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Anew simple method for the treatment of waste water containing Cu (II) and Zn(II) Ions using adsorption on dried *Conocarpus erectus* leaves

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ABSTRACT

Anew simple method for the treatment of waste water effluent containing Cu(II), Zn(II) was developed using dried*Conocarpus erectus*leavesas a low-cost natural . Batch experiments were conducted to determine the effects of varying adsorbent weight, pH, contact time, metal ion concentration and temperature of adsorption. The adsorption of cu (II) was found to be maximum (94.7%) at pH9, at 25°C, metal ion concentration 100 ppm , contact time 60 min andSpeed Shake(185rpm) . adsorption capacity of Cu (II) and Zn were found maximum (94.7% and 93.3%)respectively at optimum conditions. The order of the removal of the efficiency of these metals was found Cu> Zn. Freundlich isotherm was found to be suitable for the adsorption of Cu(II),Zn(II),functional groups[(C-N), (C-O),(C=O),(O-H)] identification was given using FTIR spectrophotoscopy.

Key words: adsorption, copper and zinc, Freudlichisotherm ,Temkin model,*Conocarpus erectus leaves*

1.NTRODUCTION

The toxicity of heavy metals in the environment is still major concerns of human life; because they accumulate in living tissues throughout the food chain which has humans at its top. The danger of these heavy metals is due to poisoning, cancer, and brain damage[1].Thetreatment of water and waste water containing heavy metal is very demanding. Such methods of treatment include precipitation [2], flotation [3], biosorption [4–6], electrolytic recovery, membrane separation [7], removal by adsorption on minerals [8,9] and activated carbon adsorption [10,11].Despite these wide methods, they have disadvantages, which include incomplete metal removal requirements and expensive equipmen. Recently many researchers the wide world investigated low-cost adsorbents with high metal binding capacities. Agricultural by-products have been widely used for the treatment of water containing heavy metal. These agricultural materials include; peat, wood, pine bark, banana pith, soybean , cotton seed hulls, peanut shells, hazelnut shell, rice husk, saw dust, orange peal, compost and leaves [12]. The present work is attempted to investigate the possibility of the utilization of one kind of tree leaves: *Conocarpus erectus* for the removal of Cu(II), Zn(II) from waste water. Optimization variables include; contact time, pH ,temperature, particle size, and initial ion concentration. The Freundlich, Langmuir and Temkin adsorption isotherms were used to investigate the adsorption process. Kinetic study was also carried out to evaluate the order of adsorption[13].

2.*Adsorption experiments*

For the adsorption experiment, the effect of adsorbent weight on the adsorption of the ions was investigated (0.5 -2g) of the adsorbent wereweighted respectively into conical flasks. 20 ml of 100 mg/L solution of each of the metal ions solution was added and the mixture was shaken at 185 rpm for 60 min. After the biosorption experiment, the biosorbent was separated from the solution by filtering through a Whatman (0.45 µm) filter paper and the filtrate was analyzed for the Cu(II), Zn(II) ions concentration. TheCu(II), Zn(II) ions concentrations before and after the biosorption were determined by using Flame Atomic Absorption Spectrophotometer (Shimadzu 6000). The equilibriumCu(II), Zn(II) ions sorptioncapacity could be calculated as the equation bellow;[14]

$$Q_e = V(C_\circ - C_e)/m \qquad (1)$$

Where ;Q_e is the equilibrium Cu(II), Zn(II)) ions sorption capacity (mg/g), V is the suspension volume (l), m is the mass of durian material (g),*Co* = Initial concentration of solution, *Ce*= Concentration of the solution after adsorption. To determine the effect of the concentration on the adsorption of the metal ions, 2g of the adsorbent, being the optimum adsorbent weight in the previous experiment was added to 50 ml each of varying concentrations (between 5 - 100 mg/L) of the metal ion solutions. The mixtures were shaken and the concentration of the metal ions adsorbed was determined. The effect of contact time was also investigated by adding 2g of the adsorbent to 20 ml of 50 mg/L of Cu(II), Zn(II) ions being their respective optimum adsorption concentrations; and shaking using varying contact times (30 –180 min) and the percentage of adsorbed ions was determined. The effect of pH on adsorption of the metals was investigated using 0.5g of the adsorbent and 20 ml of 100 mg/L of Cu (II), Zn(II) ions. The mixture was shaken for 60 min forCu (II), Zn(II) and the amount of ion adsorbed was determined.

2.1. preparation of heavyMetal ion solutions

All materials used in this experiment were provided from the Iraqi market. A solution of Cu $Cl_2.2H_2O$ and $ZnCl_2$ Were prepared with initial concentration of 100 mg/l by dissolving0. 2682 gm of Cu $Cl_2.2H_2O$ in 1000ml of distilled water and 0. 2084 gm of $ZnCl_2$ in 1000ml deionized water.

2.2.Preparation of adsorbent

Conocarpuserectus leaves were collected from the gardens Abu Al-Khaseeb, Basra, Iraq. The leaves were extensively washed with deionized water to remove dirt ,dried in an oven at 80C° for a period of 2hr, then ground and screened to obtain the average particle size 150µm.the powder was preserved in glass bottles for use as adsorbent .

2:3.FT.IR Characterization of Conocarpus ErectusLeaves

FT-IRapparatus type shimadzu (4000-400 cm^{-1}) was carried out to identify the functional groups and structural in the *Conocarpuserectus* leaf powder that might be involved in the adsorption process. FT-IR analysis was carried out in order to identify the functional groups in the *Conocarpus erectus* leaf powder that might be involved in the adsorption process. The FTIR spectrum in the range of 400-4000cm is shown in Fig.1.as shown in the figure, the spectrum displays a number of adsorption peak, which indicates the complex natural of the material examined stretching, which is consistent with the peak at 1101.28 and 1319.22 cm assigned to alcoholic C-O and C-N stretching vibration. The absorption band wave numbers of 2920.03-2852.52 cm can be assigned to CH and $–CH_2$ stretching, respectively [15].The absorption band wave number of ketone group is about 1652.88cm.thatresult of binding of this group with the cations of metal .Show table(1).

<u>3. ResultandDiscussion</u>

3.1.Effect of pH

The pH is one of the most important parameters of biosorption of heavy metals[16]. The biosorption of Cu(II),Zn(II) by*Conocarpuserectus*leaves powderat different pH values(3-10) is presented in Fig2. The optimal pH for removal of Cu(II), Zn(II) was(10-9) respectively. The removal percentages of Cu(II), Zn(II) ion on *Conocarpuserectus*powder was at an initial concentration of 100 ppm and at an initial pH=9 ,using0.5g of the adsorbentwith100mLof Cu(II),Zn(II) ionssolution(94%,90.2%.) respectively .At pH higher than 9 both metals were precipitated due to the formation of hydroxides and the removal due to the sorption was very low .The minimal adsorption at low pH may be due to the higher concentration and high mobility of the H^+, which are preferentially adsorbed rather than the metal ions [17,18]. At higher pH values, the lower number of H+ and greater number of ligands with negatives charges results in greater Cu(II), Zn(II) adsorption. For example, carboxylic groups (–COOH) are important groups for metal uptake by biological materials [19,20]. At pH higher than 3-4, carboxylic groups are deprotonated and negatively charged. Consequently, the attraction of positively charged metal ions would be enhanced [21].

3.2.Effect of adsorbent weight

One of the parameters that strongly affect the sorption capacity is the weight of the adsorbents. With the fixed metal concentration it can easily be inferred that the percent removal of metal ions increases with increasing weight of the adsorbents as shown from Fig. 3This is due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent[22] .The removal percentages of Cu(II), Zn(II) ion *Conocarpuserectus* powder at an initial concentration of 100 ppm and at an initial pH=(9) ,using at different weight of theadsorbents(0.5-3g)with50mLofCu(II), Zn(II) ions solutions(95.1-94.2) respectively.

*3.3.*Effect of Initial Concentration of Cu(II),Zn(II)ions

To study the effect of initial concentration of metal on the adsorption, the operating conditions were set as follows: Volumes of solutions used were 20ml, concentration of metal ranging between 5 and 100 mg / l ,were gently shaken with 0.5 g of*Conocarpus Erectus* leaf powder (size 150μm) for 90 min for Cu(II), Zn(II)ionswith initial pH of the solution of Cu(II), Zn(II)ions was(9). Fig. 4 shows the effect of metal concentration to the removal ofCu(II), Zn(II) ions*Conocarpuserectus* leaf powder. The heavy metals are adsorbed by specific sites provided by the acidic functional groups on the biocarbon, while with increasing metal concentrations the specific sites are saturated and the exchange sites due to excessive surface area of the biocarbon are filled[23]. It is clear that with increasing initial concentrations, the metal removal Increases. The removal percentages of Cu(II), Zn(II)ion on *Conocarpus Erectus* powder at an initial concentration from(5-100) ppm and at an initial pH=(9) ,using(0.5g of adsorbent)with 20mL of Cu(II), Zn(II) ions solutions (92.6 %,91.1%.) respectively .

3.4.Effect of contact time

Fig(5)showsthe removal percentages of Cu(II), Zn(II)ions on *Conocarpus Erectus*leaves powder at an initial concentration of 100 ppm and at an initial pH(9),using 0.5g of the adsorbent with 20mL of Cu(II), Zn(II)ionssolutions(94.7%,93.3%)respectively. From this figure, it is clear that the metal removal percentages increased with an increase in contact time before attaining equilibrium. The rate of metal removal is higher in the beginning due to a larger surface area of the adsorbent being available for the adsorption of the metal [24]. A very fast increase in the biosorption rate ofCu(II), Zn(II)ions on *Conocarpus Erectus*leaf powder may be observed in the first 30 minutes for all pH-values studies, followed by a less rapid increase and a practically constant plateau after 60 min, in all cases. .Equilibrium time was attained at 60min,for Cu(II), Zn(II)ions on *Conocarpus Erectus*leaves powder. To ensure enough time to reach equilibrium; 60 min of contact was used throughout the batch experiments.

3.5. Effect of temperature on the adsorption rate

The Increase of temperature from 30 to 60 ˚C increased the adsorption ofCu(II),Zn(II) ions indicating the process to be endothermic. The increases in uptake of Cu(II),Zn(II) ions with temperature may be due to the desolvation of the adsorbing species, the changes in the size of pores, and the enhanced rate of intraparticle diffusion of adsorbate, as diffusion is an endothermic process. The biosorption was found to increase with increase in temperature at (30-55 ^{O}C)and the sorption capacity (Q) was also found to increase. The interactions are found to be endothermic in nature [25],[26] for which the evaluation of thermodynamic.This is shown in Figure(6). The removal percentages of Cu(II), Zn(II)ions on *Conocarpus Erectus* powder was at different temperature from(30-60) and at an initial pH=9,using(0.5g of adsorbent)with 20mL of Cu(II) Zn(II)ions solutions (97.5 %,87.9%.) respectively[27].

3.6.Isotherms

Biosorption isotherms can be generated based on numerous theoretical models where Langmuir and FreundlichandTempkin models are commonly used to fit experimental data when solute uptake occurs by a monolayer biosorption [28]-[29]. Langmuir isotherms assume monolayer biosorption, and are described by equation (2):

$$Q_e = (Q_{max}bC_e)/(1+bC_e) \qquad (2)$$

The Freundlich isotherm is described by equation (3):

$$Q_e = K_fC_e^{1/n} \qquad (3)$$

Where Q_e and $Q_{max}$are the equilibrium and maximum sorption capacities (mg/g biosorbent),C_e is equilibrium concentration (mg/l solution), b is the equilibrium constant, K_F and n are Freudlich constants characteristic of the system .

While, Tempkin model Heat of adsorption and the adsorbate–adsorbate interaction on adsorption isotherms were studied by Tempkin and Pyzhev [30], who suggested that because of these interactions the energy of adsorption of all the molecules decreases linearly with coverage.

Temkin isotherm is represented by the following equation

$$Q_e = B_1 \ln K_t + B_1 \ln C_e \qquad (4)$$

Where: $B_1 = RT/b \qquad (5)$

The adsorption data can be analyzed according to equation (4). A plot of Q_e versus $\ln C_e$ enables the determination of the isotherm constants $K_t$andB_1. $K_t$is the equilibrium binding constant (l/mol) corresponding to the maximum binding energy and constant B_1 is related to the heat of adsorption..The investigation of adsorption is shown in fig (7,8,).The experimental data was better described by the Freudlich isotherm than LangmuirandTemkin isotherm. The regression coefficient (R2) was (0.955,0.924,) respectively for Cu(II), Zn(II)ionsfor the Freudlich isotherm. In contrast, the Temkin and Langmuir isothem model was less precise, with a lower R2 value .

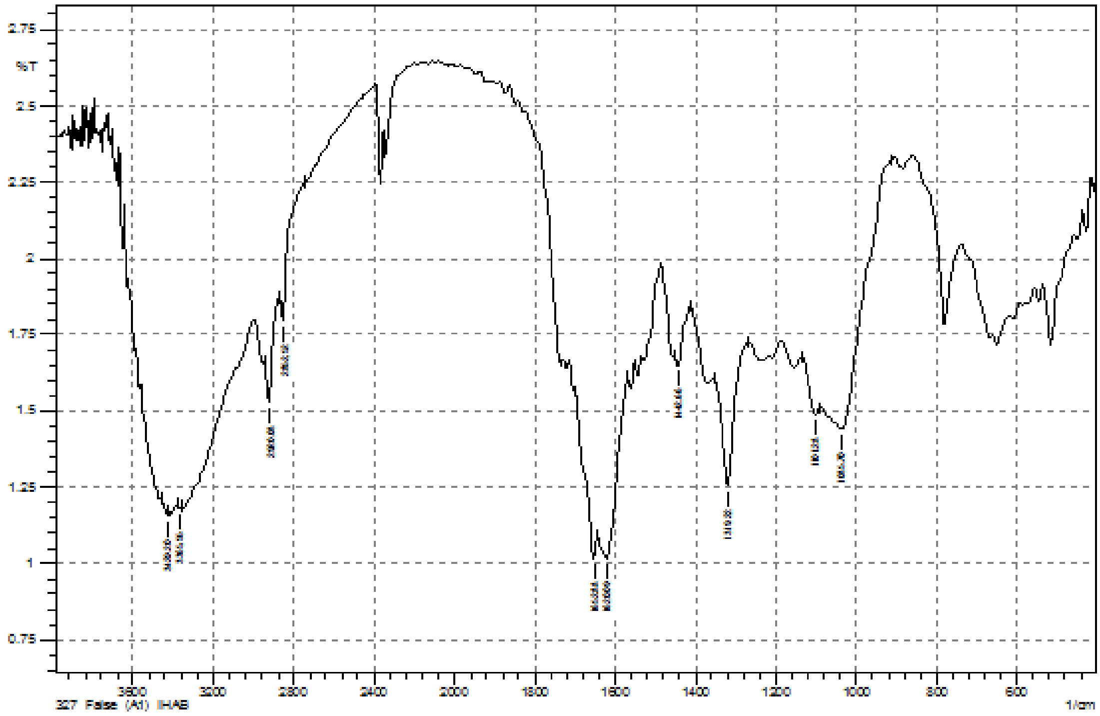


Fig (1)FT- IR of*Conocarpus erectus*leavespowder.

Table (1)explains the effective groups

Wavelength(cm^{-1})	Structural and Functional group	Functional group
1600-1660	C=O	ketone group
1700-1680	C=O	carboxylate groups
3400-2400	O-H	Hydroxyl group
2980-2870	C-H	Hydrocarbon
1340-1300	C-N	Amines
1100-1150	C-O	Carbon oxygen group

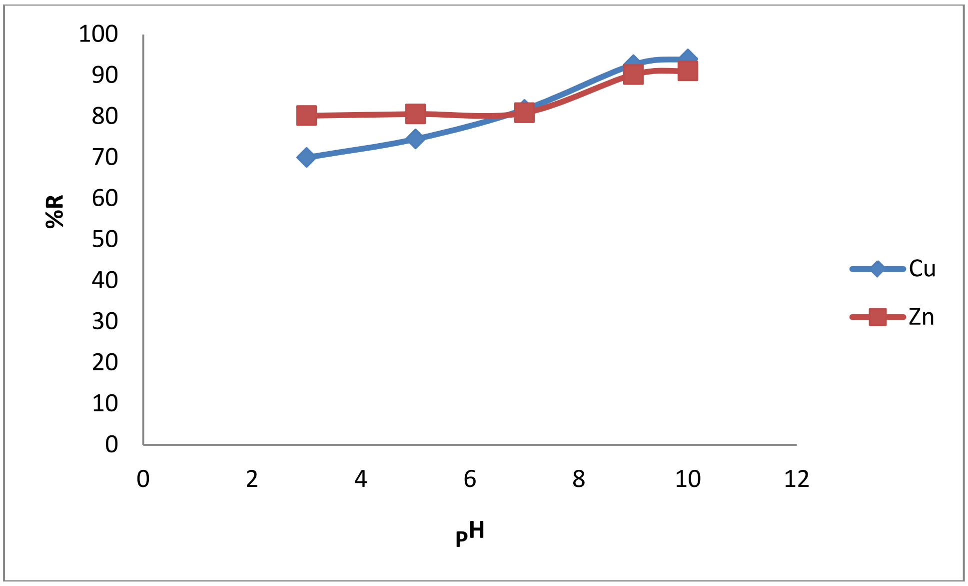


Fig (2) Effect of pH on adsorption of Cu ,Zn.

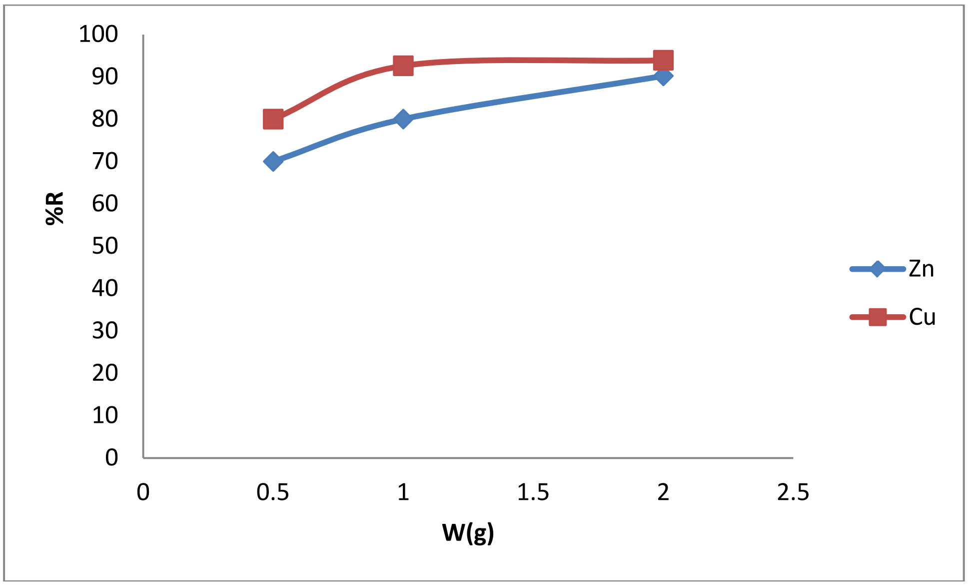


Fig (3) Effect of adsorbent weight on adsorption of Cu,Zn.

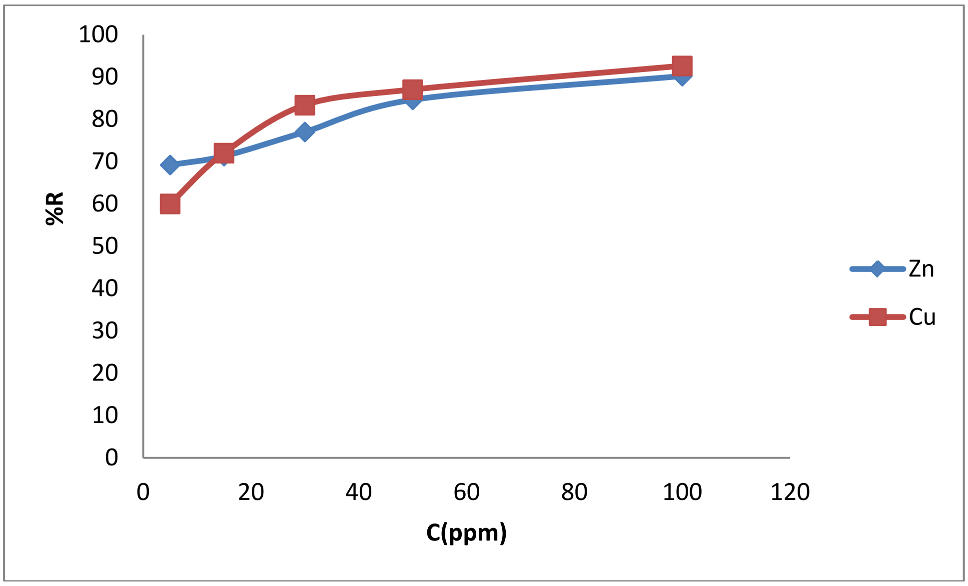
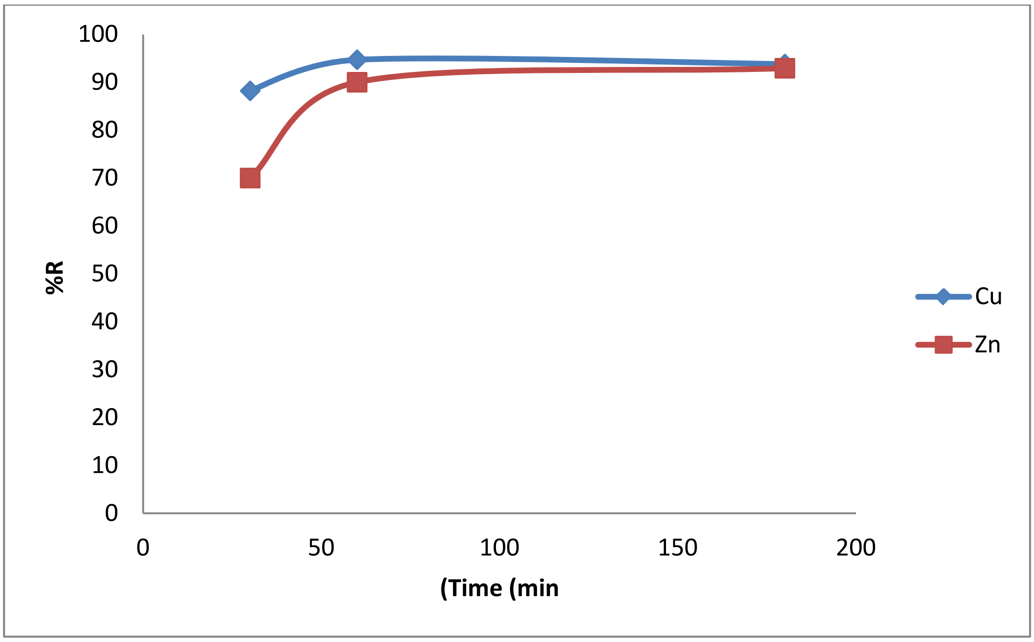
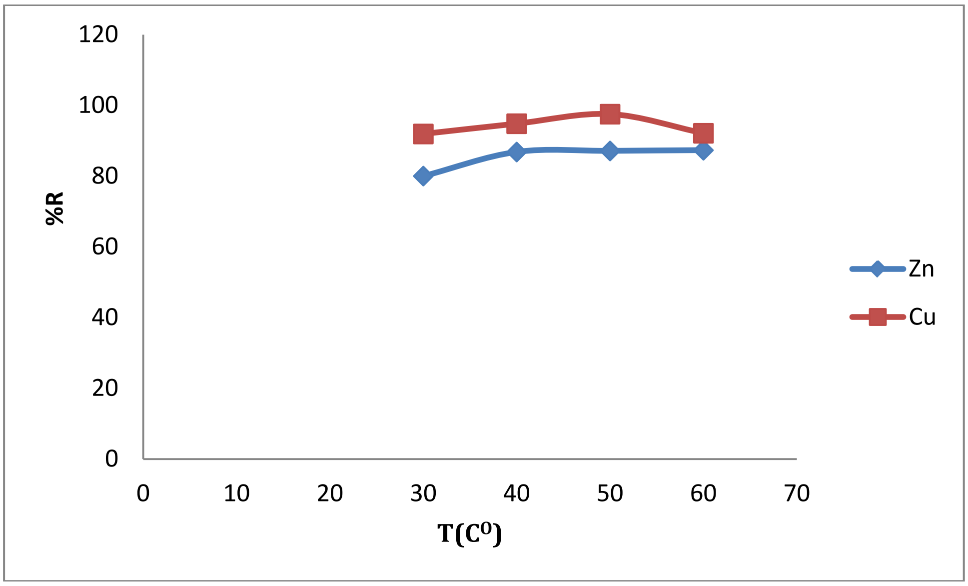


Fig (4) Effect of initial concentration on adsorption of Cu,Zn.



Fig(5) Effect of contact time on adsorption of Cu,Zn.



Fig(6)Effect of temperature on adsorption of Cu,Zn.

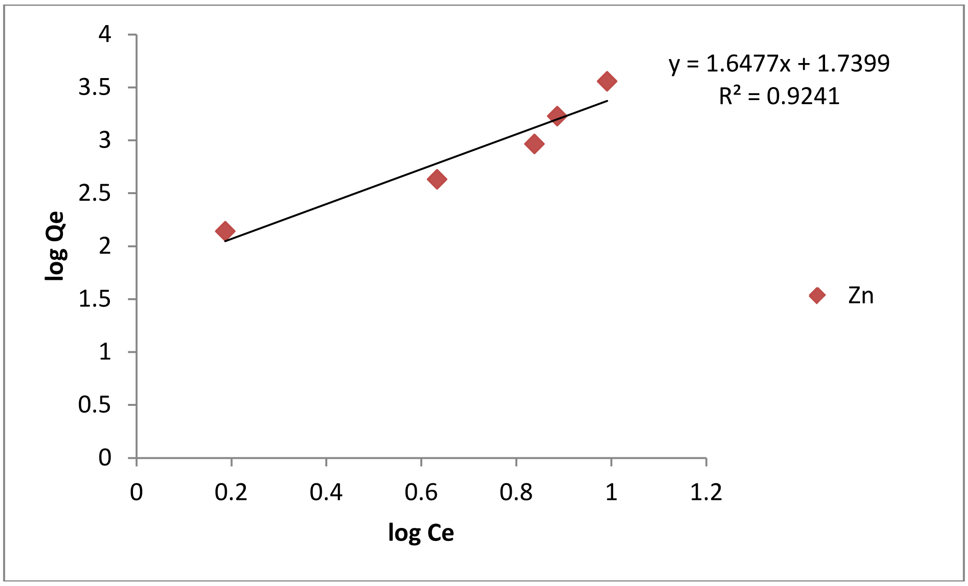
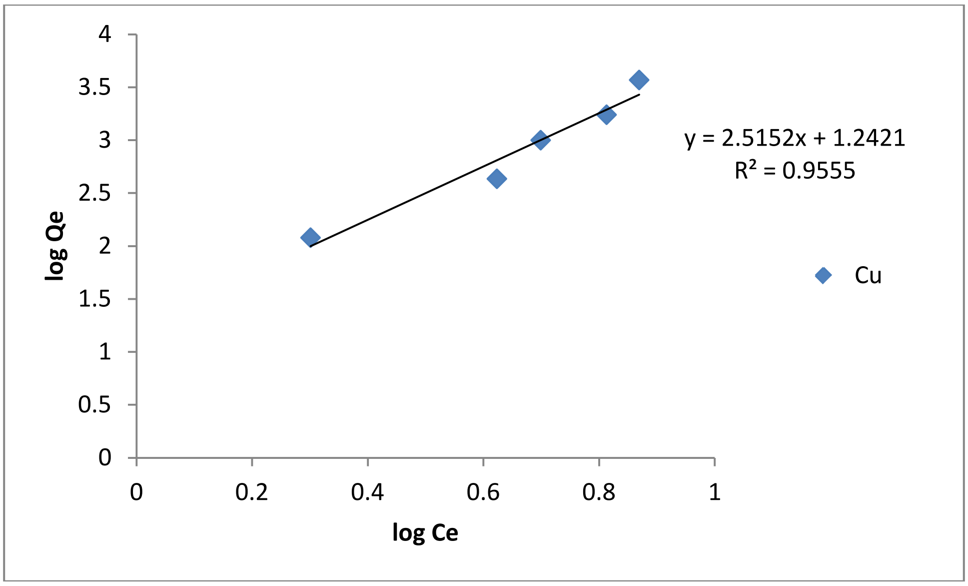


Fig (7)Freundlichisotherm for the adsorption of Zn (II) ion on*Conocarpus Erectus*leavespowder at25°cunder optimum conditions.



Fig(8)Freundlichisotherm for the adsorption of Cu (II) ion on*Conocarpus Erectus*leavespowder at25°cunder optimum conditions.

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طريقة بسيطة جديدة لمعالجة النفايات المائيةالحاوية على ايونات النحاس(II) والخارصين(II) بإستخدام الامتزاز على اوراق مجففة لشجرة الكونو كاربس

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الخلاصة

اجريت طريقة بسيطة وجديدة لمعالجة النفايات السائلة المحتوية على ايونات النحاس الثنائي والخارصين الثنائي , طورتبإستخدام اوراق مجففة *لشجرة الكونوكاربس* كمادة طبيعية منخفضة الكلفة.حيث اجريت التجارب بطريقة الدفعات لعدة مؤثرات متفاوتة في وزن المادة المازة ودرجة الحموضة وزمن الرج وتركيز ايون المعدن ودرجة الحرارة .الامتزاز في النحاس الثنائي وجد انه اعلى نسبة فيه (94.7%)عند الدالة حامضية تساوي 9 ودرجة حرارة مؤوية تساوي 25 وتركيز 100جزء بالمليون وزمن رج 60 دقيقةوسرعة رج (185دورة بالدقيقة) .ووجد ان اعلى قيمة لسعة الامتزاز للنحاس الثنائي والزنك الثنائي تساوي(94.7%93.3%) على التوالي عند افضل الظروف.حيث يكون الترتيب في كفاءة الازالة للعناصر وجدت انه (Zn<Cu) وان ايزوثرمفرندلش يكون مناسب في إمتزاز النحاس الثنائي والزنك الثنائي.وان المجاميع الفعالة [(C–N) ,(C–O),(C=O),(O–H)]تم تشخيصها باستخدام جهاز مطيافية تحت الحمراء(FT–IR) .

الكلمات المفتاحية : الامتزاز, النحاس والخارصين ,ايزوثرمفرندلش, معادلة تمكن , اوراق *شجرة الكونوكاربس*