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Removal of Chromium from Aqueous Solution using Multilayer-Mixed (Reduction/Sorption) Bed from Iron Scrap and Nutshells

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Abstract— In this research removal of chromium from an aqueous solution by multilayer-mixed (reduction/sorption) bed via scrap iron as zero valent iron and charred nutshell (walnut shell) as adsorber were studied. Both batch and continuous system were conducted. The batch system reveals that the adsorption process was of favorable type. Three models were used to describe the adsorption process. Freundlich model is matching well to the data with (R2=0.975). In the continuous system , two sets of experimental were considered, the first set (multilayer bed) conducted by fixing the characteristics of the scrap iron bed (bed height 0.2 cm, particle size 500 μm) and varying the walnut shell parameters, the optimum value of this set recorded as (bed height 2.5 cm, particle size250μm). While for the second set of experimental after fixing the optimum values of the walnut shell bed and varying the scrap iron bed characteristics, the optimum values were (height 1cm, particle size 500μm as filling). Also, the Mixed bed configuration were studied by conducting the optimum conditions for the previous experiment. it was found that at any certain time the mixed layer offers the maximum efficiency of removal rather than the multi-layer bed.

Keywords— Scrap iron, Chromium, adsorption, walnut shells.

1.   Introduction

Environment pollution is a worldwide problem and have a great potential and influence to human health [7] [14]. Pollution reaches its most serious proportions in the densely settled urban-industrial centers of the more developed countries [10]. Heavy metals can be found in dissolved form, particulate and colloidal phases, the presence of metals in water bodies can be caused by either anthropogenic origin (e.g. waste water disposal) or natural origin (e.g. leaching of ore deposits) [3][11]. Chromium is a metal that have extremely importance and variety uses in industries like: textile dying, tanneries, metallurgy, chemical and refractory industries, wood preserving, preparation of chromate compounds, metal electroplating. Hexavalent Chromium (Cr^{+6}) compounds show a high environmental mobility and have toxic effects in most living organisms [6]. Trivalent Chromium (Cr^{+3}) is undesired metals that have adverse affects on human health and can accumulate in the food chain, that will because numerous diseases. Many industries use trivalent chromium Cr^{+3} and disposed it from their effluent, such as electroplating, tanning and leather. In wastewater the max. level of Cr^{+3} is 5mg/L [4].

2.   Experimental work

This study was done to assess the use of scrap iron fillings (as a zero valent iron) to continuously reduced of Cr^{+6} to Cr^{+3} and subsequent adsorption of Cr^{+3} onto charred walnut shells. The effect of different factors and conditions on treatment process such as bed height and particle size of scrap iron and charred walnut shell, had been studied.

2.1   *2.1 Zero valent iron fillings*

Scrap iron filings was used in this study as a zero valent iron (ZVI, with oxidation number of zero, Fe0), type SELKA GmbH, Hamburg, Code 46 12.12, Germany.

2.2   *Preparation of adsorbent*

Walnut shells were collected from local markets and washed with de-ionized water for several times to remove

impurities and dirts. Wetted Walnut shells were dried at 100 ºC using electrical laboratory oven as reported by [12]. The dried Walnut shells were grinded and then charred in a laboratory furnace (type CARBOLITE-CWF 1200) set of (600 ºC) for (1 h) [12]. The resulted charred walnut shells were sieved to (250 μm, 600μm, 1mm) size using (Sieves type, S/N:0307314, Body size (200 ×500)mm, Made in Germany) to study the effect of changing the particle size on adsorption process.

2.3 *Contaminant*

The stock solution of chromium with concentration of (1000)ppm (mg/L) was set through dissolving (5.6584)g of (K2Cr2O7) potassium dichromate in (1L) volume of de-ionized water. Prepared stock solution was diluted finally to get the desired concentration of chromium ions, by using equation (1) [15].

$$W = C * V * \ (M_{(wt)})/ \ \llbracket At \rrbracket_{(wt)} \qquad ...... (1)$$

Where:

W   : the metal mass of K2Cr2O7   (mg)

C   : the required concentration   (mg/L)

V   : solution volume in (L)

At wt : the atomic weight, Cr=   51.99 gm/mole

$\mathcal{M}$wt   : the molecular weight, for potassium dichromate= 294.1846 gm/mole.

2.4 *Batch Experiment*

Batch experiment was conducted by using constant mass of one of the two waste materials with different masses for the second material; (e.g. adding 0.5 gm of scrap iron to (0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4 , 1.6, 1.8, 2 gm) of char prepared from walnut shells, then using the optimum dose of the char with different masses of scrap iron (0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1gm). Stock solution was diluted to obtain the needed concentration(25 mg/L) of chromium ion.

Samplesof (100ml) of the –known concentration-solution were placed in flasks (conical), with accurate masses of walnuts waste adsorbent and scrap iron. pH=7 (was measured), temperature = 25oC. After that 10 flasks were put in rotary shaker (No.SM-25, Edmund, Made in Germany) with speed of agitation (100rpm) for 24 hours.

2.5 *Continuous System*

Glass tube of length (35 cm) and inner diameter (4.5cm), was used with distributer to insure a good distribution of the solution over the bed. Glass mesh also was used for preventing the materials losses. When the run is on, the solution of Chromium -with known concentration- was passed through the bed. (40L) volume plastic container

was used for containing the stock solution. A flow meter was used for measuring the flow rate. Electrical pump(HP-9600D) was used to pump the chromium solution from the feed solution to the bed. The bed is packed with scrap iron and charred walnut shells in two systems (separated and mixed).

3. Results and discussion

3.1 *Batch system*

To identify the adsorption isotherm, batch process was carried out to investigate the type of agricultural waste adsorbent (charred walnut shell) equilibrium isotherm relation.

Table 1: Equilibrium isotherms for the systems of chromium ions at Co=25mg/L onto charred walnut shell adsorbent, pH= 7, contact time = 24 h, agitation speed=100 rpm and temperature= 25 °C.

Weight of scrap iron (g)	Weight of charred walnut shell adsorbent (g)	C_e (mg/L)	q_e (mg/g)
1	0.2	16	4.5
1	0.4	9.1	3.975
1	0.6	6.1	3.15
1	0.8	4.21	2.59875
1	1	3.5	2.15
1	1.2	2.6	1.86667
1	1.4	2.4	1.61429
1	1.6	1.5	1.46875
1	1.8	1.3	1.31667
1	2	0.9	1.205

Experimental data for batch experiment was fitted to Langmuir and Freundlich isotherm (equations 2, 3 respectively).

$$q_e = \frac{q_{max}*b*C_e}{(1+b*C_e)} \qquad (2)$$

Where:

qe : adsorption capacity at equilibrium (mg/g).

Ce : concentration of metal ions remaining in solution at equilibrium (mg/L).

qmax: maximum amount of metal ion per unit mass of adsorbent to form a complete monolayer (mg/g).

b : adsorption equilibrium constant (L/mg).

$$q_e = \ KC_e^{1/n} \qquad (3)$$

Where:

Ce : The concentration of metal ions remaining in solution at equilibrium (mg/L).

qe : The amount of metal ions adsorbed (mg/g).

K and n are Freundlich's adsorption constants.

1/n: is surface heterogeneity or the adsorption intensity.

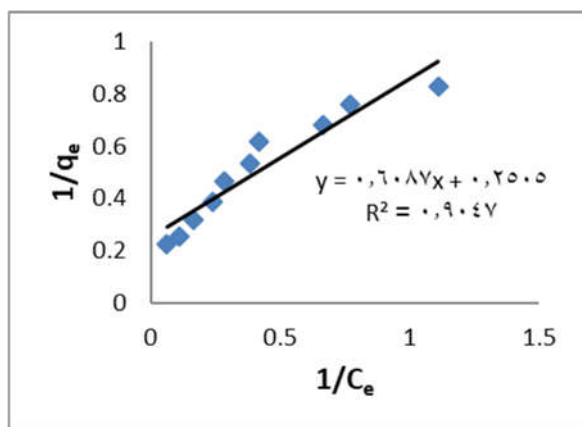It was found that Freundlich isotherm gave the best fitting according to R2 value which was equals to (0.975).
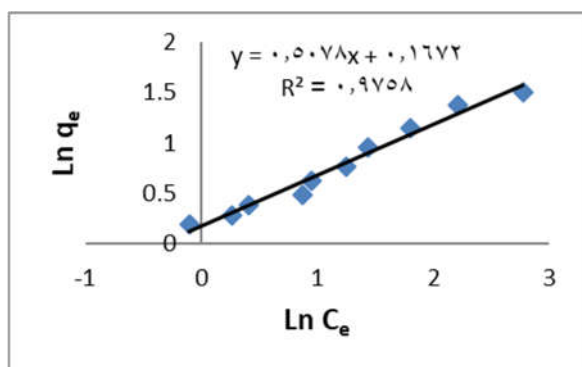

Figure 1 : Langmuir model.

Figure 2 : Freundhich model.

3.2   *Continuous system*

In the continuous operational systems different parameters were studied, shown in table 2:

Table 2: Experimental parameters

Bed height	Charred walnut shell	Scrap iron
	0.5, 1, 15, 2, 2.5 cm	0.2, 0.5, 1 cm
Particle size	250μm, 600μm, 1mm	500μm, (3-3.5mm)

3.2.1 Effect of bed height of charred walnut adsorbent

The effect of varying the bed height of the charred walnut shell adsorbent (0.5, 1, 1.5, 2, 2.5 cm) was conducted by fixing these parameters (bed height and particle size of scrap iron as (0.2) cm , and (500) μm respectively. The particle size of the charred walnut shell adsorbent was 600μm. Initial concentration was Co25(mg/L). the temperature 25ºC. pH 5.8 and flow rate 0.5 L/hr. The experimental breakthrough curves are presented in Fig.3 as Ce/Co versus time.
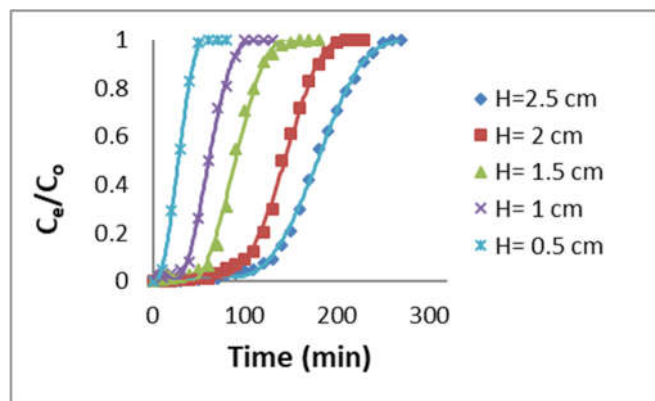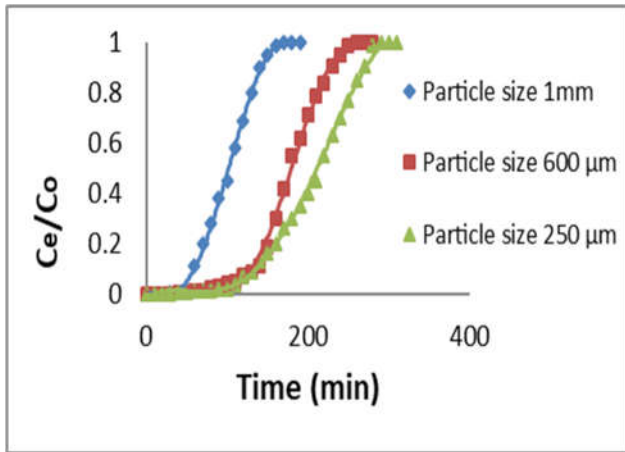

Figure 3: Breakthrough curves for different bed height of charred walnut shells adsorbent.

From this figure it is clear that when the height of bed increases, the breakpoint (in the breakthrough curve) increases. The reason is, as bed height is larg the ratio of adsorbate concentration in the effluent will be increasing slower than for a smaller bed height. Moreover, the time for saturation is increases. Greater bed heights correspond to greater mass of an adsorbent, as a result, a greater capacity for bed [5].

- Increasing the bed height will increase the contact time of the adsorbate with the bed, thus the adsorbate removal efficiency will improve. As the bed height increases, the adsorption capacity will increase too, which corresponds to extra spaces on charred walnut shell active sites. These sites will be available for the adsorbate molecules for adsorpting on these empty active sites[1].

3.2.2 Effect of particle size of charred walnut adsorbent

The effect of using various particle sizes (250μm, 600μm,1mm) of charred walnut shell on the breakthrough curves were investigated with fixing the other parameters. Bed height of charred walnut shell was 2.5 cm. Initial concentration Co was 25 mg/L. Temperature was 25ºC, pH was 5.8 and flow rate was 0.5 L/hr. Experimental breakthrough curves are shown in Fig.4.
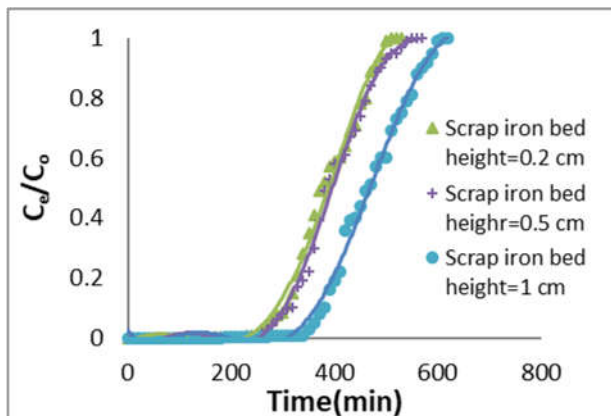
Figure 4: Breakthrough curves for different particle size of charred walnut shells adsorbent**.**

The breakthrough curves indicated that the time required for reaching breakpoint increases when particle size decreases. This occurs because that surface area available for adsorption increase with decreasing the particle size. That means more sites for adsorption and the adsorption capacity increases Figure (4) reveals that, as the particle size decreases, it will increase the time for saturation, and the film thickness that can be found around the adsorbent particle is increased. Also, inside the pore structure, the length of the path also increases. This will make the process kinetics low, the adsorbate molecules

will need more time to reach the active site on adsorbent, since the larger diffusion path inside the pores[2].

3.2.3-Effect of bed height of scrap iron

Three experiments were conducted for different bed height of scrap iron (0.2, 0.5, 1 cm) to examine breakthrough curves, with optimum conditions from the previous experiments. Experimental breakthrough curves are plotted in Fig.5**.**

Figure 5: Breakthrough curves for different bed height of scrap iron.

As it was observed from figure as the bed height of scrap iron increases, the breakpoint increases. The sorption capacity increases also as the bed height increases. This

can be attributed to the increase in specific surface of the sorbent (more binding sites), that will cause a delay in the breakthrough of the pollutant In addition, the time required for saturation and breakthrough are increased for long columns, as reported by [13].

3.2.4 Effect of shape and size of scrap iron

Effect of using different particle shape (spiral, fillings) Fig. 6, 7 respectively,

Figure 6 :Scrap iron Filling.

Figure 7: Scrap iron spiral.

With dimensions (length 3-7 mm and diameter 3-3.5 mm) for spiral, and (500 μm) for fillings scrap iron, on the breakthrough curves were studied by keeping the other parameters constant. Experimental breakthrough curves are presented in Fig.8.
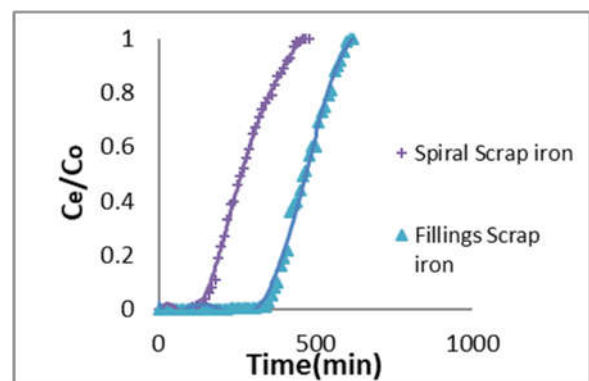
Figure 8: Breakthrough curves for different particle size of scrap iron

The previous figure indicated that when particle size of scrap iron decreases, the breakpoint will be increased. This is attributed to increasing the surface area needed for reduction. When the particle size decreases, additional sites would be available for solute and the reduction capacity increases [8].

4.   Conclusions

1- scrap iron filings (ZVI) offers a good media for reduction of Cr+6 to Cr+3 , and charred walnut shell act as a good recycled, charred media for adsorption of chromium from aqueous solution.

2- Fruendlich model describe well the adsorption data as this indicates a good agreement with the published studied and research in this field.

3- The removal efficiency of Cr increase with bed height, decrease in particle size for both scrap iron and walnut shell.

4- Using these waste materials (scrap iron and charred walnut shell) offering low cost alternatives for the conventional expensive methods in chromium removal from aqueous solution, and sustainable development benefits in terms of reuse of solid waste as well as a means of reduction disposal costs.

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إزالة الكروم من المحلول المائي باستخدام مفاعل متعدد الطبقات-مختلط   بتقنيتي (الاختزال /الأمتزاز) وباستخدام سكراب الحديد كمادة مختزلة وقشور المكسرات كمادة ممتزة

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الخلاصة – في هذا البحث يتم ازالة ايونات الكروم من المحلول المائي باستخدام مفاعل متعدد الطبقات- مختلط بتقنيتي (الاختزال/الامتزاز) وباستخدام سكراب الحديد كمادة مختزلة وقشورالمكسرات (الجوز) المتفحمة كمادة ممتزة. اجريت مجموعتين من التجارب (الدفع المتقطع و الدفع المستمر) وقد اثبتت تجارب الدفع المتقطع ((Batchان علاقة التوازن من النوع المفضل. وقد طبقت ثلاث موديلات وتم اختيار افضل موديل رياضي وهو Freundlich وهو افضل الموديلات اواكثرها انطباقاً. اما في تجارب الدفع المستمر (Continuous)فقد تم استخدام نوعين من الانظمة (مفاعل متعدد الطبقات، مفاعل مختلط)، في النوع الاول تم اجراء مجموعتين من التجارب1) تثبيت خصائص سكراب الحديد (ارتفاعه وقطر الدقائق) وتغيير عوامل وخصائص قشور الجوز المتفحمة ووجد ان افضل الظروف هي كالتالي (ارتفاع المادة المازة=2.5 سم، حجم دقائق المادة المازة=250 مايكرومتر) ،2) فقد تم تثبيت افضل العوامل والظروف التي تم الحصول عليها من التجارب السابقة مع تغيير خصائص سكراب الحديد وقد بينت التجارب ان افضل الضروف كانت (1سم ارتفاع سكراب الحديد،500 مايكروميتر قطر دقائق الحديد). كذلك تم دراسة النوع الثاني (المفاعل المختلط) ووجد ان نسب الازالة لفترة زمنية معينة كانت افضل من نسبة الازالة لنفس الفترة الزمنية في المفاعل متعدد الطبقات.

الكلمات الرئيسية – سكراب الحديد، الكروم، الامتزاز، قشور الجوز.