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# KINETIC AND ISOTHERM STUDIES OF COPPER (II) REMOVAL FROM WASTEWATER USING VARIOUS ADSORBENTS

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## ABSTRACT

The present investigation deals with the utilization of marine green algae (GA), *Ulva lactuca*, and an activated carbon prepared from green algae (CGA) as adsorbents for the removal of copper from wastewater. A series of experiments were conducted in a batch system to evaluate the effect of system variables. The effect of pH, initial copper concentration, dose of adsorbents were considered. The optimal pH value of copper (II) adsorption onto GA and CGA was found to be pH 5.0. The maximum uptake capacities were 24.5 and 32.3 mg copper (II) per gram of GA and CGA, respectively. The efficiency of removal was slightly changed by replacing an aqueous solution by saline water or wastewater containing the same copper concentration. Adsorption kinetic data were tested using pseudo-first order, pseudo-second order, Bangham's equation and intra-particle diffusion models. Kinetic studies showed that the adsorption followed a pseudo-second order reaction. Studies revealed that intra-particle diffusion played an important role in the mechanism of copper (II) adsorption. The equilibrium data were analyzed using Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich, Redlich-Peterson and Koble-Corrigan isotherm models at different doses of GA and CGA. The equilibrium data were analysed using different error analysis equations. The Freundlich and Redlich-Peterson models were found to be describing the data of GA, while Freundlich model describes the data of CGA.

## 1. INTRODUCTION

Heavy metal pollution of wastewater is a common environmental hazard, since the toxic metal ions dissolved can ultimately reach the top of the food chain and thus become a risk factor for human health. One of such heavy metal of concern is copper. It is present in the wastewater of several industries, such as metal cleaning and plating baths, refineries, paper and pulp, fertilizer, and wood preservatives (Periasamy and Namasivayam, 1996). The excessive intake of copper by man leads to severe mucosal irritation, widespread capillary damage, hepatic and renal damage, central nervous problems followed by depression, gastrointestinal irritation, and possible necrotic changes in the liver and kidney (Kalavathy *et al.*, 2005).

Effective methods for copper ion removal that have been used include ion exchange, reverse osmosis, electrochemical treatment, evaporative recovery, and adsorption. The application of such processes is often limited because of technical or economic constraints (Kumar *et al*., 2006).

Biosorption is a proven technology for the removal of copper (II) ions from synthetic and real industrial effluents. The high cost of activated carbon has motivated scientists into the search for new low cost adsorption

means. In recent years, considerable attention has been focused on the removal of copper from aqueous solution using adsorbents derived from low-cost materials. Several adsorbents, such as sawdust, silica, and iron oxide (Ajmal, *et al*., 1998), wheat shell (Basci *et al*., 2004), bagasse fly ash (Gupta and Ali, 2000), fly ash (Bois *et al*., 2003), spent activated clay (Weng *et al*., 2007) and modified goethite (Li *et al*., 2007) have been used for the treatment of copper (II) rich effluents at the solid–liquid interface.

In the present investigation marine green algae (GA) *Ulva lactuca*, and an activated carbon prepared from green algae (CGA) have been used as adsorbents for the removal of copper (II). The aim of the present work is to explore the possibility of utilizing GA and CGA for the adsorptive removal of copper (II) from wastewater. The effect of such factors as initial pH, adsorbent dose, contact time and initial concentration was investigated. The kinetics of Copper (II) adsorption on both adsorbents was analysed by various kinetic models. Experimental equilibrium data were fitted to the Langmuir, Freundlich, Tempkin, Dubinin-Radushkevich (D-R), Redlich–Peterson (R–P), and Koble-Corrigan isotherm equations to determine the best-fit isotherm equation. Different error analysis methods were used to determine the isotherm parameters for accurate elucidation of the experimental data.

## 2. MATERIALS AND METHODS

### 2.1. Adsorbent

*Ulva lactuca* was collected from Mediterranean Coast, Alexandria, Egypt. It was washed with filtered sea water several times. The clean algae were sun dried followed by oven drying at 60ºC to constant dry weight. The dried algae were milled and sieved. Part of the sieved algae was labeled (GA) and was used as adsorbent in batch adsorption experiments. Another part of the algae was suggested to carbonization according to the published methods (El-Sikaily *et al*., 2007), and was labeled (CGA).

### 2.2. Chemicals

All reagents used in this study were of analytical grade. Stock solution of copper (II) was prepared by dissolving accurately weighted amount of copper sulphate in 1000 ml distilled water. All experimental solutions were prepared by diluting the stock solution to the required concentration. The pH of each experimental solution was adjusted to the required initial pH value using 1N HCl or 1N NaOH before mixing the adsorbent. The concentration of residual copper (II) was determined with atomic absorption spectrophotometer (Perkin Elmer 2380).

### 2.3. Batch Experiments

The effect of various parameters on the removal of copper (II) onto green algae (GA) and carbon green algae (CGA) was studied, batch adsorption experiments were conducted at 25±1ºC. For each experimental run, 100 ml of copper (II) solution of known initial concentration and pH were taken in a 250 ml plugged conical flask. A suitable adsorbent dose is added to the solution and the mixture was shaken at a constant agitation speed (200 rpm). Samples were withdrawn at appropriate time intervals (5- 120 min) and the adsorbent was separated by centrifugation at 5000 rpm for 10 min. The supernatant was analyzed for residual copper (II) concentration.

The effect of dose of adsorbent on the removal of copper (II) was measured by contacting 100 ml of copper (II) solution with different amounts of GA and CGA. (2-10 g/L) till equilibrium was attained.

Adsorption equilibrium isotherms were studied using GA and CGA dosages from (2-10 g/L) per 100 ml of copper (II) solutions. Initial concentrations were ranged from (5-50 mg/L) using initial pH 5. In all sets of experiments, the plugged conical flasks were shaken at a speed of 200 rpm for 3 hours. Then, the solution was separated from the

mixture and analyzed for copper (II) concentration. The adsorption capacity was obtained by using a mass equilibrium equation as follows

$$q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where $C_0$ and $C_e$ being the initial copper (II) concentration (mg/L) and equilibrium concentration, respectively, $V$ *is* the experimental volume of copper (II) solution expressed in liters, and $m$ is the adsorbent mass expressed in grams.

The effect of pH on the rate of adsorption was investigated using copper concentration of 50 mg/L for constant GA and CGA dosages. The pH values were adjusted with 1N HCl and 1N NaOH solutions. The adsorbent-adsorbate mixture was shaken at room temperature using agitation speed (200 rpm) for 2 hours. Then, the concentration of copper in solution was determined.

### 2.4. Simulation studies

Synthetic seawater, natural sea water and real wastewater were used to examine the application of the results on the field. Synthetic sea water of 3.5% NaCl concentration was prepared, then different copper concentrations were prepared by dissolving known amounts of $CuSO_4$ in the synthetic sea water to get the required concentration. Similar concentrations were prepared using natural seawater and real wastewater instead of synthetic sea water. Natural seawater was collected from Eastern Harbor, Alexandria, Egypt and it was filtered using Whattman no. 40 filter paper before its usage. Wastewater was collected from El-Emoum Drain, where different industrial effluents are collected before its discharge to sea, Alexandria- Egypt. Similarly, the collected wastewater was filtered through Whattman no. 40 filter paper before its usage.

## 3. RESULTS AND DISCUSSION

Analysis of adsorption data is important for developing equilibrium and kinetic equations that can be used for design purposes.

### 3.1 Effect of initial pH on copper (II) adsorption:

pH is an important parameter influencing heavy metal adsorption from aqueous solutions. It affects both the surface charge of adsorbent and the degree of ionization of the heavy metal in solution (Aksu, 2005). Fig 1 represents the effect of initial pH of the solution on the adsorption of copper (II) onto GA. and CGA using 50 mg/L initial copper concentration and 2 g/L adsorbent concentration. The optimum pH was found to be pH 5.0 for both studied adsorbents. The maximum removal efficiency was 62% and 88% for GA and CGA, respectively. This may be attributed to the competition between the hydrogen and copper ions on the sorption sites, at low pH values. At pH values higher than 6.0 insoluble copper hydroxide starts precipitating from the solutions making true sorption studies impossible (Antunes *et al*., 2003). Consequently, the working pH value for copper removal onto GA and CGA was chosen as 5.0 and the other adsorption experiments were performed at this pH value.

### 3.2. Effect of adsorbent dose

The effect of varying doses of GA and CGA was investigated using 50 mg/L of initial copper concentration at initial pH 5.0. Fig. 2 shows an increase in percentage removal of copper with the increase in dose of adsorbent up to a certain limit and then it remains almost constant. Increase in the adsorption with increasing dose of adsorbent is expected due to the increase in adsorbent surface area and the availability of more adsorption sites (Mall *et al*., 2006). In contrast, the adsorption capacity of copper

onto GA and CGA decreases with the increase in dose of adsorbent. It was decreased from 14.3 to 2.3 and from 21.35 to 3.23 with an increase in the dose of adsorbent from 2 to 15 g/L for GA and CGA, respectively.

### 3.3. Effect of contact time

Effect of contact time for the removal of copper (II) by GA and CGA at 2 g/L biomass concentrations is shown in (Fig. 3). There was a rapid adsorption of copper (II) in the first 10 min and, thereafter, the rate of adsorption decreased gradually. The maximum removal was 73% and 90% and it was attained in about 60 and 45 min for GA and CGA, respectively.

### 3.4. Adsorption kinetic study

Kinetic models have been used to investigate the mechanism of sorption and potential rate controlling steps, which is helpful for selecting optimum operating conditions for the full-scale batch process (Kalavathy *et al*., 2005). Pseudo-first-order, pseudo-second-order, Bangham and intra-particle diffusion kinetic models were used.

#### *3.4.1. Pseudo-first-order model*

The pseudo-first-order rate expression based on solid capacity is generally expressed as follows (Lagergren, 1898)**:**

$$\frac{dq}{dt} = k_{1,ad}(q_e - q) \quad (2)$$

where, $q_e$ is the amount of copper (II) adsorbed at equilibrium (mg/g), $q$ is the amount adsorbed at time $t$ (mg/g), $k_{1,ad}$ is the rate constant of first order adsorption (L/min). After integration and applying boundary conditions, $t = 0$ to $t$ and $q = 0$ to $q_e$; the integrated form of equation (2) becomes:

$$\log(q_e - q) = \log(q_e) - \frac{k_{1,ad}}{2.303}t \quad (3)$$

Values of adsorption rate constant ($k_{1,ad}$) for the copper (II) adsorption onto GA and CGA were determined from the straight line plot of $\log(q_e - q)$ against $t$. The data were fitted with a poor correlation coefficient (Table 1), indicating that the rate of removal of copper onto GA and CGA does not follow the pseudo-first-order equation.

#### *3.4.2. Pseudo-second-order model*

The pseudo-second-order equation is also based on the sorption capacity of the solid phase. It predicts the behavior over the whole range of data. Furthermore, it is in agreement with chemisorption being the rate controlling step and is expressed as (Ho *et al.*, 2000):

$$\frac{dq}{dt} = k_{2,ad}(q_e - q)^2 \quad (4)$$

where $k_{2,ad}$ is the rate constant of second-order-adsorption (g/mg.min). For the same boundary conditions the integrated form of equation (4) becomes:

$$\frac{t}{q} = \frac{1}{k_2 q_e^{\,2}} + \frac{1}{q_e}t \quad (5)$$

The initial sorption rate, $h$ (mg/ g. min), at $t = 0$ is defined as

$$h = k_{2,ad} q_e^2 \quad (6)$$

where $k_{2,ad}$ and $h$ values were determined from the slope and intercept of the plots of $t/q$ against $t$ (Fig. 4). The values of the parameters and correlation coefficients are also presented in Table 1. The correlation coefficients of all examined data were found very high ($R^2$> 0.99). This shows that the model can be applied for the entire adsorption process and confirms that the sorption of

copper onto GA and CGA follows the pseudo-second-order kinetic model. Same behavior have been observed in the biosorption of copper onto agricultural waste sugar beet pulp (Aksu and Isoglu, 2005) and adsorption of copper onto $H_3PO_4^-$ activated rubber wood sawdust (Kalavathy *et al*., 2005).

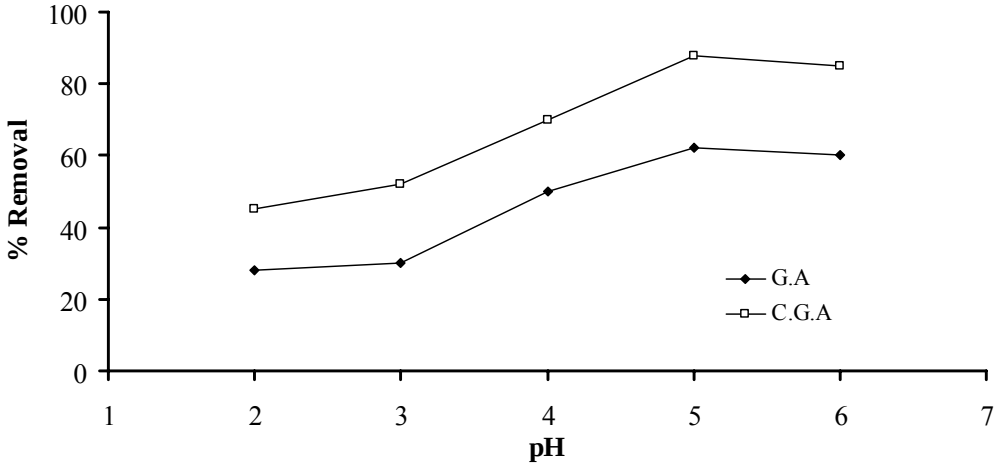



**Fig. (1): Effect of pH on copper (II) adsorption onto G.A and C.G.A.**

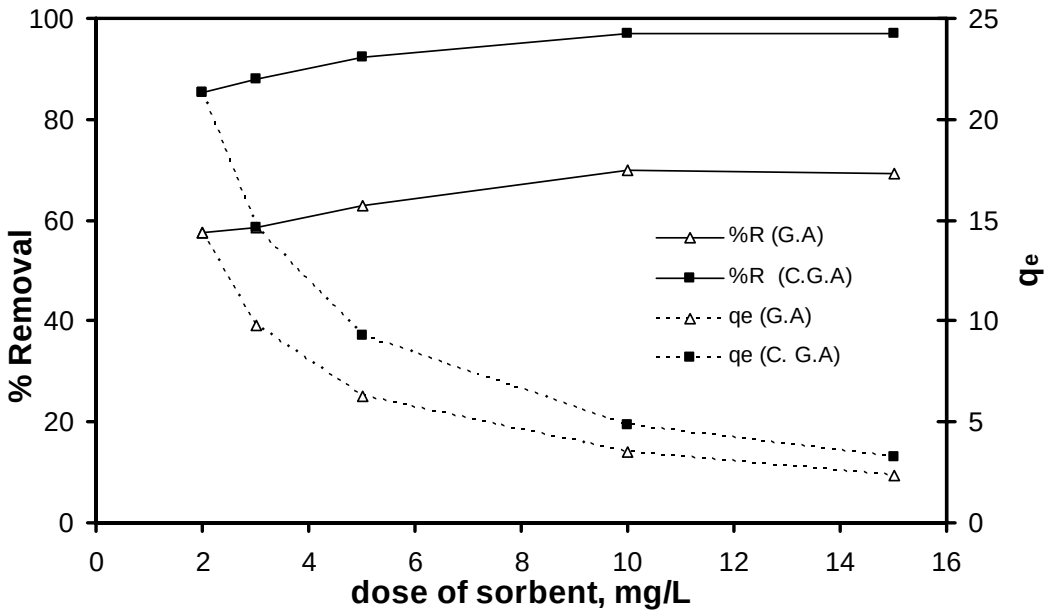



**Fig. (2): Effect of adsorbent dose on percentage copper (II) removal, R, and adsorption capacity, $q_e$ from solution.**

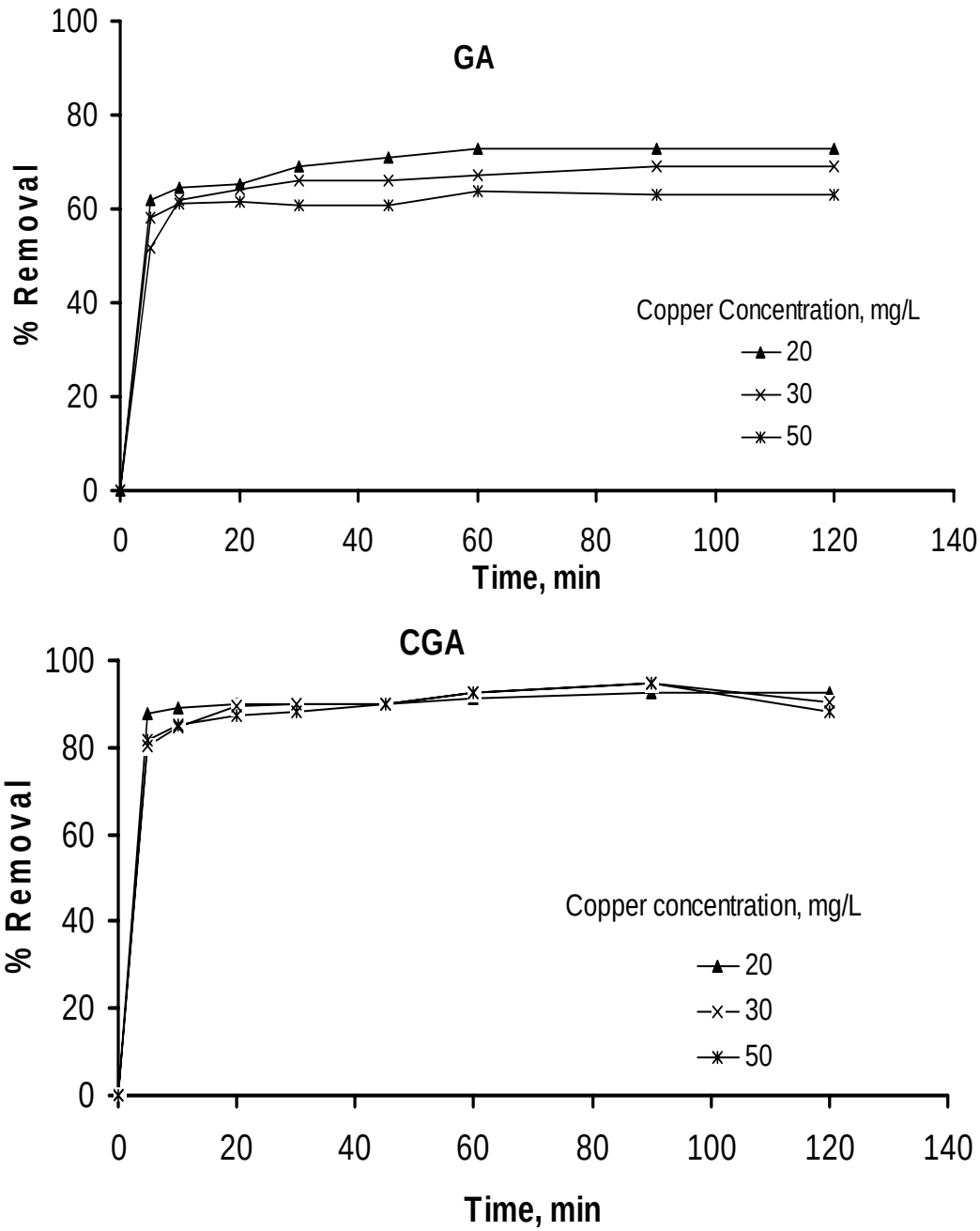
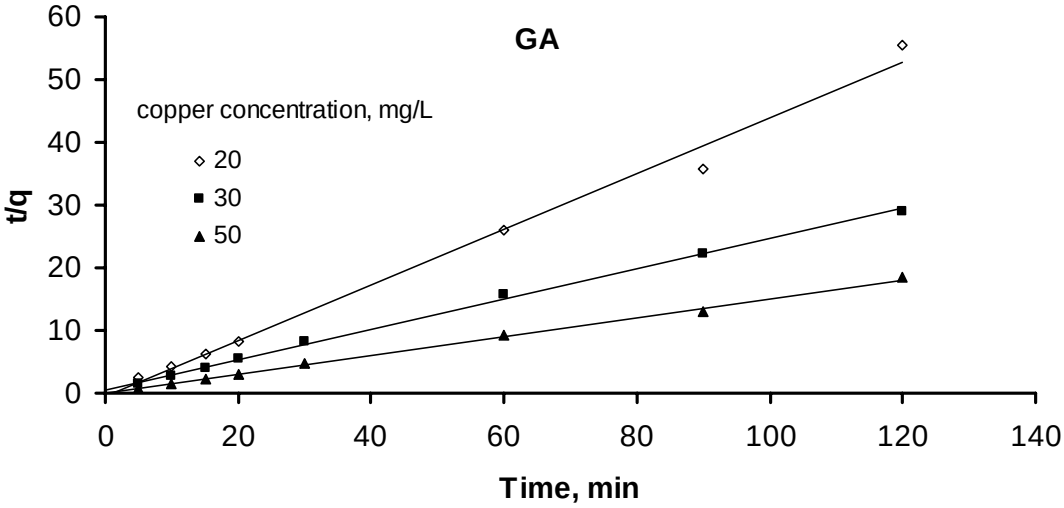



**Fig. (3): Time variation at different concentrations using 0.5 g of green algae (GA) and carbon green algae (CGA).**



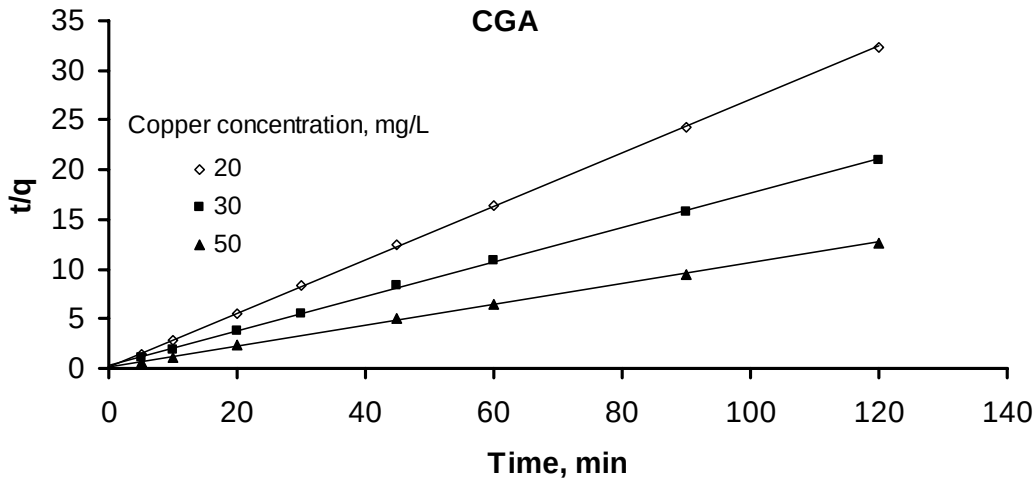




**Fig. (4): Pseudo- second order adsorption kinetic data for copper (II) onto GA and CGA.**

**Table (1): Adsorption kinetic model rate constants for GA and CGA at different doses of adsorbent**

| Adsorbent | Dose of adsorbent (g/L) | Initial Conc. of Cu (mg/L) | Pseudo first-order | | Pseudo second- order | | |
|---|---|---|---|---|---|---|---|
| | | | $k_1$ | $R^2$ | $k_2$ | h | $R^2$ |
| GA | 2 | 20 | 0.067 | 0.680 | 0.090 | 5.010 | 0.998 |
| | | 30 | 0.214 | 0.742 | 0.044 | 5.330 | 0.996 |
| | | 50 | 0.176 | 0.615 | 0.026 | 7.663 | 0.999 |
| | 3 | 20 | 0.160 | 0.874 | 0.065 | 1.906 | 0.994 |
| | | 30 | 0.130 | 0.751 | 0.042 | 2.407 | 0.998 |
| | | 50 | 0.133 | 0.626 | 0.035 | 4.785 | 0.999 |
| | 5 | 20 | 0.158 | 0.892 | 0.386 | 1.962 | 0.990 |
| | | 30 | 0.155 | 0.752 | 0.098 | 1.697 | 0.999 |
| | | 50 | 0.141 | 0.769 | 0.789 | 34.72 | 0.998 |
| | 10 | 20 | 0.158 | 0.820 | 0.704 | 1.013 | 0.996 |
| | | 30 | 0.050 | 0.764 | 0.401 | 1.488 | 0.997 |
| | | 50 | 0.132 | 0.788 | 0.457 | 4.184 | 0.994 |
| | 15 | 20 | 0.260 | 0.950 | 1.621 | 1.916 | 0.996 |
| | | 30 | 0.052 | 0.814 | 1.862 | 2.433 | 0.998 |
| | | 50 | 0.138 | 0.935 | 0.760 | 3.090 | 0.998 |
| CGA | 2 | 20 | 0.036 | 0.871 | 0.020 | 1.968 | 0.997 |
| | | 30 | 0.041 | 0.904 | 0.014 | 2.326 | 0.998 |
| | | 50 | 0.057 | 0.929 | 0.012 | 5.921 | 0.999 |
| | 5 | 20 | 0.044 | 0.481 | 0.357 | 4.948 | 0.999 |
| | | 30 | 0.044 | 0.666 | 0.103 | 3.408 | 0.999 |
| | | 50 | 0.045 | 0.703 | 0.063 | 5.804 | 0.999 |
| | 10 | 20 | 0.035 | 0.384 | 0.528 | 1.895 | 0.999 |
| | | 30 | 0.088 | 0.506 | 0.806 | 6.579 | 1.000 |
| | | 50 | 0.037 | 0.485 | 0.176 | 4.132 | 0.999 |
| | 15 | 20 | 0.040 | 0.498 | 0.635 | 1.060 | 1.000 |
| | | 30 | 0.041 | 0.372 | 0.963 | 3.529 | 0.999 |
| | | 50 | 0.050 | 0.577 | 0.419 | 4.442 | 1.000 |

### *3.4.3. Bangham's equation*

Bangham's equation (Aharoni *et al*., 1979) is given as:

$$\log\log\left(\frac{C_0}{C_0 - qm_s}\right) = \log\left(\frac{k_0 m_s}{2.303V}\right) + \alpha\log(t) \quad (7)$$

where $V$ is the volume of solution, α (<1) and $k_0$ are constants. The double logarithmic plot did not yield satisfactory linear curves for the removal of copper (II) onto GA and CGA ($R^2$ < 0.88). This shows that the film diffusion is not the only rate controlling parameter. It may be concluded that the film and pores diffusion were important to different extents in the removal process.

### *3.4.4. Intra-particle diffusion study*

The most commonly used technique for identifying the mechanism involved in the adsorption process is by using intra-particle diffusion model as (Weber and Morris, 1963):

$$q = K_d t^{1/2} + I \quad (8)$$

where $K_d$ is the intra-particle diffusion rate constant. If intra-particle diffusion occurs, then $q$ against $t^{1/2}$ will be linear and the line will pass through the origin if the intra-particle diffusion was the only rate limiting parameter controlling the process. Otherwise, some other mechanism is also involved. Fig. 5 presents intra-particle plot for copper (II) onto GA and CGA for different copper concentrations. The figure shows two linear portions, the first part of curve is attributed to boundary layer diffusion while, the final linear parts indicate effect of intra-particle diffusion. Values of $I$ give an idea about the thickness of the boundary layer. The diffusion rate parameters were shown in Table 2. The data indicate that intra-particle diffusion controls the sorption rate. Simultaneously, external mass transfer resistance cannot be neglected although this resistance is only significant for the initial period of time (Mall *et al*., 2006).

### 3.5. Adsorption Equilibrium Study

It is important to evaluate the most appropriate correlations for equilibrium curves, to optimize the design of a sorption system. Langmuir, Freundlich, Tempkin, Redlich-Peterson and Koble-Corrigan isotherm models were used to describe the adsorption equilibrium. Experimental isotherm data were conducted at an equilibrium time of 120 minutes for different dosages of adsorbate.

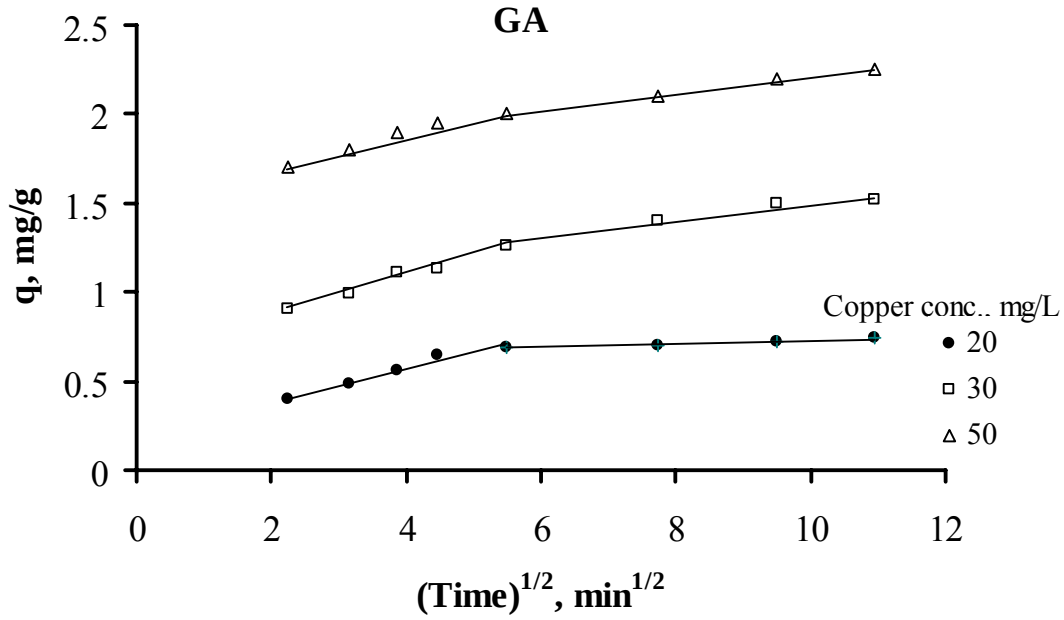
The Langmuir adsorption isotherm is based on the assumption that all sites possess equal affinity for the adsorbate. It may be represented in the linear form as follows (Langmuir, 1916):

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_m} + \frac{C_e}{Q_m} \quad (9)$$

where $Q_m$ is the maximum copper (II) uptake, mg/g, $K_L$ the Langmuir adsorption constant, L/mg. The model provides the maximum values where they could not be reached in the experiments. The values of $K_L$ were increased with increasing the dose of adsorbent for GA and CGA, respectively. High $K_L$ values indicate high adsorption affinity. The monolayer saturation capacity, Qm, were 24.5 and 32.3 mg/L for GA and CGA, respectively.

**Table (2): Intra-particle diffusion constants for copper(II) adsorption onto GA and CGA.**

| Adsorbent | Dose of adsorbent (g/L) | Initial Conc. of Cu (mg/L) | $K_{d1}$ | $I$ | $R^2$ | $K_{d2}$ | $I$ | $R^2$ |
|---|---|---|---|---|---|---|---|---|
| GA | 2 | 20 | 0.037 | 0.626 | 0.928 | 0.013 | 0.815 | 0.947 |
| | | 30 | 0.095 | 0.739 | 0.973 | 0.062 | 1.016 | 0.998 |
| | | 50 | 0.102 | 1.590 | 0.968 | 0.062 | 1.916 | 0.998 |
| | 5 | 20 | 0.057 | 1.992 | 0.926 | 0.092 | 1.865 | 0.944 |
| | | 30 | 0.087 | 3.387 | 0.914 | 0.093 | 3.121 | 0.980 |
| | | 50 | 0.102 | 6.094 | 0.932 | 0.100 | 6.322 | 0.975 |
| | 10 | 20 | 0.324 | 2.914 | 0.930 | 0.138 | 3.829 | 0.952 |
| | | 30 | 0.358 | 4.812 | 0.944 | 0.142 | 5.876 | 0.934 |
| | | 50 | 0.466 | 9.498 | 0.981 | 0.216 | 9.197 | 0.978 |
| | 15 | 20 | 0.458 | 4.531 | 0.902 | 0.109 | 6.786 | 0.990 |
| | | 30 | 0.571 | 7.407 | 0.938 | 0.172 | 8.475 | 0.958 |
| | | 50 | 1.187 | 10.37 | 0.969 | 0.235 | 15.37 | 0.968 |
| CGA | 2 | 20 | 0.521 | 5.163 | 0.995 | 0.207 | 7.364 | 0.936 |
| | | 30 | 0.725 | 6.487 | 0.954 | 0.221 | 9.221 | 0.941 |
| | | 50 | 1.037 | 13.16 | 0.988 | 0.260 | 18.67 | 0.969 |
| | 5 | 20 | 0.021 | 3.484 | 0.933 | 0.025 | 3.452 | 0.971 |
| | | 30 | 0.130 | 4.646 | 0.912 | 0.070 | 4.980 | 0.970 |
| | | 50 | 0.187 | 7.857 | 0.913 | 0.109 | 8.346 | 0.944 |
| | 10 | 20 | 0.012 | 1.750 | 0.907 | 0.019 | 1.691 | 0.983 |
| | | 30 | 0.031 | 2.627 | 0.931 | 0.020 | 2.764 | 0.951 |
| | | 50 | 0.044 | 4.363 | 0.908 | 0.048 | 4.305 | 0.954 |
| | 15 | 20 | 1.185 | 1.185 | 0.907 | 0.010 | 1.139 | 0.920 |
| | | 30 | 1.848 | 1.848 | 0.969 | 0.039 | 1.804 | 0.989 |
| | | 50 | 3.013 | 3.013 | 0.966 | 0.016 | 3.071 | 0.990 |



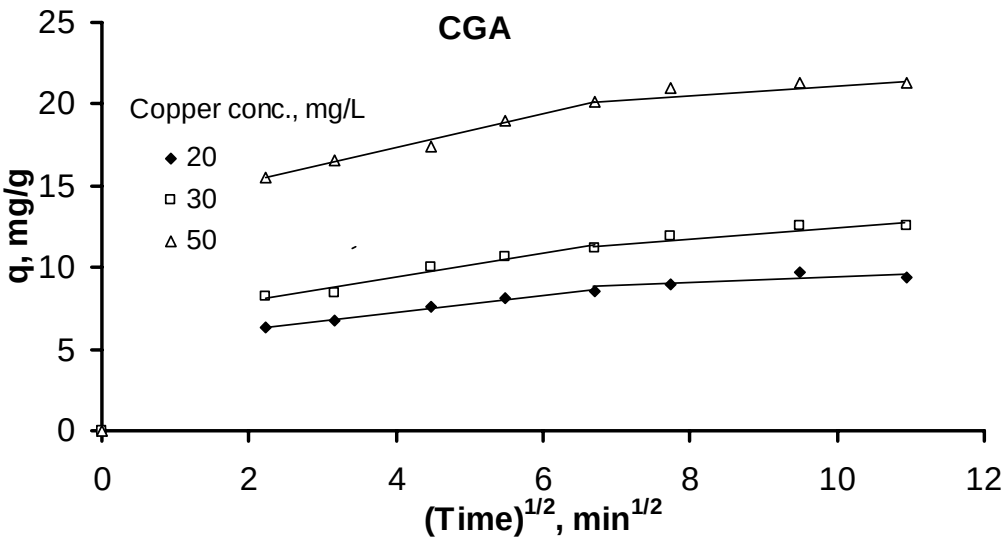




**Fig. (5): Intra-particle diffusion plots for the removal of copper onto GA and CGA at different concentrations (dosage = 2 g/L, pH = 5).**

The empirical Freundlich isotherm is based on the equilibrium relationship between heterogeneous surfaces. This isotherm is derived from the assumption that the adsorption sites are distributed exponentially with respect to the heat of adsorption. The logarithmic linear form of Freundlich isotherm may be represented as follows (Freundlich, 1906):

$$\log q_e = \log K_F + \frac{1}{n_F}\log C_e \quad (10)$$

where $K_F$ (L/g) and $1/n_F$ are the Freundlich constants, indicating the sorption capacity and sorption intensity, respectively. The magnitude of $K_F$ showed a high copper (II) adsorptive capacity of GA and CGA from aqueous solution studied. Table 3 also indicated that $0 < 1/n_F < 1$, indicating that copper (II) is favourably adsorbed by GA and CGA at all studied parameters.

Tempkin isotherm, assumes that the heat of adsorption decreases linearly with the coverage due to adsorbent-adsorbate interaction (Vijayaraghavan *et al.*, 2006). The Tempkin isotherm has generally been applied in the following linear form (Tempkin and Pyozhev, 1940):

$$q_e = B\ln A + B\ln C_e \quad (11)$$

$$B = \frac{RT}{b} \quad (12)$$

where $A$ (L/g) is Tempkin isotherm constant, $b$ (J/mol) is a constant related to heat of sorption, $R$ is the gas constant (8.314 J/mol K) and $T$ the absolute temperature (K). A plot of $q_e$ versus ln $C_e$ enables the determination of the isotherm constants A, b from the slope and intercept. The data are listed in Table 3.

Dubinin-Radushkevich (D-R) isotherm is another isotherm equation that proposed by Dubinin (Dubinin, 1960). He assumed that the characteristics of the sorption curves are related to the porosity of the adsorbent. The linear form of the isotherm can be expressed as follows:

$$\ln q_e = \ln Q_D - B_D\varepsilon^2 \quad (13)$$

where $Q_D$ is the theoretical maximum capacity (mol/g), $B_D$ is the D-R model constant ($mol^2/kJ^2$), $\varepsilon$ is the Polanyi potential and is equal to

$$\varepsilon = RT\ln(1+\frac{1}{C_e}) \quad (14)$$

The mean energy of sorption, $E$ (kJ/mol), is calculated by the following equation

$$E = \frac{1}{\sqrt{2B_D}} \quad (15)$$

The Calculated D-R constants and mean free energy for adsorption are shown in Table (3). The mean adsorption energy was found to be in the range of 0.9- 4 kJ/mol, which are in the energy range of physical adsorption reactions.

Redlich- Peterson isotherm (R- P) contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms into a single equation. The general isotherm equation can be described as follows (Redlich and Peterson, 1959):

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \quad (16)$$

where $K_R$ (L/g) and $a_R$ (L/mg) are R-P isotherm constants and $g$ is the exponent. The exponent, $g$, lies between 0 and 1. There are two limiting behaviors; Langmuir form for $g = 1$ and Henry's law for $g = 0$. The values of $K_R$ (Table 2) indicate that the adsorption capacity of GA and CGA also decreased with increasing dose of adsorbent. Furthermore, the value of g lies between 0 and 1, indicating favorable adsorption.

Koble-Corrigan model is another three parameter empirical model representing adsorption equilibrium data. It is given by

$$q_e = \frac{K_K C_e^{\alpha}}{1 + a_K C_e^{\alpha}} \quad (17)$$

where $K_K$, $a_K$ and $\alpha$ are the Koble-Corrigan parameters. This model is valid only when $\alpha > 1$ (Koble and Corrigan, 1952). The corresponding Koble- Corrigan parameters for different doses of adsorbent are also given in Table (3). The constant $\alpha$ is less than unity, meaning that the model is unable to describe the data in spite of the high value of $R^2$.

**Table (3): Isotherm constants for copper(II) adsorption onto GA and CGA.**

| Isotherm Model | parameters | Dose of green algae (g/L) | | | Dose of carbon green algae (g/L) | | |
|---|---|---|---|---|---|---|---|
| | | 2 | 5 | 10 | 2 | 5 | 10 |
| Langmuir | $Q_m$ | 24.51 | 9.074 | 4.885 | 32.26 | 12.484 | 5.935 |
| | $K_L$ | 0.058 | 0.106 | 0.147 | 0.237 | 0.333 | 0.6858 |
| | $R^2$ | 0.850 | 0.9404 | 0.966 | 0.9131 | 0.9352 | 0.8124 |
| | RMSE | 0.424 | 0.174 | 0.094 | 0.966 | 0.278 | 0.244 |
| | $X^2$ | 0.381 | 0.134 | 0.155 | 0.593 | 0.213 | 0.496 |
| Freundlich | $K_F$ | 1.739 | 1.0252 | 0.659 | 5.817 | 2.8125 | 2.0816 |
| | $1/n_F$ | 0.678 | 0.6238 | 0.6371 | 0.648 | 0.6402 | 0.5168 |
| | $R^2$ | 0.9998 | 0.9999 | 0.9821 | 0.9953 | 0.9977 | 0.9844 |
| | RMSE | 0.219 | 0.012 | 0.011 | 0.091 | 0.072 | 0.183 |
| | $X^2$ | 0.074 | 0.001 | 0.012 | 0.007 | 0.018 | 0.160 |
| Tempkin | b | 51.757 | 126.77 | 224.8 | 38.843 | 94.95 | 236.5 |
| | A | 1.028 | 1.617 | 2.072 | 4.248 | 5.527 | 18.583 |
| | $R^2$ | 0.9013 | 0.9242 | 0.9537 | 0.9013 | 0.9182 | 0.8108 |
| | RMSE | 0.916 | 0.329 | 0.144 | 1.312 | 0.493 | 0.397 |
| | $X^2$ | 2.243 | 0.645 | 0.239 | 3.303 | 1.062 | 1.445 |
| D-R | $Q_D$ | 8.396 | 3.850 | 2.231 | 13.01 | 5.646 | 2.635 |
| | E | 0.903 | 1.162 | 1.294 | 2.071 | 2.261 | 3.963 |
| | $R^2$ | 0.7207 | 0.7709 | 0.8181 | 0.8117 | 0.8577 | 0.754 |
| | RMSE | 1.911 | 0.777 | 2.513 | 2.586 | 0.975 | 3.857 |
| | $X^2$ | 5.11 | 1.867 | 40.09 | 5.830 | 1.895 | 73.37 |
| R –P | $K_R$ | 4.276 | 3.427 | 3.427 | 40.00 | 38.00 | 38.00 |
| | $a_R$ | 0.6222 | 3.645 | 3.644 | 6.006 | 13.032 | 18.929 |
| | g | 0.440 | 0.492 | 0.492 | 0.378 | 0.395 | 0.388 |
| | $R^2$ | 0.9959 | 0.9880 | 0.9880 | 0.9995 | 0.9985 | 0.9847 |
| | RMSE | 0.176 | 0.084 | 0.073 | 0.940 | 0.660 | 0.213 |
| | $X^2$ | 0.130 | 1.957 | 0.061 | 0.024 | 0.148 | 0.245 |
| Koble- Corrigon | $K_K$ | 1.12 | 0.7729 | 0.6702 | 5.925 | 3.249 | 2.524 |
| | $a_K$ | 0.0315 | 0.0707 | 0.1319 | 0.155 | 0.2109 | 0.282 |
| | $\alpha$ | 0.731 | 0.708 | 0.630 | 0.662 | 0.631 | 0.629 |
| | $R^2$ | 0.9902 | 0.9788 | 0.9813 | 0.9916 | 0.9852 | 0.9716 |
| | RMSE | 2.140 | 0.805 | 0.445 | 0.147 | 0.803 | 0.334 |
| | $X^2$ | 5.610 | 1.785 | 0.919 | 0.015 | 1.058 | 0.384 |

### 3.6. Error Analysis

The traditional methods of determining the isotherm parameters by linear regression equations appear to give very good fits to experimental data. However, the use of $R^2$ is limited to solve linear forms of isotherm equation, but not the errors in isotherm curves. Beside, the parameters of non-linear isotherm equations cannot be solved from the linear equation (Wong *et al.*, 2004). To evaluate the fit of isotherm equations to the experimental data, different error functions of non- linear regression basin were used to measure the isotherm constants and compare them with the less accurate linearized analysis values. The residual root mean square error (RMSE) and the chi- square test were used. RMSE can be defined as (Vijayaraghavan *et al.*, 2006):

$$RMSE = \sqrt{\frac{1}{n-2}\sum_{i=1}^{n}(q_{e,\exp} - q_{e,calc})^2} \quad (18)$$

The subscripts "exp" and 'calc" show the experimental and calculated values and n is the number of observations in the experimental isotherm. The small the *RMSE* value, the better the curve fitting. The chi-square test (Ho *et al.*, 2005) is given as:

$$X^2 = \sum_{i=1}^{n}\frac{(q_{e,\exp} - q_{e,calc})^2}{q_{e,\exp}} \quad (19)$$

If data from the model are similar to the experimental data, $X^2$ will be a small number; if they are different, $X^2$ will be a large number.

The values of the two error measurements were presented in Table (3). By comparing the values of the error functions, it was found that R- P and Freundlich models best fit the copper (II) adsorption onto GA. The models show high correlation coefficients and low RMSE and chi-square values. While, Freundlich isotherm best fitted the data for copper (II) removal onto CGA. Figures (6 and 7) show plots comparing different isotherm equations with experimental data for GA and CGA, respectively. Figure (6) shows an excellent fit of R-P and Freundlich models with experimental data for the removal of copper(II) onto GA, while Figure (7) shows an excellent fit of Freundlich model only with experimental data for the removal of copper(II) onto CGA. This confirms the results obtained by error analysis.

Although the Langmuir model did not show a precise fit, its sorption parameters can still provide valuable information. The maximum sorption capacity, $Q_m$ for adsorption of copper (II) onto GA and CGA were found 24.5 and 32.6 mg/g, respectively. The $Q_m$ values obtained for the present system in comparison with those reported earlier for sorption of copper (II) onto various adsorbents (Table 4) revealed that GA and CGA were effective adsorbent in removing copper.

### 3.6. Treatment of Wastewater

Three different streams; synthetic seawater, natural sea water and real wastewater were used to examine the validity of removing copper (II) from such streams using GA and CGA. Figure (8) shows a comparison between efficiency of copper (II) removal from aqueous solution and other examined solutions. The efficiency was slightly changed by replacing an aqueous solution by saline water or wastewater containing the same copper concentration indicating that there is only a little interference between ions present in salted water and wastewater with copper ions. The results suggested the applicability of using the two adsorbents GA and CGA for copper (II) removal from real wastewater effluents.

**Table (4): Comparison of adsorption capacity of Copper (II) with other adsorbents**

| Type of adsorbent | Adsorption Capacity (g/L) | reference |
|---|---|---|
| Rice bran | 33.58 | Wang and Qin, 2004 |
| Waste sugar beet Pulp | 31.4 | Aksu and Isoglu, 2005 |
| Carrot residue | 32.74 | Nasernejad *et al*., 2004 |
| Wheat shell | 10.84 | Basci *et al*., 2004 |
| Activated rubber wood sawdust | 5.73 | Kalavathy *et al*., 2005 |
| Bagasse fly ash | 2.26 | Gupta and Ali, 2000 |
| Present work | 32.3 | |

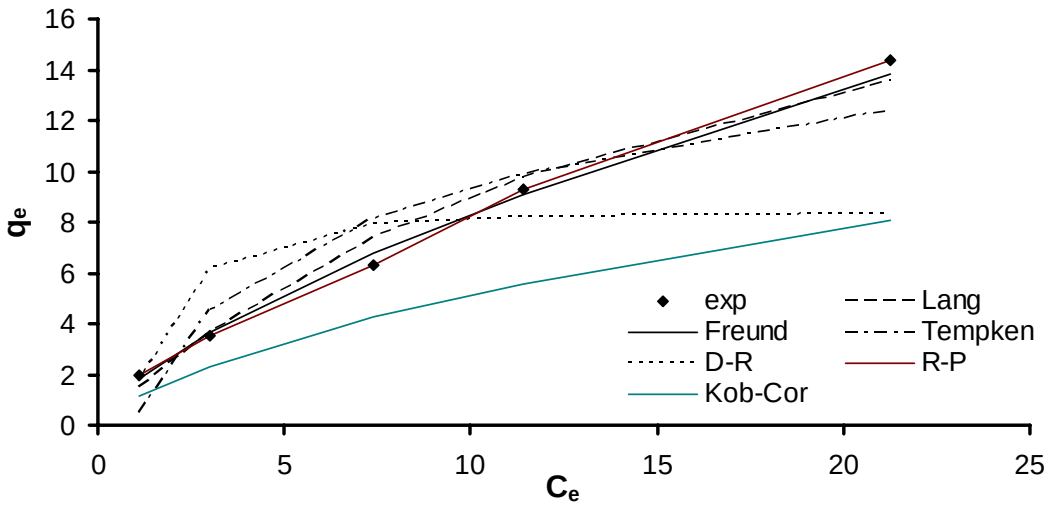



**Fig. (6): Equilibrium isotherms for the removal of copper by green algae (GA)**

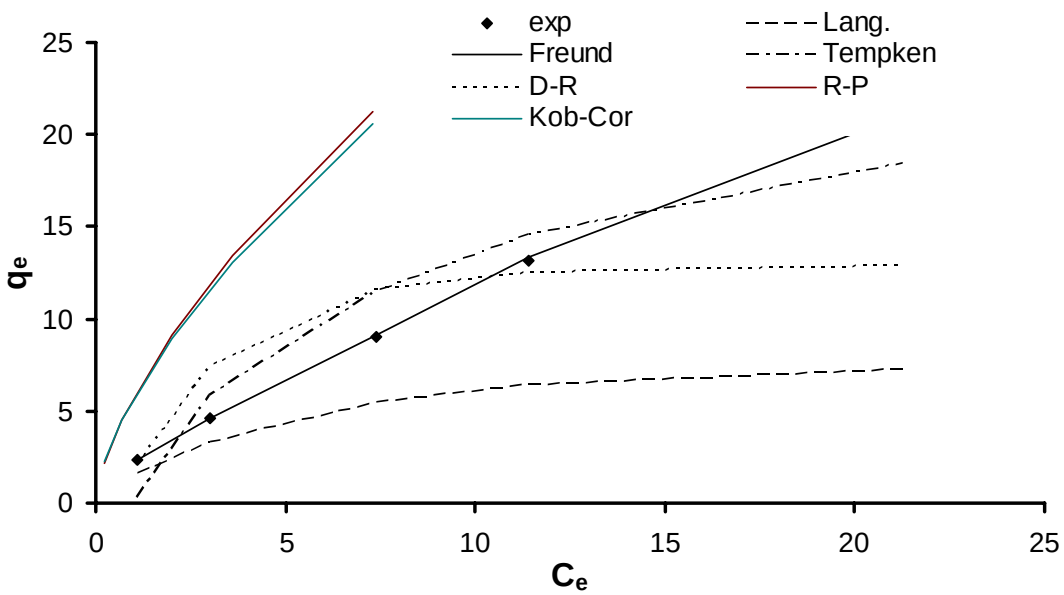



**Fig. (7): Equilibrium isotherms for the removal of copper by carbon green algae (CGA)**

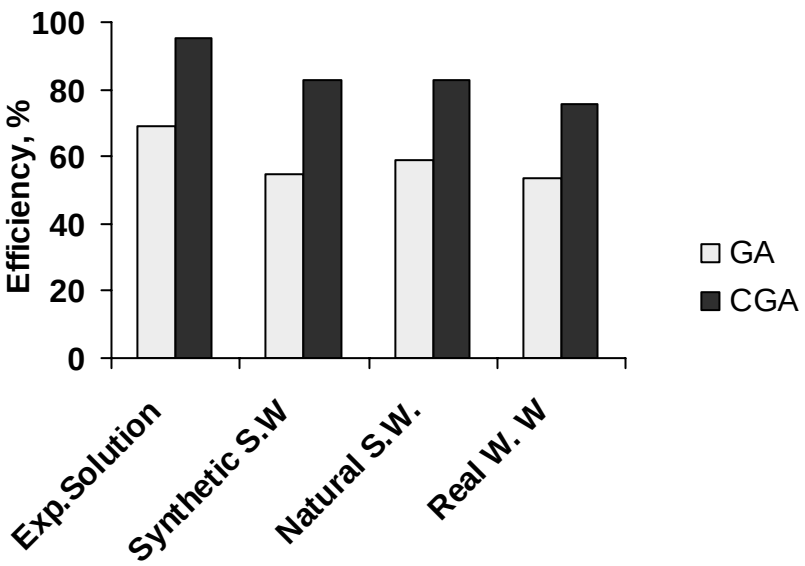



**Fig. (8): Adsorption of copper (II) from different solutions onto GA and CGA ($C_0$ = 30 mg/L, dosage of adsorbent = 5 g/L, pH = 5).**

## 4. CONCLUSIONS

Marine green algae (GA) *Ulva Lactuca*, and an activated carbon prepared from green algae (CGA) have been used as adsorbents for the removal of copper (II) from solutions. Adsorption was influenced by various parameters such as initial pH, initial copper (II) concentration and dose of adsorbents. The maximum uptake of copper (II) occurred at an initial pH of 5.0. Adsorption was increased with increasing dose of adsorbent and decreased with increasing initial copper (II) concentration. The maximum copper (II) uptake capacity was 24.5 and 32.3 mg/g for GA and CGA, respectively. It was attained at pH of 5.0 and adsorbent dosage of 2 g/L. These values are comparable to other adsorbents reported in literature for copper (II) adsorption. Kinetic and isotherm studies revealed that GA and CGA can be effectively employed for the adsorption of copper. Adsorption follows the Freundlich and R-P isotherms for GA and the Freundlich isotherm model for CGA. Adsorption was best fitted by the pseudo-second order model. Mechanism of adsorption was rather complex and is probably a combination of external mass transfer and intra-particle diffusion. The application of adsorption of copper (II) by GA and CGA had prove its efficiency in wastewater treatment applications. Since the marine green algae, the raw material used in the investigation, is freely and locally available, the adsorbent is expected to be economically viable for wastewater treatment.

## REFERENCES


Aharoni, C., Sideman, S., Hoffer, E.: 1979, "Adsorption of phosphate ions by colloid ion-coated alumina", *J. Chem. Technol. Biotechnol*. **29**: 404-412.

Ajmal, M., Khan, A.H., Ahmad, S., Ahmad A.: 1998, "Role of sawdust in the removal of copper (II) from industrial wastes", *Water Res*. **32**(10): 3085–3091.

Aksu, Z.: 2005, "Application of biosorption for the removal of organic pollutants: a review", *J. Process Biochemistry.* **40**: 997-1026.

Aksu , Z., Isoglu, I.A.: 2005, "Removal of copper(II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp", *J.Process Biochemistry*. **40**: 3031–3044.

Antunes, W.M., Luna, A.S., Henriques, C.A, Costa, A.C.: 2003, "An evaluation of copper biosorption by a brown seaweed under optimized conditions". *Electronic Journal of Biotechnology ISSN*: 0717-3458, **6**: 174- 184.

Basci, N., Kocadagistan, E., Kocadagistan, B.: 2004, "Biosorption of copper (II) from aqueous solutions by wheat shell", *Desalination.* **164**: 135-140.

Bois, L., Bonhomme, A., Ribes, A., Pais, B, Raffin, G., Tessier, F.: 2003, "Functioalized silica for heavy metal ions adsorption" *Colloids Surf. Physicochem. Eng. Aspects*. **221**: 221-230.

Dubinin, M.M.: 1960, "The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface", *Chem. Rev*. **60**: 235-266.

El-Sikaily, A., El Nemr, A., Khaled, A., Abdelwehab, O: 2007, "Removal of toxic chromium from wastewater using green alga *Ulva lactuca* and its activated carbon", *Journal of Hazardous of materials*. in press

Freundlich, H.M.F.: 1906, "u¨ber die adsorption in lo¨sungen", *Zeitschrift fu¨r Physikalische Chemie* **57**: 385–470.

Gupta, V.K., Ali, I.: 2000, "Utilization of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater", *Sep. Purif. Technol*., **18**: 131- 140.

Ho, Y.S., McKay, G., Wase, D.A.J, Foster, C.F.: 2000,"Study of the sorption of

divalent metal ions on to peat", *Adsorp. Sci. Technol*. **18**: 639–650.

Ho, Y.S., Chiu, W.T. and Wang, C.C.: 2005, "Regression analysis for the sorption isotherms of basic dyes on sugarcane dust", *Bioresource Technology*. **96**: 1285–1291

Kalavathy, M.H., Karthikeyan, T., Rajgopal, S., Miranda, L.R.: 2005, "Kinetics and isotherm studies of Cu(II) adsorption onto $H_3PO_4$- activated rubber wood sawdust", *Journal of Colloid and Interface Science*. **292**: 354-362.

Koble, R.A. and Corrigan, T.E.: 1952, "Adsorption isotherm for pure hydrocarbons", *Ind. Eng. Chem.* **44**: 383–387.

Kumar, Y.P., King, P. and Prasad, V.S.R.K.: 2006, "Removal of copper from aqueous solution using *Ulva fasciata* sp.—A marine green algae", *Journal of Hazardous Materials* **B137**: 367–373.

Lagergren,S.: 1898, "Zur theorie der sogenannten adsorption geloster stoffe kungliga svenska vetenskapsakademiens", *Handlingar*. **24**, 1–39.

Langmuir, I.: 1916, "The constitution and fundamental properties of solids and liquids", *J. Am. Chem. Soc*. **38**: 2221–2295.

Li, W., Zhang, S. and Shan, X-q,: 2007, "Surface modification of goethite by phosphate for enhancement of Cu and Cd adsorption", *Colloids and Surfaces A: Physicochem. Eng. Aspects*. **293**: 13–19.

Mall, D.I, Srivastava, V.C. and Agarwal, N.K.: 2006, "Removal of Orange- G and methyl violet dyes by adsorption onto bagasse fly ash- kinetic study and equilibrium isotherm analyses", *Dyes and pigments*. **69**: 210- 223.

Nasernejad, B., Zadeh, T.E., Pour, B.B., Bygi, M.E. and Zamani, A: 2004, "Comparison for biosorption modeling of heavy metals (Cr (III), Cu (II), Zn (II)) adsorption from wastewater by carrot residues", *Process Biochemistry*. **40**: 1319- 1322.

Periasamy, K, Namasivayam, C.: 1996, "Removal of copper(II) by adsorption onto peanut hull carbon from water and copper plating industry wastewater", *Chemosphere* **32**: 769- 789.

Redlich, O. and Peterson, D.L.: 1959, "A useful adsorption isotherm", *J. Physical Chemistry*. **63**: 1024- 1026.

Tempkin, M.J. and Pyozhev, V.: 1940, "Acta Physicochim. USSR 12: 327- 352

Vijayaraghavan, K., Padmesh, T.V.N., Palanivelu, K, Velan, M.: 2006, "Biosorption of nickel(II) ions onto Sargassum wightii: Application of two-parameter and three- parameter isotherm models", *J. of hazardous materials*; (**B133**): 304- 308.

Wang, X.S. and Qin, Y.: 2004, "Equilibrium sorption isotherms for $Cu^{2+}$ on rice bran and thermodynamic parameters", J. *Process Biochemistry*. **39**, 2183- 2191

Weber, W.J. and Morris, J.C.: 1963, "Kinetics of adsorption on carbon from solution". *Sanit Eng Div Am Soc Civ Eng*. **89**(SA2): 31-40.

Weng, C.H., Tsai, C-Z., Chu, S-H, Sharma, Y.C.: 2007, "Adsorption characteristics of copper(II) onto spent activated clay", *Separation and Purification Technology*, **54**: 187–197.

Wong, Y.C., Szeto, Y.S., Cheung, W.H., McKay, G.: 2004, "Adsorption of acid dyes on chitosan- equilibrium isotherm analyses", *Process Biochemistry*, **39**: 693-702.