المجلة العراقية
لبحوث السوق وحماية المستهلك

المجلد (9) العدد (2)
لسنة 2017

دراسة المتغيرات الحركية والامتزازية لازالة ايونات النحاس والحديد من المحاليل المائية باستعمال مخلفات المنتجات الزراعية.

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تاريخ استلام البحث: **2016 /5/22** تاريخ قبول النشر: **2017 /4/17**

الخلاصة:

عدل قش نبات الحنطة باستعمال حامض المالونك لغرض الحصول على مادة ممتزة رخيصة الثمن لها قابليه عالية لازالة ايونات النحاس والحديد من المحاليل المائية وكانت درجة الحراة للتعديل الكيميائي 120ْم وبزمن مقداره 12 ساعة ولوحظ من خلال دراسة المتغيرات التي تؤثر على سير تجارب الامتزاز ان افضل اس هيدروجيني كان 6 و 5 لكل من النحاس والحديد على التوالي. بينما افضل زمن للامتزاز كان 120 دقيقة وكذلك افضل وزن للمادة الممتزة كان 0.1 غم، وتم تحديد قيم متغيرات الامتزازوجد ان طبقا الى Langmuir (qmax كانت 54.64 و 61.7 ملغم/غم بينما قيم b كانت 0.234 و0.22 ملغم/لتر) Freundlich (Kf كانت 16.07و 18.89 ملغم/غم وقيم n كانت 2.77 و 3.16) Temkin (قيم B كانت 0.063 و 0.074 جول/مول وقيم A_t كانت 0.143 و 1.658 لتر/غم) و Dubinin-Radushkevich (قيم Kad كانت $3*10^{-6}$ و $9*10^{-7}$ و qs كانت 48.42 و 44.70 مغم/غم وقيمة E كانت 0.408 و 0.745 كيلوجول/مول) لايونات النحاس والحديد على التوالي والامتزاز لكلا الايونين هو امتزاز فيزيائي طالما ان قيمة n بمعادلة Freundlich اكبر من واحد لكلا الايونين وكذلك معدل الطاقه الحرة لمعادله Dubinin-Radushkevich ذات قيم 0.408 و 0.745 كيلو جول/ مول فضلا عن ان قيم B لمعادلة Temkin كانت 0.063 و 0.074 جول/مول.

الكلمات المفتاحية: الامتزاز ، مخلفات المنتجات الزراعية، التعديل الحراري، حامض المالونك.

STUDY OF THE KINETIC AND ADSORPTION ISOTHERM PARAMETERS FOR REMOVING COPPER AND IRON IONS FROM AQUEOUS SOLUTIONS BY USING AGRICALTURAL BY-PRODUCTS.

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ABSTRACT:

Wheat straw was modified with malonic acid in order to get low cost adsorbent have a good ability to remove copper and ferric ions from aqueous solutions, chemical modification temperature was 120°C and the time was 12 h. Parameters that affect the adsorption experiments were studied and found the optimum pH were 6 and 5 for copper and iron respectively and the time interval was 120 min and the adsorbent mass was 0.1 g. The values for adsorption isotherms parameters were determined according to Langmuir [qmax were 54.64 and 61.7 mg/g while b values were 0.234 and 0.22 mg/l] , Freundlich [Kf were 16.07 and 18.89 mg/g and n were 2.77 and 3.16], Temkin [B were 0.063 and 0.074 j/mol and A_t were 0.143 and 1.658 l/g] and for Dubinin-Radushkevich [Kad were $3*10^{6-}$ and $9*10^{7-}$, qs were 48.42 and 44.70 mg/g, E were 0.408 and 0.745 Kj/mol] for copper and iron ions respectively. The adsorption for both ions are physical since the n values in Freundlich were more than 1, the mean of free energy for Dubinin-Radushkevich were 0.408 and 0.745 Kj/mol and B values for Temkin equation B were 0.063 and 0.074 j/mol.

Key words: adsorption isotherms, agricultural by-products, thermal modification, malonic acid

INTRODUCTION:

Many toxic heavy metals have been discharged into the environment as industrial wastes, causing seriously solid and water pollution copper one of the metals that accumulate in organisms, causing numerous diseases and disorders. Copper are also common groundwater contaminant at industrial and military installation (**Kabata-Pendias, 2011**). Drinking water can contribute significant amount of copper to the body. According to The United States environmental protection agency (EPA) the tolerable copper is limited to be 1.3 mg/l, (**United State environmental Agency**). While the world health organization (WHO) tolerance for copper in drinking water is 2 mg/day (**World health organization, 1989).** The upper limit for copper is 10 mg/day in order to prevent liver damage as the critical adverse effect (**Institute of medicine, 2011**). Copper toxicity effect on aquatic environment and human health can be determined by correlation between symptoms and diagnosis and thousands of tests. Copper toxicity cannot be neglected due to a lot of health conditions like premenstrual syndrome, fatigue, migraine headache, depression anxiety, anorexia, and allergies (food and environmental allergies) (**Dave, et al.,2009**). Wide range of effects such as necrosis in kidneys and the brain, liver cirrhosis, low blood pressure, lesions, gastrointestinal distress, and fetal mortality are found in mammals because of copper toxicity (**Kabata-Pendias, 2011**). Marine and freshwater organisms like molluscs and fishes also affected by raising the level of copper in water (**Van Genderan, *et al.*, 2005**). Fishes cannot choose good mate or cannot find their way for mating areas due to impede the sense of smell by a high level of copper in water, also causing damage in liver, gills, nervous system and kidney (**Flemming, and Trevos, 1989**). Iron toxicity causing several clinical observations likes diarrhea, vomiting, and gastrointestinal bleeding (**Greentree *et al*., 1995; and Liebelt 1998**). The next stage occur After about 12 - 96 hours of initial clinical, the sign of this stage marked by lethargy, repeating of gastrointestinal signs, metabolic acidosis, shock, hypotension, tachycardia, cardiovascular collapse, coagulation deficits, hepatic necrosis, and possibly death (**Greentree *et al*., 1995; and Liebelt 1998**).Therefore, it is necessary to remove copper and iron ions from aqueous solutions. Several conventional methods used for removing copper ions from aqueous solutions, such as membrane desalination (**Clayton, 2015**), Chemical precipitation (**Negrea, *et al*., 2008**), electro coagulating (**Escobara, *et al*., 2006**), reverse osmosis (**Greenlee *et al*., 2009**), solvent extraction (**Fillipi, *et al*., 1998**), biological degradation (**Patil, and Paknikar 1999**), ion exchange (**Caputo, and Pepe, 2007**) and adsorption (**El-Ashtoukhya, *et al*., 2008**). Most of these methods suffering from some drawback such as high capital or high operation cost or disposal of resulting sludge (**Thenmozhi, and Santhi, 2013**). Among these techniques, adsorption is generally preferred due to its easy handling, high efficiency, and availability of different adsorbents. Therefore, the searching for cost-effective absorbent has become the focus of attention for many studies (**Dong, *et al*., 2010**). In this study wheat straw was used as adsorbent after been modified with malonic acid according to method applied for soya been hulls by Marshall (**Marshall, *et al*., 2000**).

MATERIAL AND METHODS

SAMPLES

Wheat straws were provided from Iraqi farms. All chemicals and reagents were supplied by Merck

Preparation of adsorbent:

Wheat straw reflexed with 2% NaOH solution, then washed with distilled water, dried and cut into segments of 2-3 mm for further treatments. Treated wheat straw subjected to chemical modification according to method described by Marshall *et al* (**Naief, 2015**).Where 0.5 gm of wheat straw mixed with 1.5 gm of malonic acid in 8 ml of distilled water. The mixture was steered for 30 minutes at 20°C then the acid straw slurry moved to porcelain dish and dried at 50°C in air oven. The thermochemical reaction was proceeding between straw and acid after 24 hours by raising the heat of oven to 120°C for 12h. After cooling the product washed with distilled water to remove any access of malonic acid. Modified wheat straw dried at 50°C till constant weight. This procedure repeated for different time and temperatures until get best yield of the product.

Preparation of solutions and adsorption experiments:

Copper and ferric ions were prepared at 40, 60, 80, 100 and 120 ppm. Batch experiment was carried out for each of these concentrations by taking 50 ml of the solution in stoppered conical flask and stirred with 0.1 gm of the adsorbent at 200 rpm. After period time interval the solution filtrated to measure the equilibrium concentration by using spectrophotometric technique (UV-9200), where copper and ferric ions measured at 435nm and 480nm respectively (**Jeffery, *et al.*, 1989**). The removal percentage of ions from aqueous solutions (%R) and the amount of adsorbed (q_e) has been calculated according to the following equation.

$$\textbf{\% Removing} = \frac{Ci - Ce}{Ci} \times 100$$

$$\textbf{Amount of adsorbed } (q_e) = \frac{Ci - Ce}{m} \times V$$

Where Ci and Ce are initial and equilibrium concentrations respectively in ppm (m) the mass of adsorption in gm and (V) is the volume in litter.

RESULTS AND DISCUSSION

Characterization of adsorbent

The main purpose of the reaction between wheat straw and malonic acid was to increase the ability of wheat straw to absorb the metal ions from the solutions. This can be occur by synthesize across linked between the straw and carboxylic groups of malonic acid. The FTIR spectra for the wheat sample before and after treating with malonic acid can show in (Figure, 1). Before acid modification process the broad band shown in 3893 cm^{-1} belongs to stretching of hydroxyl group (OH). The peak at 2893 cm^{-1} due to CH alkanes stretching. The strong peak at 1064 cm^{-1} due to ether stretching. After acid modification (Figure, 2) process the peaks in 1064 cm^{-1} due to ether. The Peak at 1739 cm^{-1} due to ester stretching. The sharp peak at 3429 cm^{-1} it's due to hydroxyl group stretching. The formation of ester and transform the (OH) peak from broad to sharp band (due to reaction most of these groups with the acid its number will become less) and absence of carboxylic groups stretching even in finger print area. All these are clear evidences for carrying out of modification between wheat straw and malonic acid.

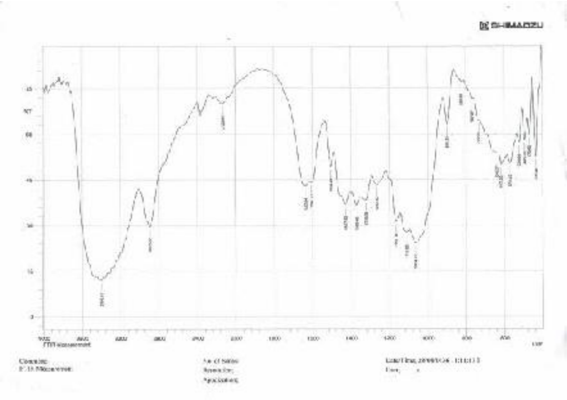

Fig (1): wheat straw

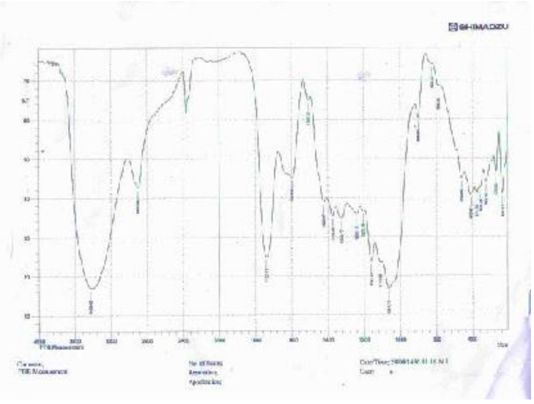

Fig (2): wheat straw modified with malonic acid

The effect of pH:

The pH of the solution can be regarded as the most important parameter that affects the adsorption of the metal ions. The effect of pH has been studied by using (inoLab pH 7110) at a range of pH from 2 to 10 (Figure, 3). The removal percentage of copper and ferric ions increase as the pH of the solution increase from 2 to 6 and 5 respectively this is because of the competitive effect of hydrogen ions in the solution. At low pH the number of hydrogen ions will be high hence it will bend to the adsorbent and fill the adsorption sites. As the pH increase the number of hydrogen ions becomes less therefore, the number of vacant sides on adsorbent increase and large number of cooper and ferric ions can bend to the adsorbent if the pH increases more than 6 for copper ions and 5 for ferric ions the removal percentage will decrease due to the precipitation of metal ions at high pH. Hence the optimum pH found to be 6 and 5 for copper and ferric ions respectively.

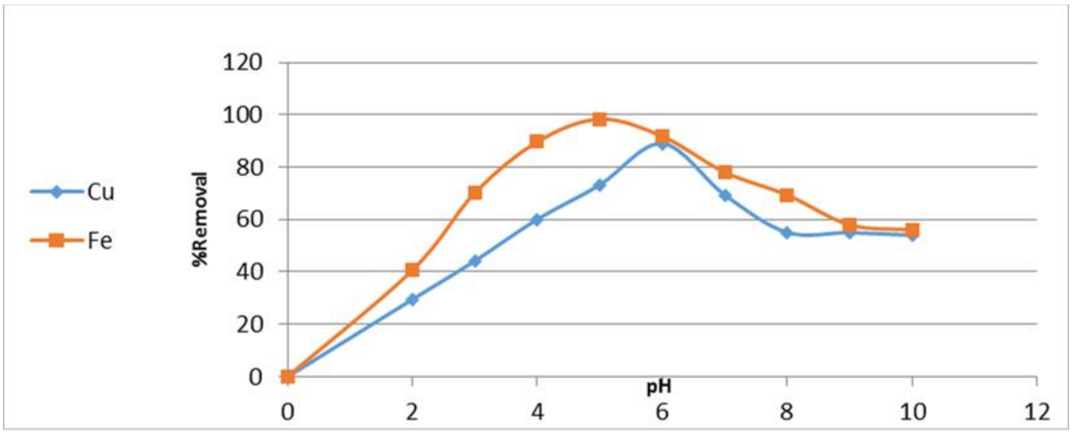

Fig (3): the effect of pH on removal percentage of copper and ferric ions in aqueous solutions.

The effect of equilibrium time:

The effect of time on removal percentage of ions has been study for 80 ppm at 6 and 5 for copper and ferric ions respectively and mass of adsorbent 0.1 gm /50 ml for different intervals. As show in the (Figure, 4) the removal percentage increase as the time in (min) increase up to 120 minutes then the removal percentage didn't change so the optimum time for adsorption found to be 120 min.

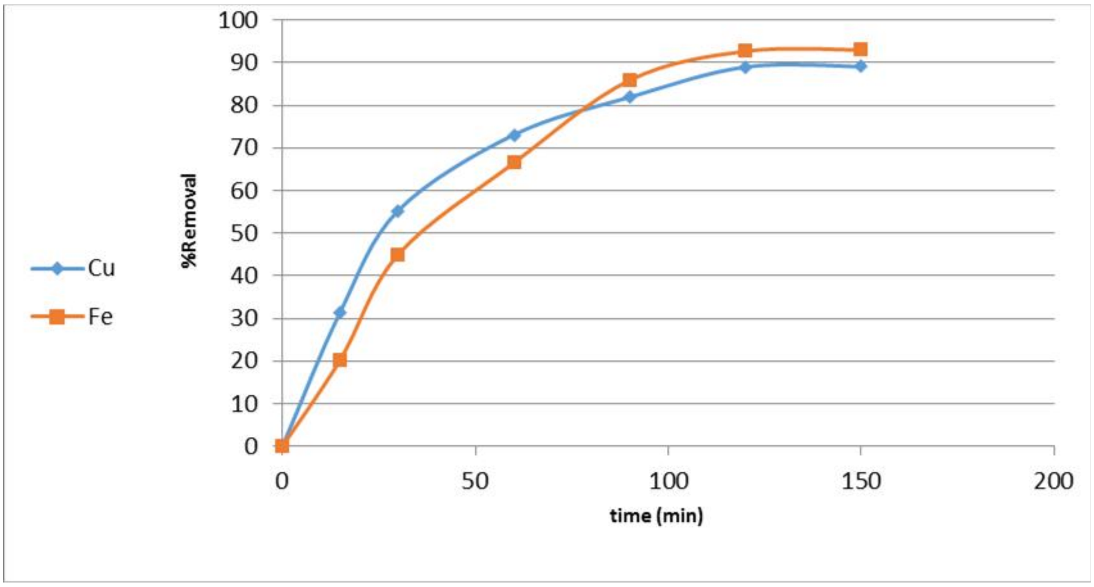

Fig (4): the effect of equilibrium time on the removal percentage of copper and ferric ions in aqueous solutions.

The effect of absorbent mass

The optimum absorbent mass was studied by varying the amount of adsorbent in the range from 0.02 g to 0.12 g in 50 ml of solution. it is appeared from (Figure, 5) that the removal percentage of copper and ferric ions in aqueous solutions increases with increases the mass of absorbent because of the number of adsorption vacant sites become higher. At low adsorbent mass the number of ions become higher than the vacant adsorption sites hence little number of ions will bend to these sites.

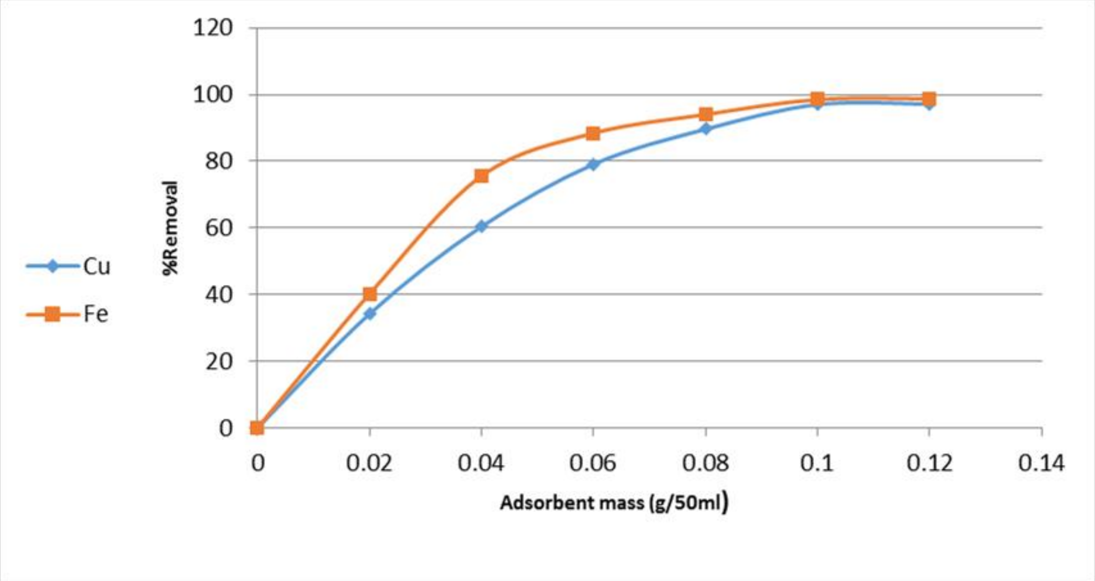

Fig (5): the effect of mass of absorbent on removal percentage of copper and ferric ions in aqueous solutions.

Adsorption isotherms:

Adsorption isotherm can be defined as pile up of atoms or ions of adsorpte on the surface of adsorbent (**Parameswara Murthy, and Andra Naidu, 2009**). There are more than one model described adsorption isotherms. In this study we focused on four models which are Langmuir, Freundlich, Temkin and Dubinin-Radushkevich.

Langmuir adsorption isotherm:

This type of adsorption assumes that all adsorption sites on adsorbent are identical and the adsorption occur on this sites. Each of these sites are occupied by only one adsorbate therefor, one monolayer is deposed (**Yıldırım Erbil, 2006**). Langmuir equation can be represented as.

$$\frac{Ce}{qe} = \frac{1}{qmax\, b} + \frac{Ce}{qmax}$$

Where b and q_{max} are Langmuir constants which are represented energy of adsorption and maximum adsorption capacity respectively. Ce and qe represent the equilibrium concentration (mg/L) and the amount adsorbed at equilibrium time (mg/g). The values of q and b can be calculated from the slop and intercept of the plotting $\frac{Ce}{qe}$ vs C_e (Figure 6). From the plotting. Maximum adsorption capacity q_{max} found to be 54.46 and 61.7 (mg/g) for copper and ferric ions respectively, while the energy of adsorption b is 0.234(mg/l) and 0.22 (mg/l) for copper and ferric ions respectively.

Freundlich adsorption isotherms:

This is one of the oldest adsorption isotherm developed by Freundlich. it's useful for adsorption from aqueous solutions and chemisorption isotherms (**Yıldırım Erbil, 2006**). Freundlich equation can represented as

$$\ln(q_e) = \ln(Kf) + \frac{1}{n} \ln c_e$$

Where q_e and C_e represented the amount of adsorbed per gram of adsorbent (mg/g) and equilibrium concentration (mg/l) respectively. Kf and n were empirical Freundlich constants which represent capacity of adsorbent (mg/g) and adsorption favorability respectively.by plotting ln(qe) vs lnCe (Figure 7) Kf values found to be 16.07and 18.89 (mg/g) for copper and ferric ions respectively. The n values are 2.77 and 3.16 for copper and ferric ions respectively. The value of n determines where the adsorption is favorable or unfavorable. If n value lie between one and ten then the adsorption is favorable if n less than one the adsorption in unfavorable. Hence the n values are 2.77 and 3.16 that's indicating the adsorption is favorable.

Temkin adsorption isotherm:

This type of isotherms assumes that all sites are not energetically equivalent (**Yıldırım Erbil, 2006**). The heat of adsorption for molecules lies in the same layer decreased linearly with coverage rather than logarithmic if the low and large Value of concentration are ignored. This adsorption contains a factor which is important into account of adsorbent-adsorbate interaction (**Tempkin, and Pyzhev, 1940; Aharoni, and Ungarish, 1977**). The equation of this model is given bellow

$$qe = B \ln At + B \ln Ce$$

$$B = \frac{RT}{bt}$$

Where At and b_t are temkin isotherm equilibrium binding constant (L/g) and temkin isotherm constant respectively. B is a constant related to heat of sorption (J/mol). R and T represents universal gas constant (8.314 J/mol) and temperature at 293K. By plotting qe vs ln Ce (Figure 8) B values are found to be 0.063 and 0.0745 (J/mol) for copper and ferric ions respectively. At Values are 0.143 and 1.658 (L/g) respectively for copper and iron and bt values are 40600 and 32697.98 for copper and iron respectively. This adsorption is physical adsorption since B values (indicate of heat sorption) are 0.063 and 0.0745 (J/mol).

Dubinin- radushkevich isotherm:

This isotherm is used to express the adsorption mechanism with Gaussian energy distribution onto heterogeneous surface (**Aharoni, Ungarish, 2007; Dabrowski, 2001**). This model also fitted at high activity of solute and intermediate range of concentration. This isotherm describe by the following equation.

$$\ln q_e = \ln q_s - (K_{ad}\varepsilon^2)$$

Where q_s theoretical isotherm saturation capacity (mg/g). K_{ad} and ε represent Dubinin-Radushkevich isotherm constants. The values of qs and K_{ad} can be calculated by plotting ln q_e vs ε^2 (Figure 9). The mean free energy E per molecule of adsorption can be calculated from the equation bellow (**Dubinin, M.M. 1960; Hobson, J.P. 1969**).

$$E = \frac{1}{\sqrt{2\,Kad}}$$

While ε can calculate through the equation.

$$\varepsilon = RT \ln\left[1 + \frac{1}{Ce}\right]$$

From the plotting the value of theoretical isotherm (qs) was 48.42 and 44.7 (mg/g) and the mean free energy was 0.408 and 0.745 J/mol respectively for copper and iron.

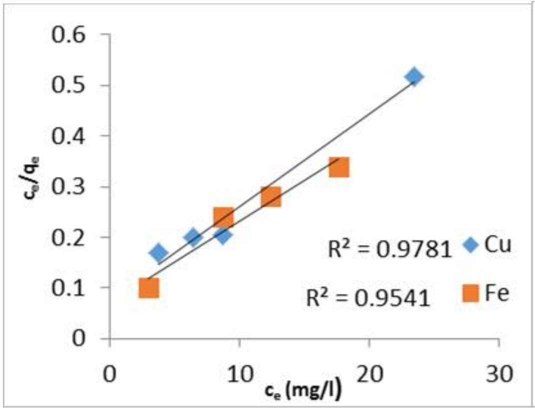

Fig (6): Langmuir adsorption isotherm.

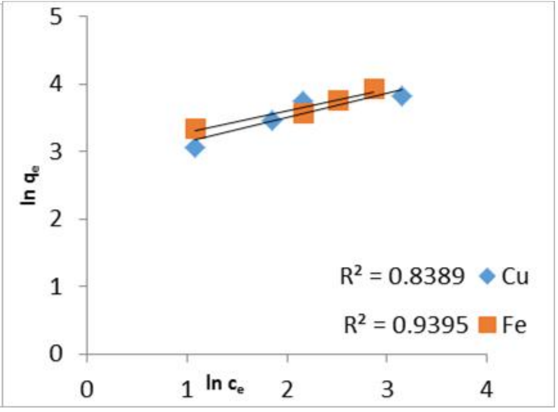

Fig (7): Freundlich adsorption isotherm.

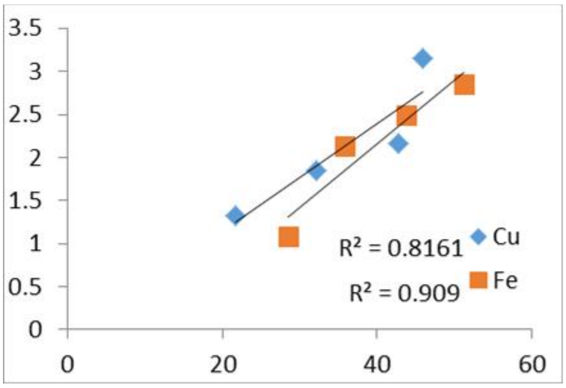

Fig (8): Temkin adsorption isotherm.

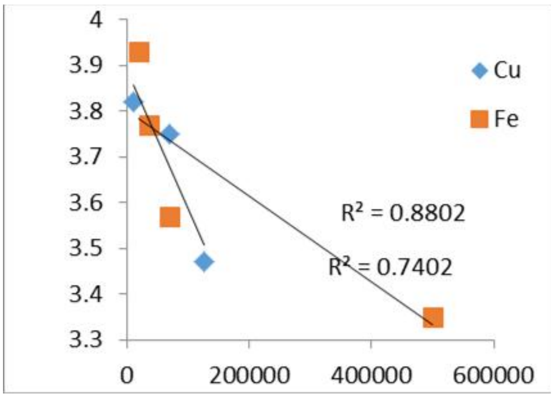

Fig (9): Dubinin- radushkevich adsorption Isotherm.

CONCLUSION

In this study the ability of wheat straw for removing of copper and iron ions from aqueous solutions were enhanced by forming cross-linking with malonic acid at temperature of

120°C and time 12h. The adsorption is favorable for Langmuir science the b values are 0.22 and 0.23mg/l for copper and iron respectively. The n values in Freundlich isotherms are more than one that is indicate the adsorption is favorable and its physical adsorption ((If n= 1 the adsorption is linear, if n >1 the adsorption is physical, if n< 1. The adsorption is chemical). Since B values (indicate of heat sorption) is 0.063 and 0.0745 (J/mol), then this adsorption is physical adsorption.

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