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A Simple Method For Treatment Of Waste Water Containingcu(II),Pb(II),Mn(II) And Co(II)Ions Using Adsorption On Dried Leaves

Jameel M. Dhabab[1], hiend A. Abbas[1]
[1]Department of Chemistry, College of Science, Al-Mustansyria University, Baghdad, Iraq

ABSTRACT:

Anew simple method for treatment of waste water effluent containing Cu(II),Pb(II),Mn(II), Co(II) was developed using Myrtuscommunis as 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 Pb (II) was found to be maximum (98.8%) at pH4, temperature of 25°C, metal ion concentration 50 ppm and contact time 90 min. Adsorption capacity of Cu (II) Mn(II), and Co(II)were found maximum (92.4%,84.1% and 79.7%) respectively at optimum conditions. The order of removal efficiency of these metals was found Pb> Cu>Mn>Co. Freundlich isotherm was found to be suitable for the adsorption of Cu(II),Pb(II),Mn(II), Co(II). Adsorption kinetics data were found pseudo-first and pseudo-second order. The results indicate that the second-order model best describes adsorption kinetic data. factional groups(O-H,C-O and C-N) identification were given using FTIR spectrophotoscopy.

Keywords:Myrtuscommunis;heavymetals; adsorption; isotherm models

INTRODUCTION

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].Therefor treatment 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 equipment. Recently many researchers in the world wide investigated low-cost adsorbents with high metal binding capacities. Agricultural by-products have been widely used for treatment of water containing heavy metal. These agricultural materials include; peat, wood, pine bark, banana pith, soybean and cotton seed hulls, peanut shells, hazelnut shell, rice husk, saw dust, wool, orange peel, compost and leaves [12]. The present work is attempted to investigate the possibility of the utilization of one kind of tree leaves: myrtus-communis(MC) for removal of Cu(II),Pb(II),Mn(II), Co(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.

Experimental:

Chemical, reagent procedure and instruments

Chemicals: all chemical used Cu (II), Pb(II),Mn(II), Co(II) nitrate) were used and obtains as AnalR(Obtained from Fluke)and these metal ions were standardized against Na_2EDTA. Distal deionize water was used for all preparations .Hydrochloric acid and sodium hydroxide were all pure solution (Obtained from Fluke)

Instrumentations:

All the following instruments were calibrated by using standard solutions or reference material to obtain the satisfaction:

1- Atomic absorption spectrophotometer used was Shimadzu AA-6200.
2- FT-IR spectrophotometer – Shimadzu.
3-pH meter was Research pH meter Radiometer, Copenhagen, Denmark.
4-Shaker was BS-11 digital, JEIO TECH, Korea.

Procedures:

1-Preparation of adsorbent; MC leaves were collected from gardens of AL-mustansriy University, Baghdad, Iraq. The leaves were extensively washed with deionize water to remove dirt ,dried in an oven at 80Cº for a period of 3hr, then ground and screened to obtain the average particle size (300,500,700µm).The powder was preserved in glass bottles for use as adsorbent .

2-Prepartion of spiked wastewater; Prepare series of diluted Cu (II), Pb(II), Mn(II) and Co(II) solutions (10-50mg/L) from stock solution(each metal ion was prepared separately).All measurements of metal ions before and after adsorption were measured by atomic absorption spectrophotometric (shemadzu AA 6200).

3-Batch adsorption procedures; to measure the adsorption of metal ions on MC different weights of adsorbents were used at concentration of 10-50 mg/L. all parameters (pH, contact time, weight of adsorbent, temperature,intial concentration and particle size) were kept constant except one which was variable. Measure concentration of metal ions before and after adsorption by flame atomic absorption.

4-calculation of adsorption efficiency and distribution coefficient (kd).

The adsorption capacity may be calculated by the flowing equation;

Q_e= v (c_o-c_e)/m….1 (14)

Q_e =adsorption capacity ,v= suspension volume ,m= mass of adsorbent material (g),c_o=initial concentration ,c_e=final concentration.

kd can be defined as a measure of the efficiency of binding for bounded to the surface of adsorbent. The kd may be calculated by the flowing equation;

$K_d = r_{ws} (C_o – C_e) /C_e$….2

$r_{ws;}$the ratio between the volume of the adsorbent solution to the weight of adsorbent(ml/g), C_o and C_e are primary and

final concentration of adsorbed material, respectively (mg / L).

5-FT.IR Characterization of MC:FTIR apparatus type shimadzu (4000-400 cm^{-1}) was carried out in order to identify the functional groups in the MC leaf powder that might be involved in the adsorption process.

Results and discussion:

FTIRcharcterization:The**e**Characterization of MC powdered was given in fig 1.In this fig the following beaks were 3419.56, ,2929.67 and 1739.67 cm^{-1} which were assigned to alcoholic O-H, stretching,CH –CH_2 and ketonic C-O respectively [15]. It is clear from this characterization that the mc adsorbent has the activity to bind with the action by the function group which contains one pairs of electrons which explain the capacity of this adsorbent.

Optimization results:

Effect of pH; The pH is considered one of the most important parameters of biosorption of heavy metals[16].however Theadsorption of these heavy metals Cu(II),Pb(II),Mn(II),and Co(II) on by mc powder were found different at pH values 2-6 and results were given in Fig 2. From this Fig, the order of pH adsorption was 6, 4, 3 and 4 respectively.Using2.0goftheadsorbentwith50mLofCu (II),Pb(II),Mn(II),Co(II)ions solution ,the percentage of adsorption were 89.52%,97.24%,82.72%,70.8% respectively. At pH higher than 6 both metals were precipitated due to the formation of hydroxides and removal due to 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),Pb(II),Mn(II), Co(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].In summary, the order of adsorption efficiency as follows;Pb(II)>Cu(II)>Mn(II)>Co(II).

Effect of adsorbent weight: To obtain the highest percentage removal of heavy metals different amounts (0.5-3g) of adsorbent were examined at optimum conditions. Results are given in fig 3.The removal percentages of Cu(II),Pb(II),Mn(II), Co(II) ion on MC powder were Pb(II)98.8%,>Cu(II)92.4%,. >Mn(II),84..37%,> Co(II)72.2%.).The difference in adsorption capacity of these metal ions may be explained due to the greater availability of the exchangeable sites or surface area at higher concentration of the adsorbent [22] .

Effect of Initial Concentration of Cu (II),Pb(II),Mn(II), Co(II)ions: In order to achieve maximum adsorption the initial concentration of metal ion should is optimum at fixed conditions. Therefor different concentration of metal ions (10-50 mg/l). Following general procedure given previously (procedure 2).results are given in fig 4.from the results the sequence of adsorption was found ;Pb(II(98.8%) >Cu(II)(92.4%) >(Mn(II)(84.37%) >Co (II)(72.2 %.) and these results are achieved at initial concentration (10-50 mg/l). Such results may be due to the adsorption of heavy metals 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].

Effect of contact time: This parameter is important as it is affecting the removal percentage of metal ions, therefor effect of contact time was studied by fixing all parametersexpect time which was varied to 90 min. results are given at Fig5 which shows that maximum removal was attained at 90 min. the compression of the four ions were found; Pb(II)94.4 %) > Cu(II) 89.6%>(Mn(II) 84.16% > Co(II) 69.6%.The rate of metal removal was found higher at beginning due to a larger surface area of the adsorbent being available for the adsorption of the metal [24].Equilibrium time was found to be different in each metal ions duo to physical and chemical properties of each metal.

Effect of Temperature: Temperature is another parameter has been studied to obtain maximum removal of heavy metals. By fixing all parameters expect temperature was varied from 25 to 70ºC.Results are given in fig 6.results show that the removal percentage of heavy metals was found: Pb(II(97.16%)>Cu(II)(92.08%) > (Mn(II)(83.14%)> Co(II)(79.72%.).It is obvious that optimum temperature is 25ºC for Co(II),Mn(II) metal ions and 60,70 ºC for Cu(II),Pb(II) metal ions respectively . The interactions were found to be exothermic and endothermic in nature [25-26] the Pattern of the process is endothermic for Cu(II),Pb(II) metal ions; therefore increase in uptake of metal ions was increased with temperature while the Pattern of the process is exothermic for Co(II),Mn(II) metal ions .

Adsorption models

Langmuir, Freundlich and Temkin models are commonly used to follow experimental data [28-29].

The final results of adsorption were found to fit Freundlich isotherm model better than Langmuir andTemkin isotherm. To compare the adsorption model of metals, figures 7-10 show that the regression coefficient (R2) were found (0.999,0.990,0.996 and 0.997) for Cu(II),Pb(II),Mn(II) , and Co(II) ions respectively.

The Freundlich isotherm is described by equation below;

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

Where q_e is the amount of adsorbate, C_e is the equilibrium concentration of metal ion, while n and K_F are empirical Freundlich constants. n was found from slop of the curve .K_F was calculated from the intercept. The values of these constants, listed in table (1).Kd value for lead ions was higher than other metals ions (1.59) .the squance of capacity of metal ions were founded to be in the order; Pb> Cu>Mn>Co.

Adsorption Kinetics:

Fig. 11shows the behavior of adsorption(II), Pb(II),Mn(II), and (II)ions on MC leaf powder at optimum conditions . All curves proved that adsorption was linear and pseudo-second order equation [31 - 32].The sequence of adsorption are Mn>Pb>Co>Cu. This difference in adsorption can be used for separation of these metal ions using other technique.

Distribution coefficient (kd)

By applying the equation 2 to calculate kd values in table 2 explained that kd values of cupper is low (278.94-644.44),for cobalt ,kd values are smaller (26.25-30.45); for manganese kd values were also low (111.6-181.61) . Therefor adsorption efficiency for Co and Mn are weak but for Cu is higher than Co and Mn ions. Only lead ions have higher kd.

Therefore this adsorbent (mc) can be used for separation of lead in the presence metals ions. Although kd values for Cu, Co and Mn are low but Mc still useful for removal of heavy metals.

Conclusion;

MC was proved successful for removal of Cu (II), Pb(II),Mn(II), and Co (II)ions from waste water (72.2-98.8%). The Freundlich isotherm model was better used to represent the experimental data. From the results different kd values are shown and the selectivity was founds in the following sequence; Pb> Cu>Mn>Co, therefore separation can be achieved using other technique such as ion exchange chromatography. Kd values were found less than 1000 for Cu, Mn and Co but higher than 1000 for Pb ions.

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Table (1) Freundlich parameter for the adsorption of heavy metals on myrtus communis leaves powder

Absorbate	Parameters		R^2
Cu	N	1.57	0.999
	K_f	0.57	
Co	N	1.1	0.997
	K_f	0.035	
Pb	N	1.59	0.991
	K_f	1.01	
Mn	N	1.34	0.996
	K_f	0.2	

Table (2); Distribution coefficient of Cu,Co,Pb and Mn ions on MCleaf powder at25c°under optimum condition.

Ions	Co mg/l	Ce mg/l	r ws	Kd
Cu	10	0.72	50	644.44
	20	2.08		430.76
	30	3.72		353.22
	40	5.6		307.14
	50	7.6		278.94
Co	10	3.964	20	30.45
	20	8		30
	30	12.01		29.95
	40	17.05		26.92
	50	21.62		26.25
Pb	10	0.12	25	2058.33
	20	0.28		1760.71
	30	0.59		1246.18
	40	0.94		1038.82

	50	1.4		867.85
Mn	10	1.21	25	181.61
	20	2.7		160.18
	30	4.58		138.75
	40	6.98		118.26
	50	9.16		111.46

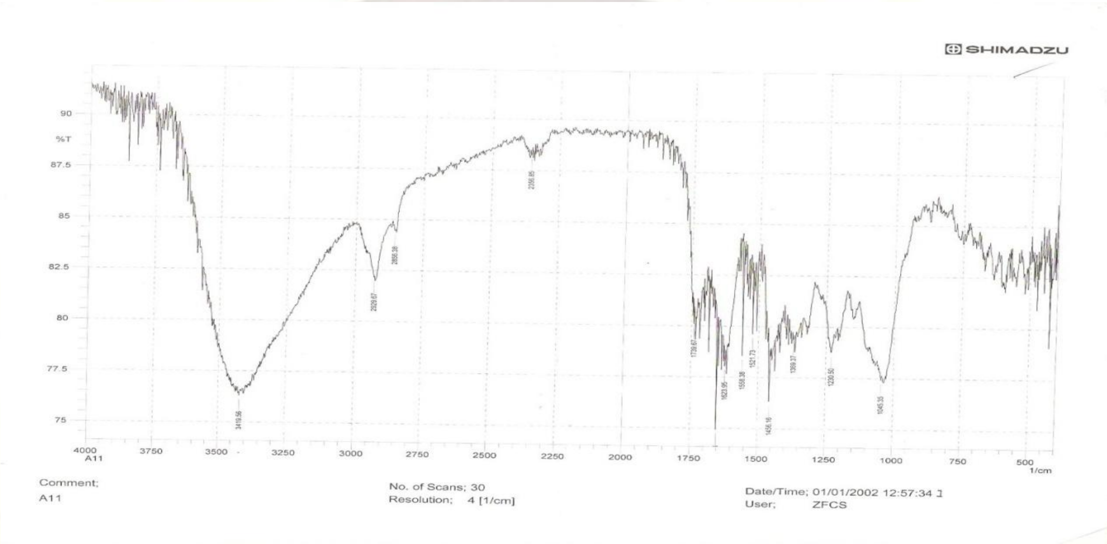


Fig (1) FTIR of MC leaf powder

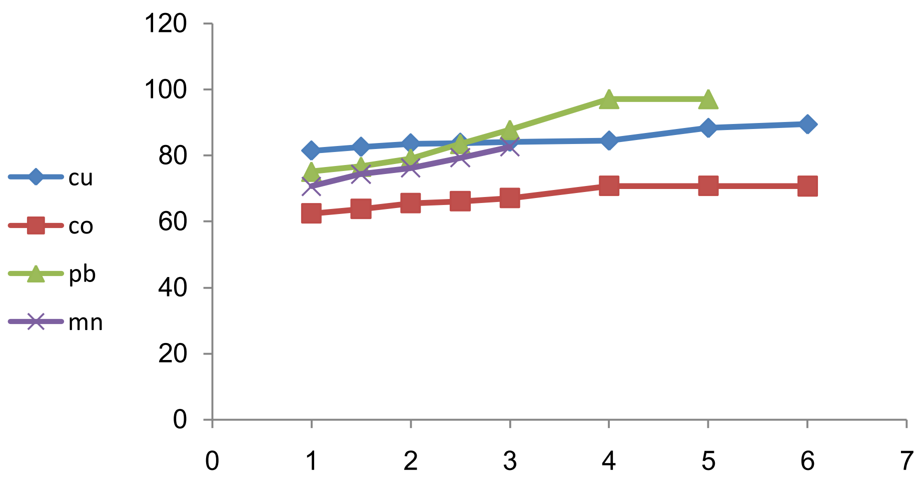


Fig (2) Effect of pH on adsorption of Cu, Co, Pb and Mn

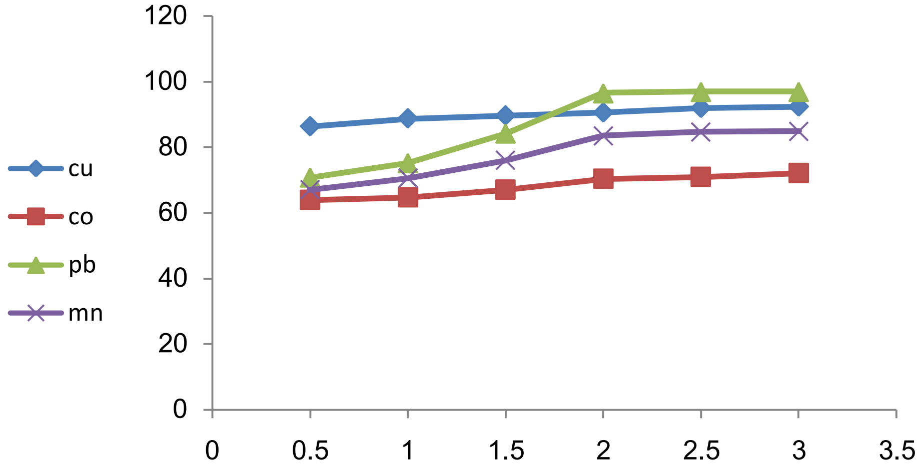


Fig (3) Effect of adsorbent weight on adsorption of Cu, Co, Pb andMn

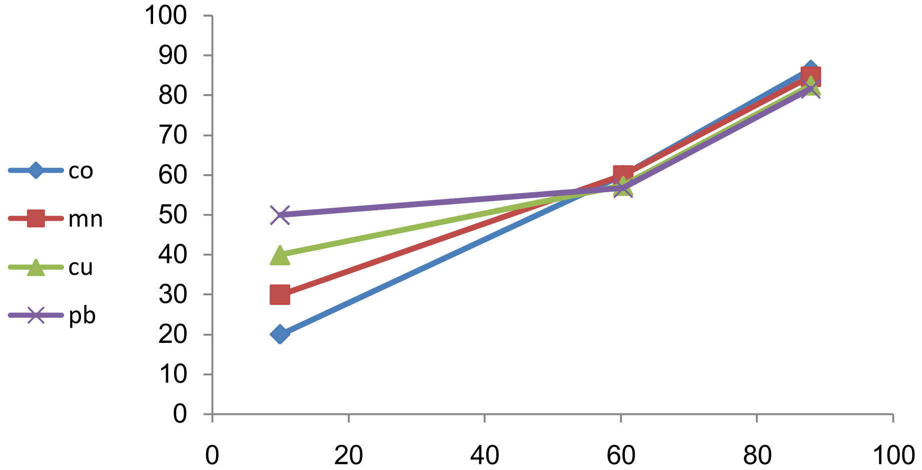


Fig (4) Effect of concentration on adsorption of Cu, Co, Pb and Mn

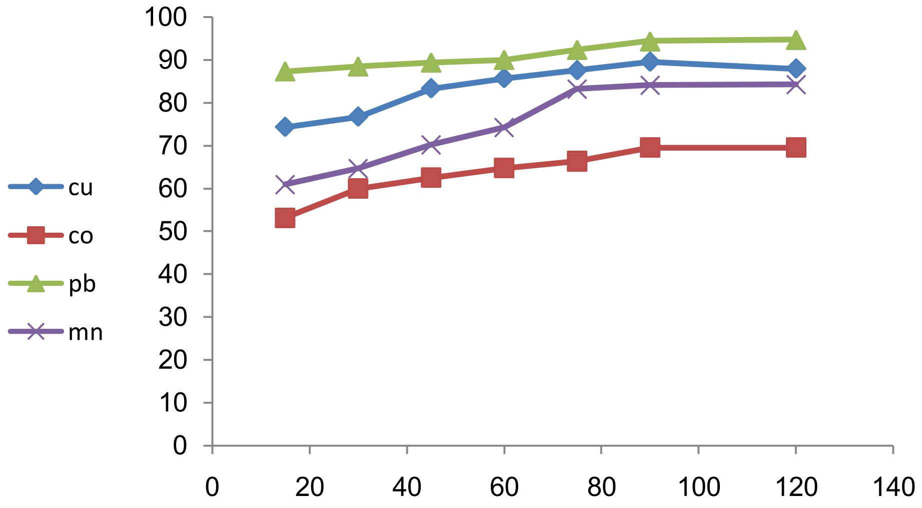


Fig (5) Effect of contact time on adsorption of Cu,Co,Pb and Mn

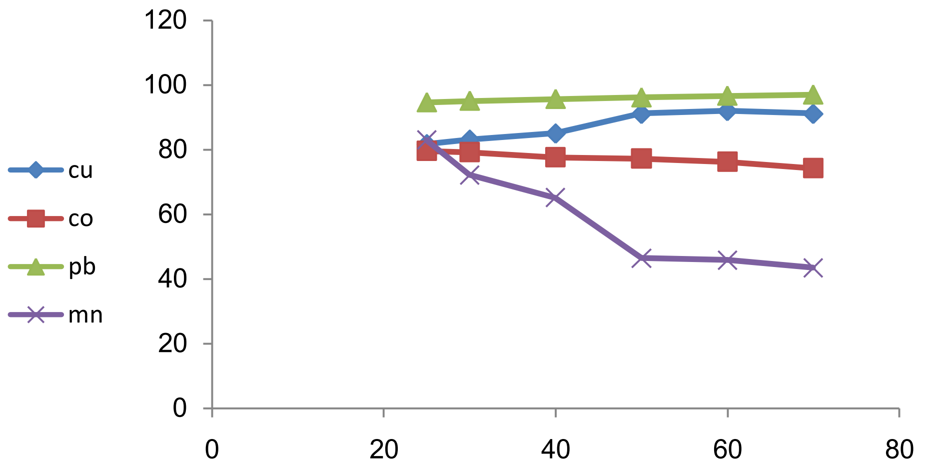


Fig (6) effect of temperature on adsorption of Cu,Co,Pb and Mn

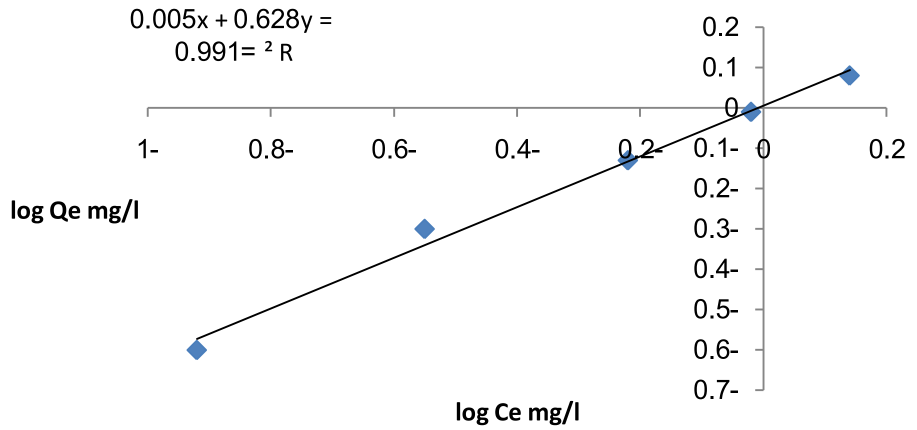


Fig (7)Freundlich isotherm for the adsorption of Pb (II) ion on MC leaf powder at25c°under optimum conditions

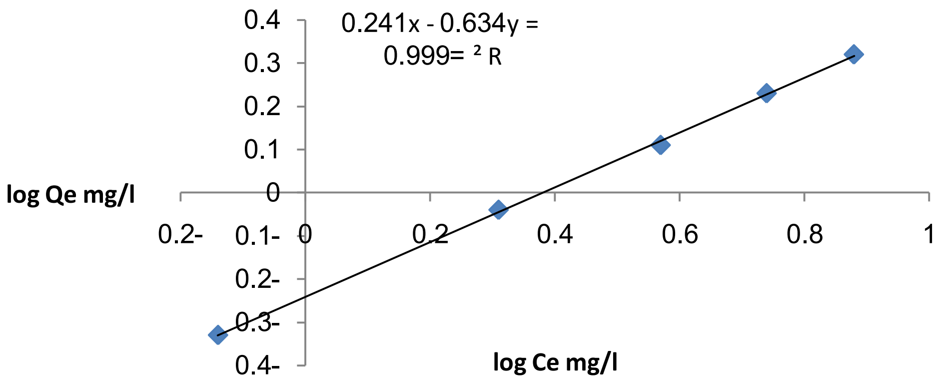
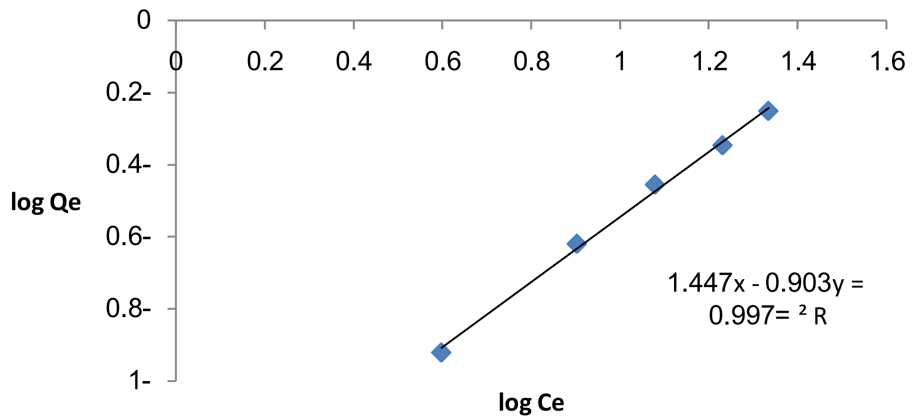


Fig (8)Freundlich isotherm for the adsorption of Cu (II) ion on MC leaf powder at25c°under optimum conditions



Fig(9)Freundlich isotherm for the adsorption of Co (II) ion on Mc powder at25c°under optimum conditions

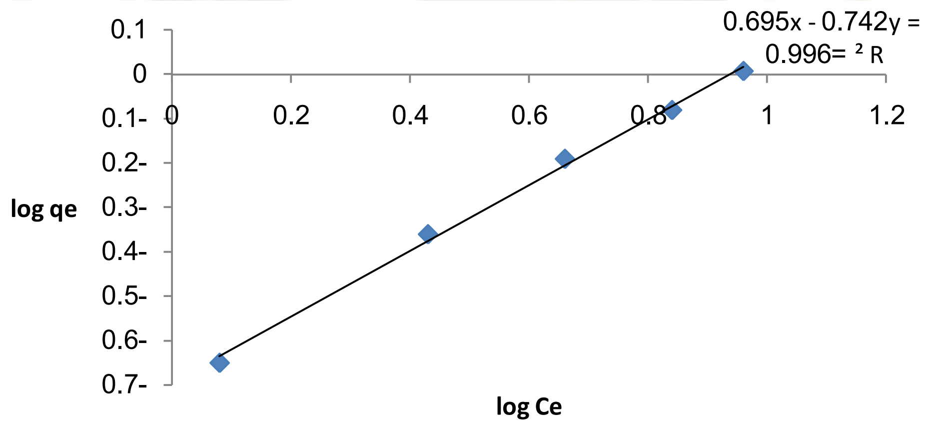


Fig (10)Freundlichisotherm for the adsorption ofMn (II) ion on MC leaf powder at25c°under optimum conditions

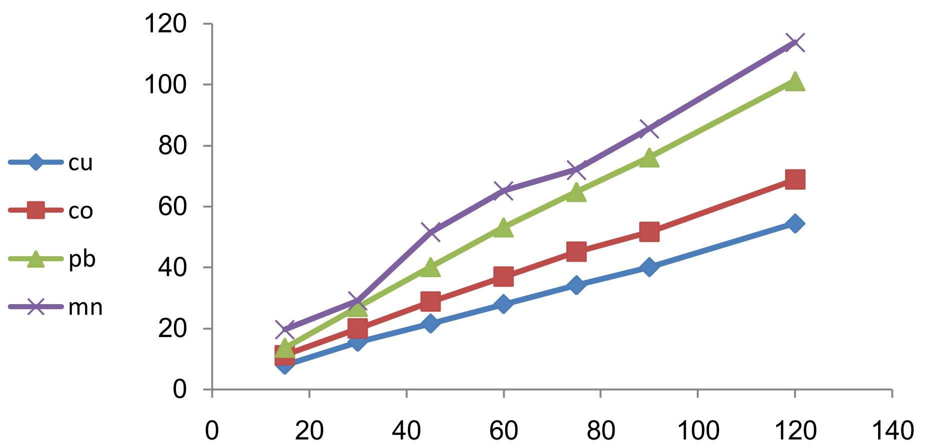


Fig (11) second order for the adsorption ofCu (II), CO (II),Pb(II), Mn(II)ions on MC leaf powder at25c°under optimum conditions