REMOVAL OF COPPER IONS FROM WASTE WATER BY ADSORPTION WITH MODIFIED AND UNMODIFIED SUNFLOWER STALKS

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ABSTRACT

Unmodified and modified sunflower stalks were examined for adsorption as a replacement of expensive activated carbon which has been recognized as a highly effective adsorbent for the removal of heavy metal-ion.

Two modes of operation were used, batch mode and fixed bed mode. In batch experiment the effect of sunflower stalk doses (2,3,4,5 and 6g/L) with constant initial copper concentration of 100 mg/L and constant particle size less than1.18 mm was studied.

Batch kinetics experiments showed that the adsorption rate of copper ion by sunflower stalks was rapid and reached equilibrium within 60 min. Adsorption models Freundlich, Langmuir and Freundlich-Langmuir were fitted to experimental data and the goodness of their fit for adsorption was compared. In the fixed bed isothermal adsorption column, the effect of particle size (1.18-2.36, 2.36-4.75 and 4.75-9.00) mm, influent flow rate (2,4and 6) L/hr, bed depth (25, 30 and 35) cm and initial metal concentration (100 and 150) mg/L was studied. In addition, the modification of sunflower stalks could enhance their natural capacity. Sunflower stalks were modified by activation with nitric acid. The results of this study show that sunflower stalk, both modified and unmodified, is an efficient adsorbent for the removal of copper from waste water. Percent removal of copper reaches 100% when particle size (2.36-4.75)mm ,bed depth 35 cm and influent flow rate 4 L/hr.

الخلاصة:

قد تم في هذا البحث دراسة امكانية جعل سيقان نبات عباد الشمس المعامل وغير المعامل كبديل لمادة الكاربون المنشط والتي تعد مادة فعالة جدا في امتزاز المعادن الثقيلة.

تم استخدام نمطين من التشغيل في هذا البحث وهي تجارب النمط الدفعي وتجارب النمط المستمر. تم اجراء تجارب دفعية لدراسة تأثير كمية عباد الشمس (2، 3، 4، 5 و6)غم/ لتر بثبوت التركيز الابتدائي لايون النحاس (100 ملغم/ لتر) وحجم ثابت لجسيمات المادة الممتزة الذي هو اقل من1.18 ملم، أظهرت النتائج ان نسبة ازالة المعدن تزداد بزيادة كمية سيقان عباد الشمس و الزمن. كذلك أظهرت النتائج ان الوصول الى حالة التعادل تستتغرق تقريباً (60) دقيقة، تم تحليل النتائج باستعمال موديلات (Langmuir, Freundlich and Langmuir-Freundlich) وأظهرت النتائج ان جميع الموديلات ذات تقارب جيد. كذلك اجريت تجارب النمط المستمر وتم دراسة تأثير تركيز المعدن الابتدائي (100 و150 ملغم/ لتر) وحجم جسيمات المادة الممتزة (1.18-2.36 و 2.36-4.75 و4.75-9.00ملم) بمعدل جريان الداخل (2 و4 و6 لتر/ ساعة) وارتفاع عمود الامتزاز (25، 30،35 سنتمتر) وبالاضافة الى ذلك تم دراسة تاثير معاملة سيقان عباد الشمس بحامض النتريك. لقد أظهرت النتائج ان سيقان عباد الشمس المعاملة وغير المعاملة هي فعالة في امتزاز المعادن من مياه الصرف وكانت نسبة ازالة النحاس تصل الى 100% عندما يكون حجم جسيمات المادة الممتزة (2.36-4.75) ملم ومعدل جريان الداخل 4 لتر/ساعة وارتفاع عمود الامتزاز 35 سنتمتر.

KEY WORDS:

Wastewater, Adsorption, Sunflower stalks, heavy metals removal, copper, low cost adsorbent.

INTRODUCTION

The idea of using various agricultural products and byproducts for the removal of heavy metals from solution has been investigated by number of authors. Friedman and Waiss, (1972), Radalletal et al. (1974) and Henderson et al.(1977) have investigated the efficiency of number of different organic waste materials as sorbents for heavy metals. The obvious advantages of this method compared to other are lower cost involved when organic waste materials are used. Activated carbon adsorption appears to be a particularly competitive and effective process for the removal of heavy metals at trace quantities (Huang and Blankenship, 1984). However, the use of activated carbon is not suitable for developing countries because of its high cost (Panday et al., 1985).For that reason, the uses of low cost materials as possible media for metal removal from wastewater have been highlighted. These materials range from industrial products such rubber tyres (Knocke and Hempill (1981))., industrial wastes and some natural material including agricultural product and by-product as mentioned earlier.

Sunflower stalks have reasonable maximum adsorption capacities (Sun and Shi, 1998). Residues, which are mainly ligno-cellulosic materials, can inherently adsorb waste chemicals such as dyes and cations in water due to the Coulombic interaction between the two substrates and physical absorption. They are renewable agricultural wastes available abundantly at no or low cost. Disposal of the agricultural biomasses in California and many states is the major obstacle to the sustainable agriculture and environment utilization of the biomasses has been studied extensively and some alternatives have been developed. Among many new technologies, utilizing plant residues as adsorbents for the removal of toxic chemicals in waste water is a prominent technology (McKay et al.,1987; El-Geundi, 1991).which have proven relatively strong Coulombic adsorption to cations such as organic bases as well as intrinsic adsorption to other materials such as acidic and anionic compounds (Sun and Xu, 1997). Sunflower stalks have relatively large surface areas that can provide intrinsic adsorptive sites to many substrates. On the basis of the structural analysis of the sunflower stalks, it was expected that the adsorbents should be able to remove cationic metal ions as well

The adsorbents are usually used in the fixed bed process because of the ease of operation. To design and operate a fixed bed adsorption process successfully, the column dynamics must be understood, that is the breakthrough curves under specific operating conditions must be predictable (Markovska and Meshkoco, 2001). The location of the breakpoint and the shape of the breakthrough curve (degree of concavity) are influenced by many parameters pertaining to the nature of the adsorption equilibrium isotherm and the mass transfer rate (Basheer and Najjar, 1996).

This paper presents a study on adsorption of copper ions on sunflower stalks as adsorbent. Contact time and adsorbent surface area were identified preliminarily as the most important variables that affect the adsorption of copper ions.

EXPERIMENTAL WORK

Materials:

Adsorbent

All of the used sun flower stalks were analytical grade, purchased and applied without further purification. The fibrous part was removed, crushed in a mill, washed with de-ionized water and air-dried. Then it was sieved to different sizes and activated with 2% (v/v) nitric acid for 24 hr and washed with deionized water. The air dried adsorbent was divided into two parts, one part was modified and the other left unmodified.

The Sunflower stalks were sieved to produce a particle size of 1.18-2.36, 2.36-4.75and 4.75-9.00 mm.

Adsorbate

Copper sulfate ($CuSO_4.5H_2O$) solution was used as adsorbate.

EXPERIMENTAL

Batch Experiments

Batch experiments were used to obtain the equilibrium isotherm curves and then the equilibrium data. In batch mode the effect of sunflower stalks weight on adsorption process and equilibrium isotherm experiments were studied.

All experiments were carried out at $25C^o$ ±1 ,rpm 120 and PH 4.2 because It was found that the adsorption of copper remains almost unchanged regardless of any change in the temperature and the maximum adsorption start at pH 4.2 (Sun and Shi, 1998) . Five 1 L flasks were used for experiments conducted with an initial copper concentration of 100 mg/L, sun flower stalks dosage was used for 2, 3, 4, 5 and 6 g/L. Samples were collected and tested. A metal ion that was lost from the solution was assumed to be adsorbed onto the adsorbents. Data obtained from batch tests fitted to Freundlich, Langmuir and Freundlich-Langmuir adsorption isotherm equations as shown in figures.

Fixed Bed Column Experiments

Column experiments were carried out for various particle sizes (dp), flow rates (Q), bed depths (H), initial metal concentrations (C_o) and the nature of the adsorbate to measure the breakthrough curves for the systems.

The fixed bed adsorber studies were carried out in Q.V.F. glass column of 8.75cm I.D. and 50 cm in height. The sun flower stalks was confined in the column by fine mesh at the bottom to avoid loss the adsorbent. The influent solution was introduced to the column through a small water distributor to ensure a uniform distribution of influent through the adsorbent, fixed at the top of the column.

The schematic representation of experimental equipment is shown in **Fig 1**.

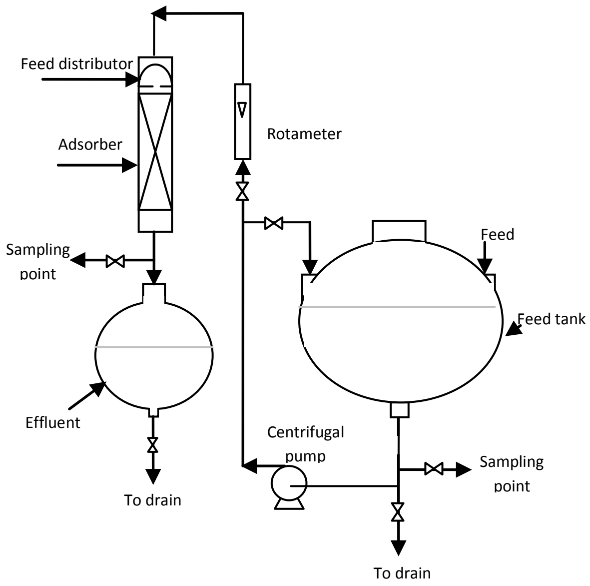

Fig. 1, Schematic representation of experimental equipment

RESULTS AND DISCUTION:

Batch Experiments:

Adsorption Isotherms:

Adsorption isotherm studies were performed to obtain equilibrium isotherm curves and data required for the design and operation of fixed bed adsorber. The adsorption isotherm curves were obtained by plotting the weight of the solute adsorbed per unit weight of the adsorbent (q_e) against the equilibrium concentration of the solute (c_e). **Fig. 2** shows the adsorption isotherm curve for adsorption of copper on unmodified sun flower stalks at 25 C^o

The obtained data was correlated with Langmuir, Freundlich and Langmuir-Freundlich models. The Langmuir model describing adsorption showed in **eq. (1)**

$$\frac{x}{m} = \frac{abC_e}{1+aC_e} \tag{1}$$

Eq. (2) described the Freundlich adsorption model):

$$\frac{x}{m} = kC_e^{1/n} \tag{2}$$

Combination of Langmuir-Freundlich Isotherm Model, i.e. the Sips model for single component adsorption presented by **eq.(3)** (Sips, 1984) .

$$q_e = \frac{bq_mC_e^{1/n}}{1+b\,C_e^{1/n}} \tag{3}$$

The parameters for each model obtained from non-linear statistical fit of the equation to the experimental data. All parameters with their correlation coefficients are summarized in **Table 1**.

From the statistical analysis “Excel program” it was found that adsorption of metal by sun flower stalks could be well described by the three isotherm models. The correlation coefficients were in the range of (0.983 -0.999 %) for initial copper concentration 100 mg/l. The correlation coefficient value was higher for Langmuir-Freundlich than other correlations. This indicates that the Langmuir-Freundlich isotherm is clearly the better fitting isotherm to the experimental data.

Effect of Mass of Unmodified Sunflower Stalks on the Adsorption Process:

The effect of mass of unmodified sun flower stalks on adsorption of copper at constant adsorbate concentration was studied for the purpose of determining the best adsorbent mass that will bring a best removal. The results of the dependence of copper on the mass of unmodified sun flower stalks of size 1.18-2.35 mm at 25 C^o is shown in **Figs. 3and4**. These figures represent the plotting concentration of copper with time and the percentage removal of copper against the mass of unmodified sunflower stalks.

The percent removal of copper increases with increasing weight of sunflower stalks up to a certain value, depending on adsorption sites. These figures can clearly show that the increase in the percent removal of copper is due to the greater availability of adsorption sites or surface area of adsorbent. An identical trend was observed by other investigations ((Sun and Xu, 1997; Maruf et al., 2006)

Table 1, Isotherm Parameters for Copper Adsorption onto Unmodified Sun Flower Stalks with the Correlation Coefficient.

Model	Parameters	Values
Langmuir (1)	a, L/mg	0.0077
	b, mg/g	142.8
	Correlation coefficient (R^2)	0.983
Freundlich (2)	K, L/g	1.6
	n,	1.2136
	Correlation coefficient (R^2)	0.99
Combination of Langmuir-Freundlich (3)	q_m, mg/g	196.79
	b, mg/g	0,0057
	n,	1.03
	Correlation coefficient (R^2)	0.999

FIXED BED EXPERIMENTS:

Effect of Volumetric Flow Rate

In a design of fixed bed adsorption column, the contact time is the most significant variable and therefore the bed depth and the metal solution flow rate are the major design parameters (Markovska, 2001). The effect of varying volumetric flow rate was investigated at constant concentration 100 ppm and particle size 2.35-4.75 mm and bed depth 30 cm and the breakthrough curves are presented in **Fig.5**. It is obvious that increasing the flow rate decreases the volume treated. This is due to decreasing contact time between the metal and the adsorbent at higher flow rate. Increasing the flow rate may be expected to make reduction of the surface film. Therefore, this will decrease the resistance to mass transfer and increase the mass transfer rate. But, according to **Fig.5**, the mass transfer rate decreases with increasing the flow rate .This is because the reduction in the surface film is due to the disturbance created when the film of the bed increased resulting of easy passage of the adsorbate molecules through the particles and entering easily to the voids. The easy entering of molecules decreased contact time between metal and sunflower stalks at high flow rate. These results agree with those obtained by Kim et al.(2003a)and Maruf et al.(2006).

Effect of Bed Depth:

The effect of bed depth was investigated for copper adsorption on sun flower stalks. The experimental breakthrough curves are presented in **Fig. 6.** The breakthrough curve was obtained for different bed depth of sun flower stalks at constant flow rate (4 l/h), constant particle size (2.35-4.75) mm and constant copper concentration (100 ppm). It is clear that the increase in bed depth increases the breakthrough time and the residence time of the solute in the column, due to the availability greater surface area (Malkoc and Nugoglu, 2006).

Thus, the residence time in the column is more important than fluid velocity in improving removal efficiency.

Effect of Particle Size:

In case of using an adsorbent particles of much smaller size, that will eliminate inter particle mass transfer resistance. This means that the rate determining step is diffusion through film around each particle. The experimental breakthrough curves are presented in **Fig. 7** were obtained for different particle size (1.18-2.36, 2.36-4.75 and 4.75-9.00 mm) at constant initial concentration of copper (100 ppm), bed depth of sun flower stalks (30 cm) and constant flow rate (4 l/h). The experimental results showed that fine particle sizes (1.18-2.36 mm) gave a higher metal removal than others particle sizes. This was due to large surface area of fine particles.

Effect of initial copper concentration:

The initial copper concentration of the influent is important since a given mass of adsorbent can only adsorb a fixed amount of metal. Therefore, the more concentrated an influent, the smaller is the volume of effluent that a fixed mass of adsorbent can purify. So, experiments were under taken to study the effect of varying the initial metal concentration on the rate of metal adsorption and they are presented in **Fig. 8**. The effect of the initial concentration in the inlet flow is one of the limitation factors and a main process parameter. Increasing the inlet concentration increases the slope of the breakthrough curve and makes it much steeper, reducing the volume of the effluent treated and reducing the throughput until breakthrough. This may be caused by saturation of adsorbent more quickly with high concentration, thereby decreasing the breakthrough time .Since the rate of diffusion is controlled by the concentration gradient, it takes a longer contact time to reach saturation for the case of low value of initial solute concentration. Wastewater treatment is limited by the breakthrough point or the dynamics of reaching that point. These systems have a small time delay with higher concentrations in the inlet, so the metal solutions have to be diluted before separation for better removal. The same conclusion was obtained by Markovska, 2001 and Maruf et.al, 2006.

Effect of Modification of Adsorbate:

Sunflower stalk is an environmental pollutant has been found to be a good adsorbent for the removal of Cu (II) ions from aqueous solutions. The modification of the adsorbent by nitric acid has been shown to enhance the adsorption capacity as illustrated in **Fig.9.**

The high binding capacities of cationic species on the adsorbents are mainly the results of columbic interactions (Weixing et al., 1998). Although sunflower stalks showed to be effective adsorbent for a wide range of solutes, particularly divalent metals cations, crop residues suffer from at least two major drawback: low exchange or sorption capacity, and poor physical stability (i.e. partial solubility) (Laszlo and Dintzis, 1994). In order to overcome these problems, chemical modification and/or activation of the raw adsorbents are required.

CONCLUSIONS:

- Unmodified and modified Sun flower stalks were effective in adsorbing copper from wastewater.
- In batch experiment the percent removal of copper increases (70 -80 %) with increasing in sunflower stalks dose (2 - 6 g/l).
- Batch kinetics experiments showed that equilibrium time was about 60 min with mechanical mixing 120 rpm, initial concentration 100 ppm and adsorbent weight 4 gm/l.
- The isotherm models (Langmiur, Freundlich and Langmiur- Freundlich) gave good fitting for the adsorption capacity of sunflower stalks versus equilibrium concentration of copper ions. The correlation coefficients (R^2) obtained from Excel program for these models were in the range of 98.3- 99.9% but the Langmiur- Freundlich model gave the best fitting for adsorption capacity.
- In fixed bed experiment, the percent removal of copper increases with increasing contact time (reducing the flow rate), adsorbent surface area, and bed height.
- Modification of the sun flower stalks by nitric acid enhances the adsorption capacity to some extent.

NOMENCLATURE:

a	Langmiur constant (L/mg)
b	Langmiur constant (mg/g)
C	concentration of solute in solution at any time (mg/l)
C_e	concentration of solute in solution at equilibrium (mg/l)
C_0	initial concentration of adsorbate (mg/l)
k	Freundlich equilibrium constant indicative of adsorption capacity
m	mass of solute adsorbent (g)
n	Freundlich constant indicative of adsorption intensity
H	bed depth (m)
Q	flow rate (l/h)
q_e	amount of metal ion adsorbed at equilibrium (mg/g)
R^2	correlation coefficient
t	time (min)
x	mass of solute adsorbed (mg)
d_p	particle size (mm)
qm	maximum amount of metal ion adsorbed at equilibrium (mg/g)

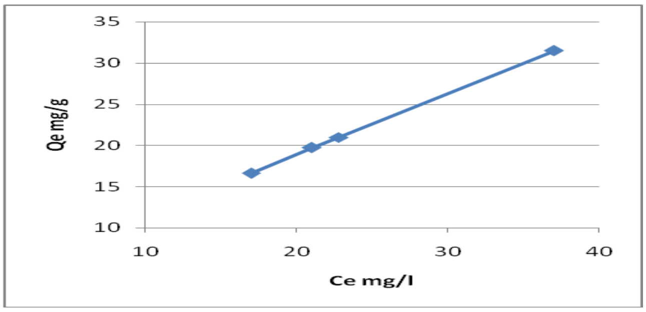

Fig. 2, Adsorption isotherm for Copper onto Sunflower Stalks (C_o=100mg/L,Temp.=25C^o, particle size =1.18 mm)

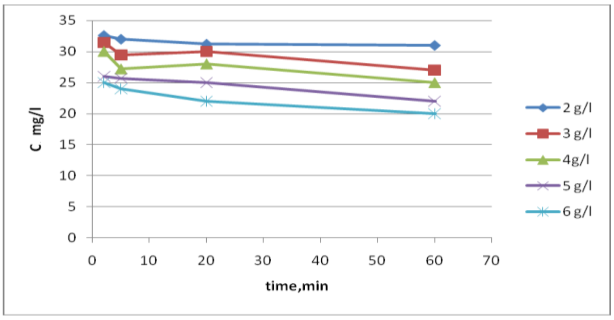

Fig.3, Change in Copper Concentration with Time of Batch Tests (C_o=100mg/L, Temp. =25C^o, particle size=1.18 mm)

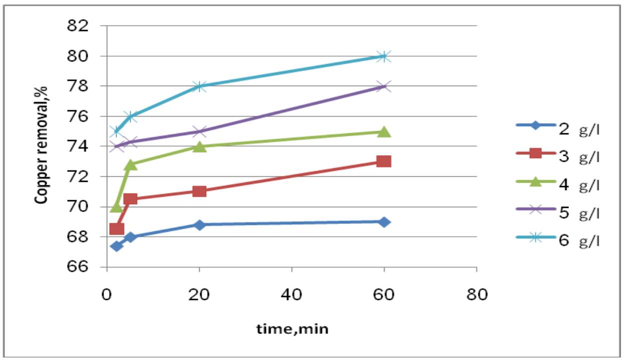

Fig. 4, The Effect of Sunflower Stalks on Copper Removal of Batch Tests (Co=100mg/L, Temp. =25Co, particle size=1.18mm)

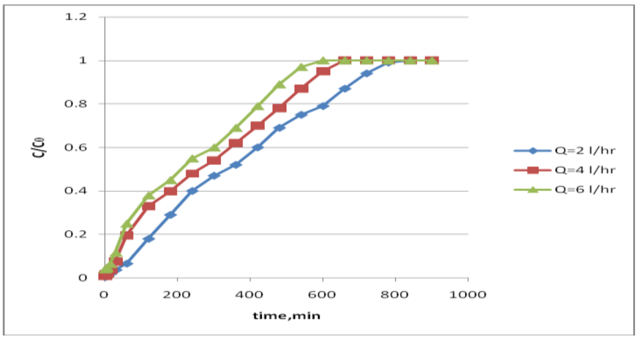

Fig.5, Experimental Breakthrough Curves for Adsorption Copper on Unmodified Sunflower Stalks for Different Flow Rates (H=0.30 cm, d_p=0.35 cm,C_0=100 ppm)

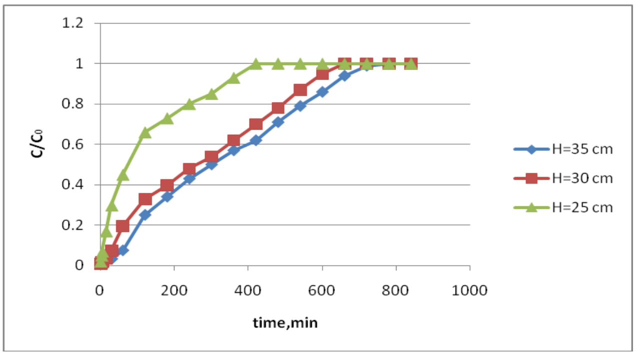

Fig.6, Experimental Breakthrough Curves for Adsorption Copper on Unmodified Sunflower Stalks for Different Bed Depths (Q=4 l/hr, d_p=0.35 cm,C_0=100 ppm)

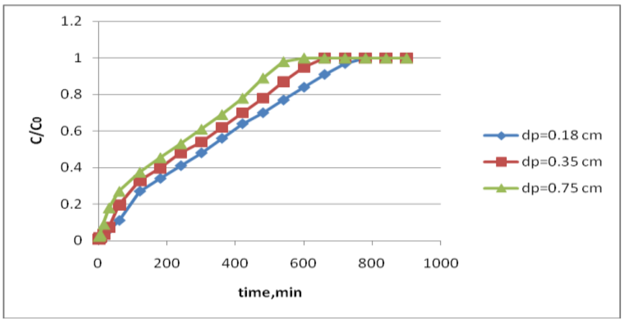

Fig.7, Experimental Breakthrough Curves for Adsorption Copper on Unmodified Sunflower Stalks for Different Particle Sizes(Q=4 l/hr, H=30 cm,C_0=100 ppm)

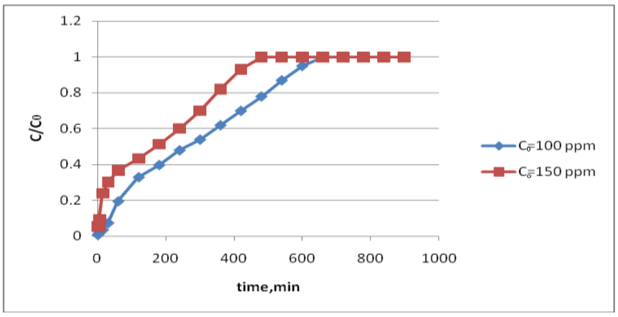

Fig.8, Experimental Breakthrough Curves for Adsorption Copper on Unmodified Sun Flower Stalks for Different Initial Concentrations (Q=4 l/hr, H=30 cm ,d_p=0.35 cm)

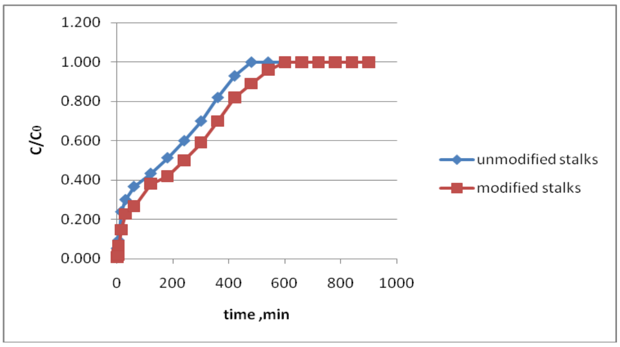

Fig.9, Experimental Breakthrough Curves for Adsorption Copper on Modified and Unmodified Sun Flower Stalks (Q=4 l/hr, H=30 cm,dp=0.35 cm ,C_0=150 ppm)

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