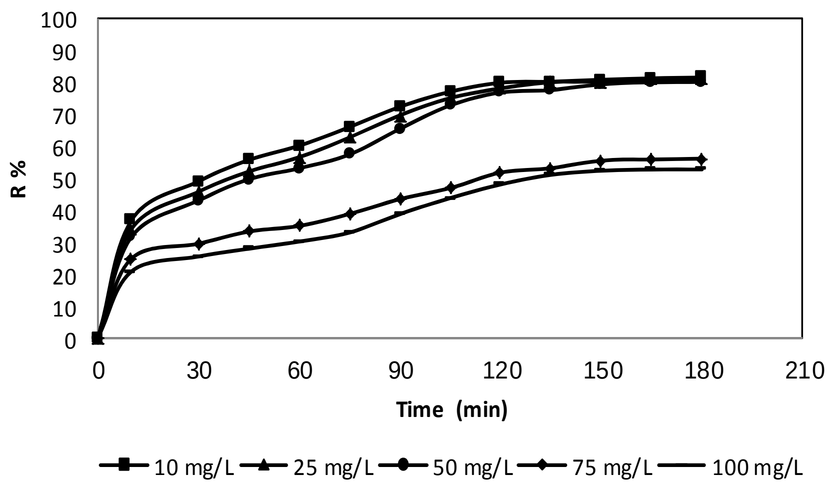


Fig. 2 Effect of contact time on the removal efficiency of Cu(II) ions onto dry walnut shells at different initial concentrations ( pH= 6 and adsorbent dose= 0.5 gm).

The effect of varying the adsorbent dose on the removal of Cu(II) ions at different initial concentrations is shown in Fig. 3. It is clearly seen that the removal efficiency increases as the dry walnut shells mass increases. As the dry walnut shells mass increases the number of binding sites for the ions also increases. After some point, adsorption capacity was steady due to a screen effect between adsorbent, this produced a block of the adsorbent active sites by an increase of adsorbate (heavy metal ions) in the system [10, 13]. Fig. 3 shows that by increase in of the adsorbent dose from 0.125 to 0.5 g a significant increase of removal efficiency is obtained for different initial concentrations of Cu(II) ions and after that the increase is negligible. So it can be considered that 0.5 g of the dry walnut shells per 50 mL of solution is the best dose economically because the increase the percentage in the adsorption efficiency is small at other large adsorbent doses.

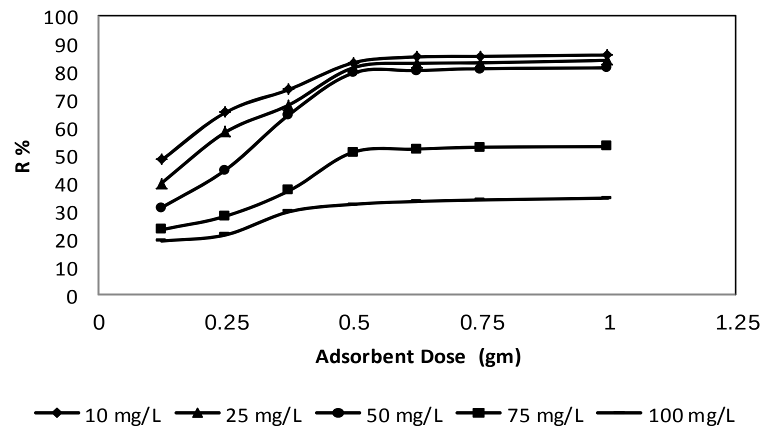


Fig. 3 Effect of adsorbent dose on the removal efficiency of Cu(II) ions onto dry walnut shells at different initial concentrations ( pH=6 and contact time = 150 min).

**Adsorption isotherm models**

Some of most widely adsorption models isotherm such as Freundlich, Langmuir are disscused [14, 15]. Freundlich and Langmuir isotherm models showed that adsorption from solution could be described in by equations (2) and (3) respectively:

$$q_e = KC_e^{1/n} \tag{2}$$

Where $q_e$ is the adsorbed metal ions (mg/g), $C_e$ is metal ions concentration in the solution at equilibrium (mg /L), $K$ (mg/g) (L/mg) $^{1/n}$ and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively.

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{3}$$

Where: $q_e$ is the adsorbed metal ions (mg/g), $q_m$ is the maximum sorption capacity for monolayer coverage (mg/g), $b$ is the constant related to the affinity of the binding site (L/mg), and $C_e$ is metal ions concentration in the solution at equilibrium (mg /L).

*Table 1*

**Parameters of adsorption isotherm models for Cu(II) ions onto Walnut Shells.**

| Model | Parameters | Cu(II) |
|---|---|---|
| Freundlich Equation (2) | K, (mg/g)(L/mg)$^{(1/n)}$ | 1.1739 |
| | n | 2.5816 |
| | $R^2$ | 0.9145 |
| Langmuir Equation (3) | $q_m$(mg/g) | 4.6198 |
| | b(L/mg) | 0.1231 |
| | $R^2$ | 0.9548 |

The data in table 1 shows that Langmuir model described the adsorption data better than Freundlich model depending on the value of correlation coefficients. Fig. 4 shows the linearized Langmuir isotherm model for adsorption of Cu(II) ions into dry walnut shells.

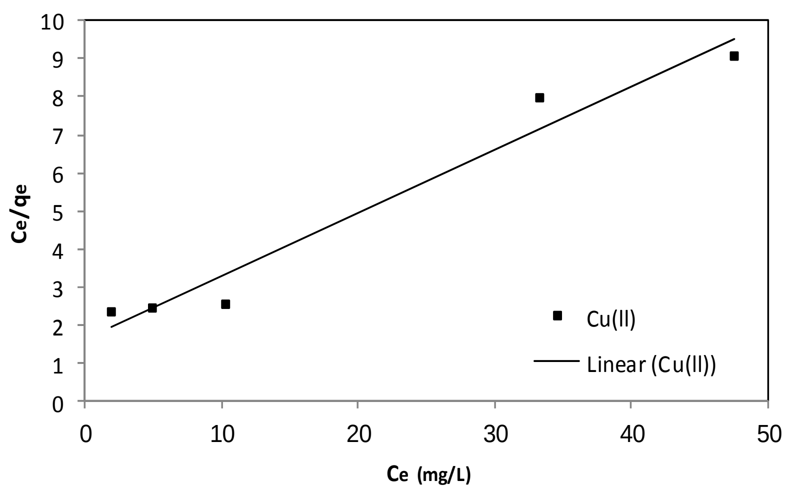


Fig. 4 Langmuir isotherm model of batch adsorption for Cu(II) ions onto dry walnut shells.

**Adsorption Kinetic models**

The kinetics of batch adsorption system of Cu(II) ions adsorption onto walnut shells was analyzed using pseudo-first-order and pseudo-second-order models [16, 17]. A linearized pseudo-first-order equation is described in equation (4):

$$\ln(q_{eq} - q_t) = \ln q_{eq} - k_1 t \tag{4}$$

Where: $q_{eq}$ is the amount of pollutant adsorbed at equilibrium (mg/g); $q_t$ is the amount of pollutant adsorbed at time $t$ (mg/g); and $k_1$ is the equilibrium rate constant of pseudo-first sorption (1/min). This pseudo-first-order equation is applicable because a plot of $\ln(q_e - q_t)$ against t is a straight line and because $q_{eq}$ and $k_1$ can be determined from the slope and intercept, respectively.

Adsorption data were analyzed with the following linearized pseudo-second-order equation):

$$\frac{t}{q_t} = \frac{1}{k_s q^2_{eq}} + \frac{t}{q_{eq}} \tag{5}$$

Where $k_2$ is the rate constant of adsorption, (g/mg.min), $q_{eq}$ is the amount of pollutant adsorbed at equilibrium, (mg/g), $q_t$ is amount of adsorbate on the surface of the adsorbent at any time, $t$, (mg/g). $k_2$ and $q_{eq}$ are the slope and intercept of the $t/q_t$ vs. $t$ plot, respectively.

Table 2 demonstrates the results of these models. The data obtained separately for each of the kinetic models from the slopes of plots show a good compliance with the pseudo second-order equation. Fig. 5 show that correlation coefficient value of pseudo second-order for the linear plots being higher than 0.97 with sorption uptake equal to 4.89 mg/g for Cu(II) ions.

*Table 2.*

**Parameters of adsorption kinetic models for Cu(II) ions Walnut Shells.**

| Model | Parameters | Cu(II) |
|---|---|---|
| Pseudo-first-order Equation (4) | $q_{eq}$(mg/g) | 4.8138 |
| | $K_L$(L/min) | 0.0266 |
| | $R^2$ | 0.8899 |
| Pseudo-second-order Equation (5) | $q_{eq}$ (mg/g) | 4.8971 |
| | $K_s$(g/mg.min) | 0.0052 |
| | $R^2$ | 0.9769 |

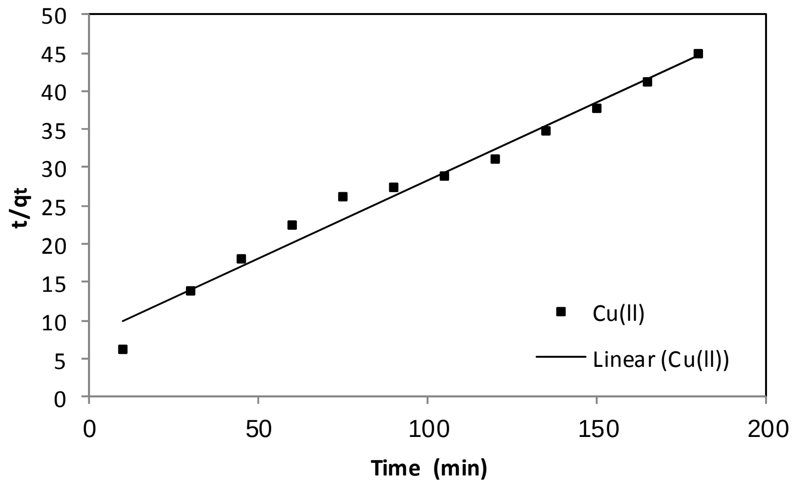


Fig. 5 Pseudo-second order kinetic model for batch adsorption for Cu(II) ions onto dry walnut shells.

**FTIR analyses**

FTIR spectroscopy analysis offers excellent information on the nature of the functional groups present on the surface of the natural adsorbent materials [10,17]. Numerous chemical functional groups have been identified as potential sorption sites to be responsible for binding heavy metals. Figs. 6 and 7 show the spectra of raw and treated dry walnut shells samples when using FTIR, spectrophotometer, TENSOR 27, BRUKER, Germany. Peak displacement decreasing define the change in the structure with Cu(II) imply the related functional groups to be responsible for the adsorption process. The bands of hydroxyl and carbonyl groups shifted to higher transmission (peaks of adsorption) and therefore it plays the major role in adsorption of these ions and this is apparent in the Figs. 6 and 7.

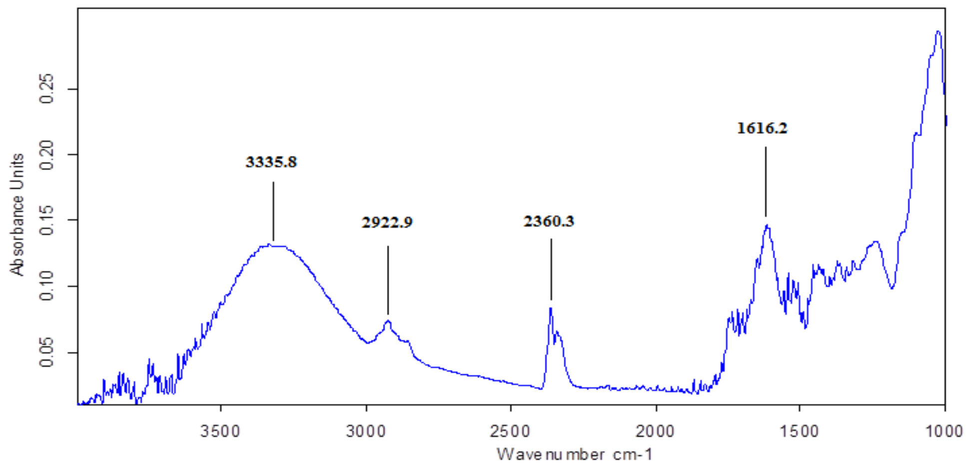


Fig. 6 FTIR analysis of dry walnut shells before loaded by Cu(II) ion .

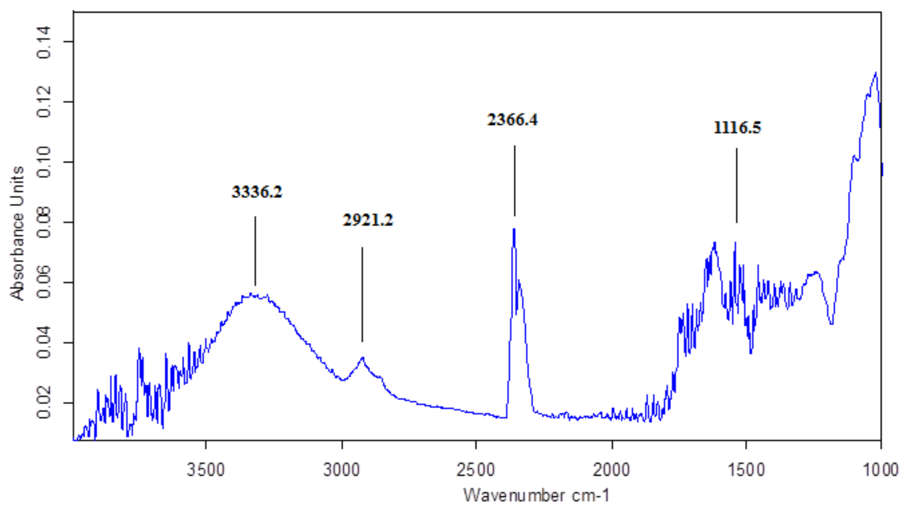


Fig. 7 FTIR analysis of dry walnut shells after loaded by Cu(II) ion.

## 4. Conclusions:

In this manuscript, the results obtained in the removal of copper ions from industrial wastewater using walnut shells are presented. Effects of various parameters such as pH, contact time and adsorbent dose were monitored. The highest removal efficiency of copper ions obtained was 79.54 %, at best operating conditions of pH 6, contact time 150 min and adsorbent dose 0.5 g / 50 mL of solution). By applying the isotherm model to the experimental data, it was found that Langmuir model is better than Freundlich model. The adsorption kinetics of Cu(II) ions onto dry walnut shells agree very well with pseudo-second order model depending on the correlation coefficient values which was calculated from the experimental data.

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