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Research Article

ADSORPTION OF Cu(II) IONS FROM AQUEOUS SOLUTION USING MICROWAVE ASSISTED *PTEROCARPUS MARSUPIUM* BARK CARBON

G. Abinaya, S. Sivajiganesan*, V. Nandhakumar, S. Surya
PG & Research Department of Chemistry, A.V.V.M. Sri Pushpam College
(Affiliated to Bharathidasan University), Poondi, Thanjavur (Dt), Tamil Nadu, India
**Corresponding author: avvmspcssg@gmail.com*

ABSTRACT

An effective adsorbent was prepared from bark of *Pterocarpus Marsupium* tree and its various adsorption characteristics were studied for removal of Cu(II) ions from aqueous solution. Optimized conditions for the preparation of effective activated carbon were found to be microwave radiation power 850W, radiation time 15 min, 50% of $ZnCl_2$ and impregnation time 24 hours. Batch mode adsorption experiments were carried out. Influence of the parameters such as Dose of the adsorbent, agitation time, initial dye concentration, pH of the solution and temperature on adsorption were studied. Kinetics of the system was studied with linearised forms of Lagergren, Ho and Webber Morris models. Equilibrium data were fitted with Langmuir and Freundlichisotherms. The order of best describing isotherms was given based on R^2 value.

Keywords: Adsorption, Isotherms, Kinetics, Activated microwave carbon.

1. INTRODUCTION

Heavy metals are discharged into water from various industries. They can be toxic or carcinogenic in nature and can cause severe problems for humans and aquatic ecosystems. Thus, the removal of heavy metals from wastewater is a serious problem [1]. Heavy metals cannot be degraded or destroyed. Heavy metal toxicity could result, for instance, from drinking-water contamination (*e.g.* lead pipes), increased ambient air concentrations near sources of emission, or ingestion via the food chain [2]. Among the most toxic metals are Cu, Cd, Pb, Zn, and Ni. These metals have been reported by researchers to have negative health effect on humans, aquatic life, plant, and the environment at large [3-6]. The adsorption process is widely used for the removal of heavy metals from wastewater because of its low cost, availability and eco-friendly nature [1]. The aim of this study was to evaluate adsorption isotherms and kinetics parameters of Cu(II) ions from aqueous solutions through adsorption technique using activated carbon prepared from *Pterocarpus Marsupium* bark by using microwave oven with simultaneous activation method. The prepared carbon was designated as Microwave assisted *Pterocarpus Marsupium* Bark (MWPMBC Carbon). Experiments were carried out in a batch process. Effect of pH, activated carbon dosage and contact time with different initial Cu(II) ion concentrations were investigated.

2. MATERIAL AND METHODS

2.1. Preparation of Activated Carbon

The MWPMBC carbon was prepared from *Pterocarpus Marsupium* bark through microwave oven. Firstly; *Pterocarpus Marsupium* bark were collected and cut into small pieces. The materials were then thoroughly mixed with different % concentration of $ZnCl_2$ [7] solution and heat-treated at 850 W in microwave oven [8] for 15 minutes. After that, the found samples were washed away thoroughly with dilute hydrochloric acid (HCl) and deionized water till the pH values reached 7.0 and finally dried at 105°C.

2.2. Preparation of adsorbates solution

Standard solutions of 1000 mg/L were prepared by dissolving 3.9294 g of $CuSO_4{\cdot}5H_2O$ in one liter of distilled water.

2.3. Adsorption Experiments

The effect of functions such as adsorbent dose, solution pH, initial concentration of adsorbate and contact time was investigated by batch technique. A 250 ml iodine flask, 50 ml and a pre-determined concentration of the adsorbate solution were transferred into the container.

Then the content was rotated in a cycle using a cycle for a prearranged duration of 180 min. The effect of pH was calculated via bringing the preferred pH of the solutions by adding con. 0.1 N HCl/0.1N NaOH solution. The kinetics investigates were performed with the working pH 7 and for contact times 5, 10, 20, 40, 60, 80, 100, 120 and 140 minutes. All investigates were conducted in the batch system. The batch system was chosen due to its simplicity and reliability. To ensure the equivalent mixture, throughout the test, there was no strain (180 RPM) for each run. Concentration of metal ions before and after adsorption was measured using a double beam UV Visible spectrophotometer. Standards for the establishing of calibration curves were prepared by weakening the stock solutions so as to have 10, 15, 20, 25 and 30 mg/L of the metal ions and the absorbance of the solution at the respective wave lengths were recorded. The wave length of extreme absorbance for the Cu(II) ion is 580 nm.

The amount of Cu(II) ion ions adsorbed in milligram per gram of adsorbent was determined by using the following mass balance equation:

$$qe = (Ci-Ce)V/W$$

Where Ci and Ce are Cu(II) ion concentrations (mg/L) before and after adsorption, respectively, V is the volume of adsorbate in litre and m is the weight of the adsorbent in grams. The percentage of removal of Cu(II) ion was calculated using the following equation:

$$\text{Removal } (\%) = (Ci-Ce)/Ci \times 100$$

3. MATERIAL AND METHODS

3.1. Effect of pH on metal ion

It is well known fact that the adsorption of heavy metal ions depends on the pH of the aqueous solution.

Removal of Cu(II) ions by MWPMBC increases with increase in pH and attains a maximum in the pH range 5.0 to 6.0 shown in fig. 1. Afterwards, it was found to decrease. Both adsorption and precipitation processes would have been occurred at pH >6 [9]. The decrease in the percentage of removal above the pH 6 might probably be due to the precipitate blocking the adsorbent sites leading to a reduced uptake by adsorption. The influence of pH on Cu(II) removal can be explained on the basis of an electrostatic interaction mode. $pH_{zpc}$of the MWPMBC is 6.78. As the pH decreases below the pH $_{zpc}$ of the adsorbent, the surface of the carbon exhibits increasing positive characteristics. Since the species to be adsorbed, Cu^{2+}, was also positive, the adsorption is not favoured [10]. Besides this, H^+ ions present at a higher concentration in the reaction mixture compete with Cu^{2+} ions for the adsorption sites resulting in the reduced uptake of Cu(II). On the contrary, as pH increases the adsorbent surface becomes more and more negatively charged and therefore the adsorption of positively charged Cu^{2+} and $Cu(OH)^+$ species is more favourable. The mechanism of adsorption of Cu(II) may also be explained based on ion exchange model [11]. A pure carbon surface is considered to be nonpolar, but in actual practice some carbon-oxygen complexes (C_xO, CO_x and C_xO_2) are usually present, which render the surface slightly polar. Since there is no satisfactory method for determining the polar character of the surface quantitatively, the above statement is relative [12].

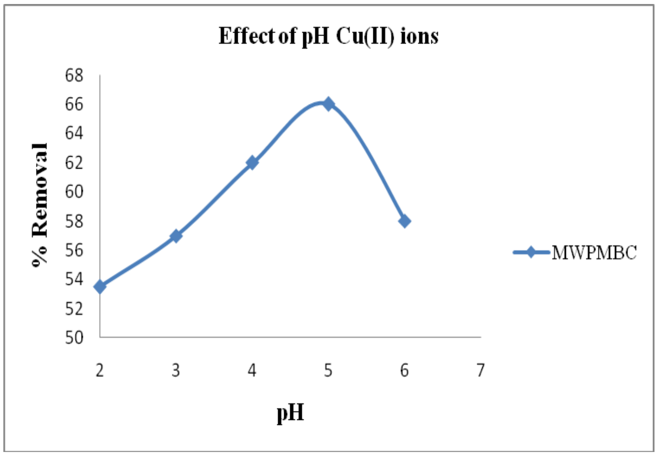

Fig. 1: Effect of pH for Cu(II) ions onto MWPMBC

3.2. Effect of adsorbent dosage

Effect of adsorbent dosage was studied by varying the carbon dose from 10 to 100 mg, taking 50 mL of adsorbate solution. The aliquots were stirred in a rotary shaking machine at 180 rpm for 180 minutes. The percentage of removal of adsorbate from aqueous solution increased with an increase of carbon dose in all the cases which was shown in fig. 2. This is due to the increased carbon surface area and the availability of moreadsorption sites

3.3. Effect of the contact time and initial concentration

The adsorption process was characterized by a rapid uptake of the adsorbate at the initial stages. The rate of percentage removal was found to decrease afterwards as the contact time increases and become constant after attaining equilibrium stage in all the cases was shown in fig. 3.

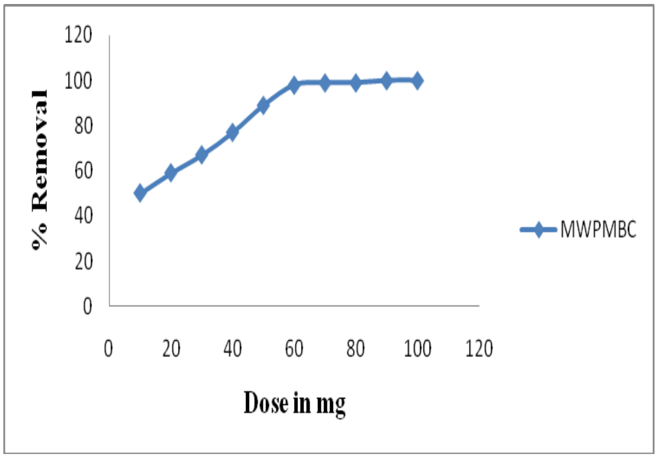

Fig. 2: Effect of Dose for Cu(II) ions onto MWPMBC

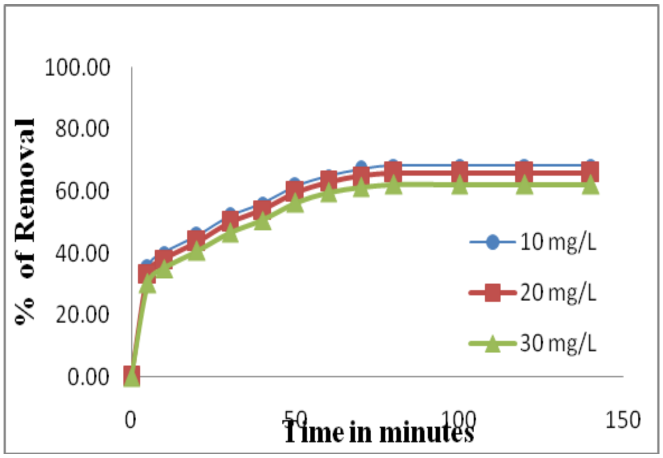

Fig. 3: Effect of Contact times and with different initial concentrations

3.4. Isotherm studies

The presence of equilibrium between two phases (liquid and solid phase) is rationalized by adsorption isotherm. The equilibrium data obtained from the experiments were processed with the following isotherm equations such as Langmuir and Freundlich adsorption isotherm models [13].

3.4.1. Langmuir isotherm

It is a widespread-used model for describing heavy metal ion/dye sorption onto adsorbent. Langmuir equation relates to the coverage of molecules on a solid surface and the concentration of contacting solution at a fixed temperature.

This isotherm is based on the following assumptions such as adsorption limited to monolayer coverage, all surface sites being alike one site accommodates one species of the adsorbates and the ability of a molecule to be adsorbed on a given site independent of its neighboring sites occupancy.

Langmuir equation is written in the following form [14]:

$$Q_e = Q_m b\, C_e / 1 + b\, C_e$$

This equation is often written in linear form as

$$C_e / Q_e = 1/Q_m b + C_e / Q_m$$

Where, Q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e the equilibrium concentration of solute in the bulk solution (mg/L), Q_m is the maximum monolayer adsorption capacity or saturation capacity (mg/g) and bis the adsorption energy, bis the reciprocal of the concentration at which half saturation of the adsorbent is reached. The linear equation is often preferred because of its simplicity and convenience.

The mono layer adsorption capacity Q_m values (mg/g) for adsorption of Copper (II) ions onto MWPMBC system ranged from 43.478 to 52.083 were given in table 1 and shown in fig. 4. MWPMBC seems to have a higher adsorption capacity with respect to the adsorption of Copper (II) ions for all the studied temperatures.

Table 1: Isotherm parameters for removal of Copper (II) ions onto MWPMBC

Temperature (K)	**Q_m** (mg/g)	**B** (L/mg)	**R^2**
305	43.478	0.048	0.9937
315	46.296	0.056	0.9915
325	49.020	0.064	0.9869
335	52.083	0.076	0.9817

The essential characteristics of Langmuir isotherm can be described by a separation factor, R_L, which is defined by the following equation

$$R_L = 1 / (1 + bC_i)$$

Where C_i is the initial concentration of the adsorbate solution. The separation factor R_L indicates the shape of the isotherm and the nature of the adsorption process as given below:

R_L value	**Nature of the process**
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The dimensionless separation factor R_L values calculated for various initial concentrations at different temperatures are lie between 0 and 1 which indicates the favourable adsorption of Copper (II) ions onto MWPMBC. These R_L values are presented in table 2.

Table 2: R_L values for removal of Copper (II) ions onto MWPMBC

Temperature	C_i	R_L
305	10	0.674
	20	0.508
	30	0.407
315	10	0.642
	20	0.473
	30	0.374
325	10	0.609
	20	0.438
	30	0.342
335	10	0.568
	20	0.397
	30	0.305

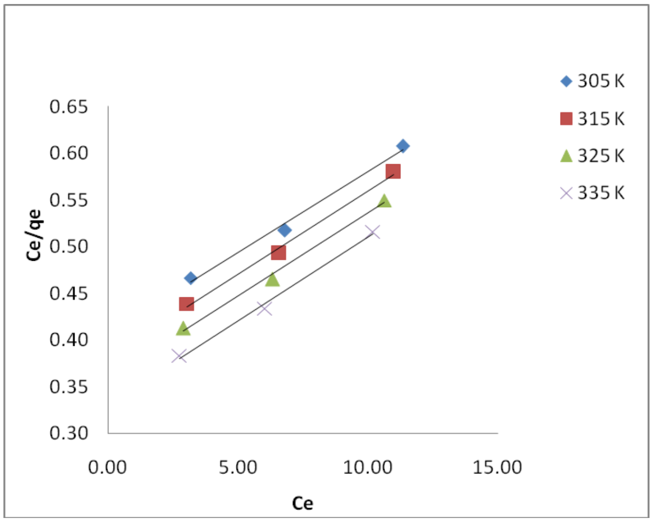

Fig. 4: Langmuir - Isotherm for Cu(II) ions onto MWPMBC

3.4.2. Freundlich Isotherm

Freundlich isotherm is an empirical equation. It is the most popular model for a single solute system based on the distribution of solute between the solid phase and aqueous phase at equilibrium. It also suggests that sorption energy exponentially decreases on completion of the sorptional centres of an adsorbent. The Freundlich model describes the adsorption within a restricted range only. It is capable of describing the adsorption of organic and inorganic compounds on a wide variety of adsorbents.

This equation has the following form [14]:

$$\log q_e = \log K_f + 1/n \log C_e$$

Where q_e is the amount of adsorbate adsorbed (mg/g) at equilibrium, C_e is the equilibrium concentration of adsorbate in solution (mg/L) and K_f and n are the constants incorporating all factors affecting the adsorption capacity and intensity of adsorption respectively.

Freundlich constant K_f (mg/g) for adsorption of Cu(II) ions onto MWPMC system, the values ranged from 3.0019 to 3.8362 were given in Table 3 and shown in fig. 5.The adsorption intensity constant 'n' values are ranged from 1.3490 to 1.4747 for all the studied systems, i.e., between 1 and 10, which indicates the favourable physical adsorption. 'n' value increases with an increase of temperature for all the studied systems.

Table 3: Freundlich isotherm constants for the adsorption of metal ions

Temperature (K)	n	K_f(mg/g)	R^2
305	1.3490	3.0019	0.9931
315	1.3864	3.2397	0.9886
325	1.4257	3.5035	0.9840
335	1.4747	3.8362	0.9771

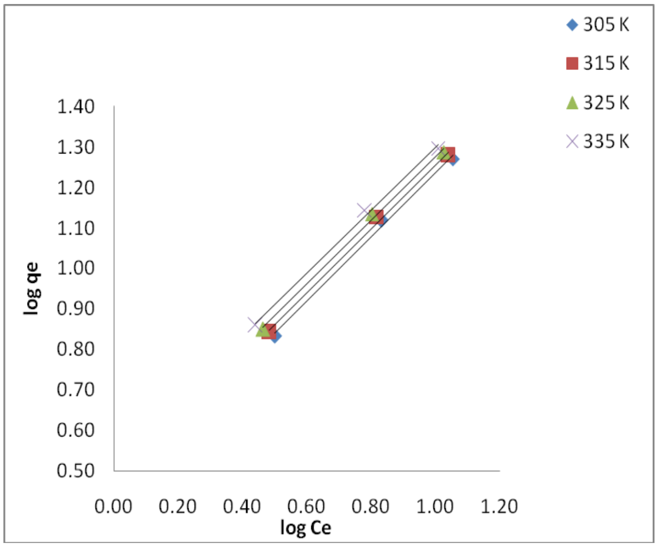

Fig. 5: Freundlich Isotherm for Cu(II) ions onto MWPMBC

3.5. Kinetic study

Generally, several steps are involved in the sorption process by porous sorbent particles: (i) Bulk diffusion; (ii) External mass transfer (boundary layer or film diffusion) between the external surface of the sorbent particle and the surrounding fluid phase; (iii) Intraparticle transport within the particle and (iv) Reaction kinetics at phase boundaries [15].

In practice, kinetic studies were carried out in batch reactions using various initial sorbate concentrations. Sorption kinetic models have been proposed to clarify the mechanism of sorption from aqueous solution to on an adsorbent. Several adsorption kinetic models have been established to understand the adsorption kinetics and rate-limiting step. These include pseudo-first and second-order rate model, Weber and Morris sorption kinetic models.

3.5.1. Pseudo first order kinetics

The linearised form of the pseudo-first order equation of Legergren is generally expressed as follows [15]

$$\log (q_e-q_t)=\log q_e - k_1 /2.303 \times t$$

Where, q_e and q_t are the adsorption capacity at equilibrium and at time respectively (mg/g). k_1 is the rate constant of pseudo first-order adsorption. The plot of log (q_e -q_t) versus t should give a linear relationship; k_1 and q_e can be calculated from the slope and intercept of the plot, respectively.

3.5.2. Pseudo second order kinetics

The pseudo second order kinetic model (Ho equation) is represented by the following linear equation [15]

$$t/q_t = 1/ k_2.q_e^2 +1/q_e\, t$$

Where, q_e and q_t are the adsorption capacity at equilibrium and at time respectively (mg/g).

The initial adsorption rate, h (mg/(g min)), as t⟶0 can be defined as

$$h = k_2 q_e^2$$

The Plot is drawn between of t/q_t and t. Theoretical adsorption capacity (q_e), and the second-order rate constants k_2 (g/(mg min)) can be determined experimentally from the slope and intercept of plots.

3.5.3. Intra particle diffusion

The mechanism of adsorption of a sorbate on a sorbent follows a series of steps. The slowest of these steps control the overall rate of the process. Generally, pore and intra particle diffusion are often ratelimiting in a batch reactor while for a continuous flow system, film diffusion is the rate limiting step [14, 15].

The effect of contact time experimental results can be used to study the rate limiting step in the adsorption process, as shown by Weber and Morris. According to Weber and Morris, an intra-particle diffusion co-efficient K_p is defined by the equation:

$$q_t = k_p t^{0.5} + C$$

Weber and Morris plots were drawn between q_t and $t^{0.5}$ to understand the intra particle diffusion. Where K_p ($mg/g/min^{0.5}$) is the intra particle diffusion rate constant and C is the thickness of the boundary film. The K_p and C values were obtained from the slope and intercept of the linear portions of the Weber and Morris plots.

3.5.4. Test for kinetics models

Best fitting kinetic model can be determined by comparing the theoretically calculated adsorption capacity at equilibrium ($q_{e(cal)}$) values from the respective kinetic models with the experimentally determined adsorption capacity($q_{e(exp)}$). The kinetic model which gives the closer '$q_{e(cal)}$' values with the experimental '$q_{e(exp)}$' values can be considered as the best fitting kinetic model. This can be known from the statistical tool 'Sum of Squared Error' (SSE)as evaluated by the following formula [14,15];

$$SSE = \sqrt{\sum[(q_e)_{exp}-(q_e)_{cal}]^2 / N}$$

Where N is the number of data points, (q_e)exp is the experimental q_e and (q_e) calis the calculated q_e. The theoretical adsorption capacity ($q_{e(cal)}$) values for the pseudo first order kinetic model can be calculated from the intercepts of the linear Legergren plots. In the case of pseudo second order kinetic modeltheoretical adsorption capacity ($q_{e(cal)}$) value can be calculated from the slope of the Ho linear plots.

The analysis of the results obtained in the present study with two kinetic models is presented in table 4 and 5 and shown in fig. 6 & 7. Between the first order and second order, second order kinetic model seems to best describe the above adsorption system as it has R^2 value which was very close to unity.

Table 4: First order kinetic parameters for the adsorption of metal ions

C_i (mg/L)	k_1 (10^{-2} min^{-1})	$q_{e(cal)}$ (mg/g)	$q_{e(exp)}$ (mg/g)	R^2	SSE
10	0.0288	14.3648	6.82	0.9982	4.54
20	0.0288	11.0510	13.18	0.9977	
30	0.0286	7.5336	18.66	0.9971	
40	0.0283	3.7993	23.20	0.997	

Table 5: Second order kinetic parametersfor theadsorptionof metal ions

C_i (mg/L)	k_2 (10^{-2} g/mg.min)	$q_{e(cal)}$ (mg/g)	$q_{e(exp)}$ (mg/g)	H	R^2	SSE
10	0.0189	7.24	6.82	0.99	0.9922	0.52
20	0.0095	14.03	13.18	1.86	0.9918	
30	0.0064	19.92	18.66	2.53	0.9911	
40	0.0047	24.94	23.20	2.94	0.9899	

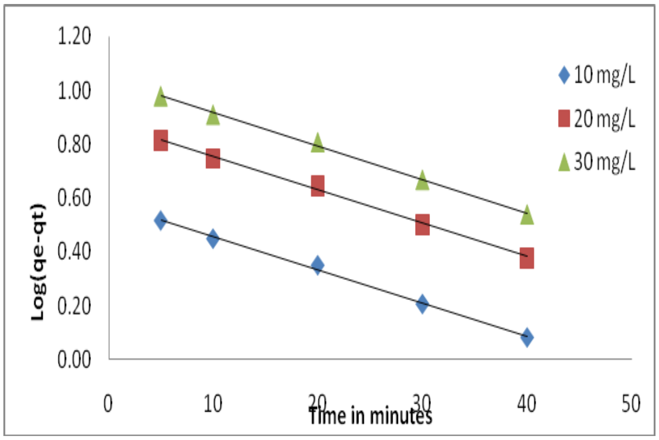

Fig. 6: Lagergren plot for Cu(II) ions onto MWPMBC

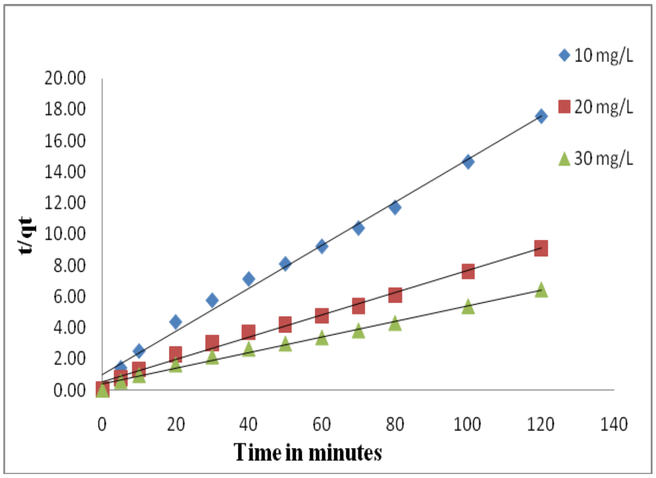

Fig. 7: Ho plot for Cu(II) ions onto MWPMBC

Moreover, the difference between calculated adsorption capacity (qe_{cal}) and experimental adsorption capacity (qe_{exp}) values of second order is little when compared to first order kinetic model for the both Cu(II) ions onto MWPMBC system for each initial concentrations.

Statistically it is tested with the tool sum of error squares) (SSE %). The Δqe and SSE % values were given in table 4 and 5 which it was concluded that the second order kinetic model was more appropriate rather than the first order kinetic model. The conformance of this plot to the pseudo second order is extremely high.

The most commonly used technique for identifying the mechanism involved in the sorption process is by fitting the experimental data in an intra-particle diffusion plot as suggested by Webber-Morris. Calculated intra particle diffusion coefficient K_p (mg/g $min^{0.5}$) values for the adsorption metal ions are presented in the table 6 and shown in fig.8. The increase of K_p values with a rise in initial concentration shows that pore diffusion limits the rate of the adsorption.

Table 6: Intra Particle Diffusion parameters for the adsorption of metal ions

Concentration (mg/L)	Intra Particle Diffusion	
	k_p (mg/g.min)	R^2
10	0.5969	0.994
20	1.1865	0.9938
30	1.7471	0.9932

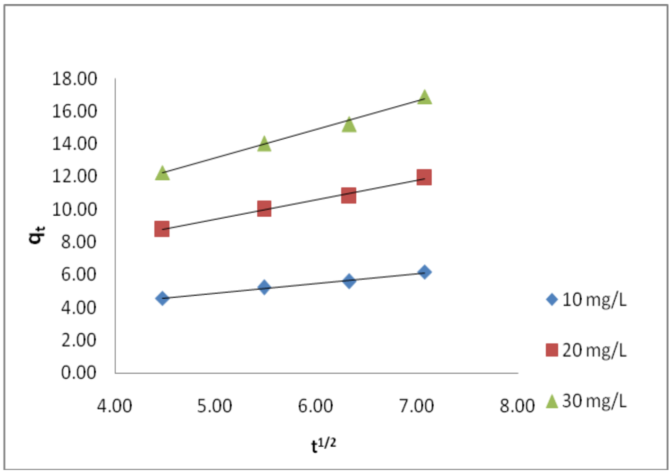

Fig. 8: Weber and Morris plot for Cu(II) ions onto MWPMBC

4. CONCLUSION

This study show that activated carbon prepared from bark of *Pterocarpus Marsupium* act as a good adsorbent to remove Cu(II)ions from aqueous solution. The application of Langmuir isotherms to experimental data shows that copper adsorption increases with increase of temperature for Cu(II)ions onto MWPMBC system. Experiments conducted in this work show that the maximum copper adsorption capacity depends on the ionic strength and the predominant copper species in the aqueous solution. The binding of these metal ions was observed to be a feasible and corresponds with the Langmuir isotherm model. The binding was also observed to be in agreement with pseudo-second-order and intraparticle diffusion model.

Conflict of interest

None declared

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