Removal of Hexavalent Chromium from Aqueous Solutions by Adsorption on Thermally Modified and Non-Modified Eggshells

Asst. Lect. Suheila abd alreda akkar
Department of Chemical Engineering
College of Engineering- Baghdad University
Email: suheila_akkar@yahoo.com

ABSTRACT:

Removal of heavy metals from waste water has received a great deal of attention. The compare Cr (VI) adsorption characteristics removing from wastewater by using thermally modified and non-modified eggshells were examined. Adsorption experiments were carried out in a batch process and various experimental Parameters such as effect of pH, adsorbent dosage, contact time, and initial chromium ion concentration on percentage removal have been studied. The modification of eggshells obtained by calcination which was performed in a furnace at 800°C for 2h after crushing of the dried eggshells. The adsorption of chromium ions from solutions containing different initial Cr^{+6} concentrations (50,100,150) mg/L. The results show that all factors have a significant effect on the percentage removal of Cr^{+6} ions from aqueous solutions and the optimum pH, weight and time of treatment are (8, 5.8), (0.5, 0.01) g and (120 ,60) min respectively for non-modify and modify eggshell. The present study was also aimed to evaluate the equilibrium of adsorption process using Langmuir and freundlich isotherms. The Langmuir isotherm was the best for correlation of adsorption data, showing maximum capacities of 16.6 and 159 mg/g for non-modified and modified eggshells, respectively. Meanwhile, the kinetics of (Cr^{+6}) adsorption on eggshell and modified of eggshells also analyzed using pseudo-first order.

Key words: Waste Eggshells; CaO; Adsorption; Removal of Cr^{+6}

ازالة ايون الكروم السداسي من المحلول المائي بواسطه امتزازه بقشور البيض المعالجه وغير المعالجه حراريا

م.م سهيله عبد الرضا عكار

قسم الهندسه الكيمياويه /كلية الهندسة/ جامعة بغداد

الخلاصه

ازالة المعادن الثقيلة من الماء والمياه الملوثه حظيت باهتمام كبير، حيث سوف يتم مقارنه بين ازالة ايون الكروم السداسي بواسطة قشور البيض المعالجه وغير المعالجه حراريا من الماء الملوث . واجريت التجارب في منظومه دفعيه وتم فيها دراسه المعاملات التاليه الاس الهيدروجيني، وزن الماده المازه، زمن الخلط وتركيز الاولي وتاثيرها على نسبة الازالة. يتم معالجه وتطوير قشور البيض بواسطه عمليه الكلسنه وذلك بادخال قشور البيض الى الفرن بدرجه حراره 800 درجه سيلزيه ولمده ساعتين وذلك بعد تجفيف وسحق وطحن قشور البيض. امتزاز ايونات الكروم من المحاليل التي تحوي تراكيز بدائية مختلفة من الكروم (50,100,150) ملغم/لتر وقد اثبتت النتائج ان الظروف المثالية للتخلص من ايون الكروم السداسي هو عند اس هيدروجيني ، وزن الماده المازه،والزمن هي الاتي(8,5.8)، (0.5، 0.01) غرام، (120,60) دقيقه على التوالي بالنسبه لقشور البيض غير المعالجه والمعالجه حراريا.وفي هذا الدراسة تم تحليل الايزوثيرم باستخدام لونك ماير والفريندلش وقد اظهرت النتائج ان لونك ماير مطابقة للنتائج العمليه اعلى سعة هي (16.6,159) ملغم/غم لقشور البيض المعالج وغير المعالج بالتتابع اماالنماذج الحركيه فاستخدمنا البسيدو من الدرجه الاولى لتحليل النتائج

الكلمات الرئيسيه: قشور البيض، اوكسيد الكالسيوم، الامتزاز، ازاله ايون الكروم

1. INTRODUCTION

Industrial waste water contaminated with heavy metals is commonly produced from many kinds of industrial processes therefore, if this waste water is not treated with a suitable process, it can cause a serious environmental problem in the natural eco-system [Ayad,2012 et al, park heung,et al. 2007].

Tannery effluent is a major source of aquatic pollution in Iraq with high hexavalent chromium. There are a large number of tanneries scattered all over Iraq. But the main areas of their concentration are al-qa`im ,haditha and hit and also in Baghdad in Al-Nahrawan .[Mohammed Nsaif, et al. 2013].

Water of high quality is essential to human life and of acceptable quality is essential for agriculture industrial, domestic and commercial uses. All these activities are also responsible for polluting the water. Billions of gallons of waste from all these sources are thrown to fresh water bodies every day [Muhammed Ali et al., 2012].

The requirement for water is increasing while slowly all the water resources are becoming unfit for use due to improper waste disposal [Suresh, et al. 2013]. The task of providing proper treatment facility for all polluting sources is difficult and also expensive; hence there is pressing demand for innovative technologies which are low cost, require low maintenance and are energy efficient [Rajendran, A. et al. 2011]. The adsorption technique is economically favorable and technically easy to separate as the requirement of the control system is minimum [Renge V.C et al., 2012].

Hexavalent chromium [Cr(VI)] compounds are being used in a wide variety of commercial processes and unregulated disposal of the chromium containing effluent has led to the contamination of soil, sediment, surface and ground waters. In trace amounts, chromium is considered an essential nutrient for numerous organisms, but at higher level, it is toxic and mutagenic. Nearly 80% of the tanneries are engaged in the chrome tanning processes. Most of them discharge untreated wastewater into the environment. In such aqueous waste, Cr (VI) is present as either dichromate $Cr_2O_7{}^{-2}$ *in* acidic environments or as chromate ($CrO_4{}^{-1}$) in alkaline environments. Chromium compounds were employed in textile coloring and leather tanning processes. The principal chromium emissions into surface waters are from metal finishing processes such as electroplating, pickling and bright dipping [Rajendran, 2010].

ollution of soils occurs as a result of the dumping of chromate wastes such as those from tanneries or electroplating and from sewage sludge disposal on land [Ambasht, 1983]. Uncontrolled emissions have greater potential for contaminating the fresh waters with relatively toxic form of Cr (VI), which exist only as oxy species and is strongly oxidizing other small discharges of Cr (VI) are from the additive in circulating waters, laundry chemicals [Anandakrishnanadar et al., 1992].

In this article, the technical feasibility of low cost (adsorption) , and locally available adsorbent (eggshell) for heavy metal removal (Cr^{+6}), from contaminated water has been reviewed.

This work is intended to remove Cr (VI) from aqueous solutions onto eggshells as an effective and low-cost. This also represents a serious problem for egg processing industries due to stricter environmental regulations and high landfill costs. Therefore, this paper aimed to present eggshells as porous adsorbents since it is feasible to grind the eggshell agro waste in the preparation of fine powders, which might pave the way for available materials. Moreover, Cr (VI) were successfully removed from water samples under the recommended conditions.

In the present investigation, to estimate the amount of chromium ions present in its aqueous solutions after treatment and the removal of chromium from wastewater using eggshell as an adsorbent is attempted. Though many conventional adsorbent are used for the effective removal of heavy metal ions, egg shell has been chosen as adsorbents with an aim to use waste pollutant material as adsorbent.

The present work is also aimed at fixing the optimal conditions such as, pH, equilibrium time (for batch mode technique), dosages of adsorbent and initial concentration on the adsorption efficiency of (Cr^{+6}) from waste water by non-modified eggshells and modify eggshells besides for effective removal of chromium. To evaluate the equilibrium of adsorption process using Langmuir and freundlich isotherms. Meanwhile, the kinetics of (Cr^{+6}) adsorption on eggshell and modify of eggshells also analyzed using pseudo-first order kinetic models.

2. EXPERIMENTAL WORK

2.1 Preparation of Adsorbent.

Chicken eggshells were collected. To remove impurity and interference material such as organics and salts, the sample was rinsed several times with deionized water. Then the sample was dried at 100°C for 24 h in the dry oven after that, the inner thin layer was removed from dried eggshell by hand. Then crushing eggshells were ground to a powder in a grinder, and sieved to obtain under 75µm size particles. Thermal modification of eggshells by calcination was performed in a furnace at 800 °C for 2h. After calcination the structure has been change and much developed pore was observed from the emission of co_2 . The formation of co_2 was assumed to follow an endothermic reaction as described in reaction (1).

$$caco_3 \longrightarrow \text{cao} + co_2 \qquad (1)$$

The sample were then packed into desicater for future use.

2.2 Preparation of Metal Solutions.

A stock solution of chromium (VI) is prepared by dissolving 2.8287g of potassium dichromate ($k_2cr_2o_7$) in 1000 ml of distilled water. This solution is diluted as required to obtain standerd solutions containing (50, 100, 150) mg/L of chromium (VI).

The pH was adjusted with 0.1M NaOH and 0.1M Hcl solution and measured by pH meter.

The concentration of chromium (VI) ions in the effluent was determined spectrophotometrically by developing a purple-violet color with 1, 5-diphenyl carbazide in acidic solution as an complexing agent. The absorbance of the purple-violet colored solution is read at 540 nm after 10 min.

3. RESULTS and DISCUSSION

3.1 Equilibrium Study

To select optimal operating conditions for full-scale batch processing. The graph plotted in **Fig.1** shows that a contact time of 120 min was sufficient to achieve equilibrium and that the adsorption did not change significantly with further increases in the contact time. Therefore, the removal of chromium concentrations at the end of 120 min are given as the equilibrium values of non-modify eggshell.

It is evident that time has significant influence on the adsorption chromium ion **Fig.2** till 60min, the percentage removal of chromium ion. from aqueous solution increases rapidly and reached up to 99% for modify eggshell. A further increase in contact time has neglected effect on the percentage removal. When compare **Fig.2** with **Fig.1** the modify eggshell can remove the chromium ion (Cr^{+6}) through 10 min with (99%) percentage removal of (Cr^{+6}) of 50 mg/L concentration ofCr^{+6}. While the non-modify eggshell can remove 72% at the same time. The adsorption efficiency of chromium ions can be calculated as:

$$\text{Removal percentage} = ((C_o - Ce)/C_o)*100 \qquad (2)$$

Where C_o is the adsorbent initial concentration (mg/L), Ce is the adsorbent concentration at equilibrium (mg/L).

3.2 Effect of pH Value on Adsorption.

The pH of aqueous solution is an important controlling parameter that strongly affects the adsorption of metals on the surface of eggshells. All batch experimental were conducted at room temperature (25°C). The results depicted in **Fig. 3** illustrate that the maximum adsorption removal was attained at pH of 8. The distribution of species clearly indicates that between pH values of 2 and 4, the complex compound is adsorbed on eggshell, but that between pH values of 4 and 6, chromium is adsorbed principally, through cation exchange mechanism.

At pH 3, adsorption can be explained by ion-exchange mechanism in which the important role is played by carbonate groups that have cation-exchange properties, as has been reported. At lower pH < 3, the metal adsorption was diminished which may be attributed to the fact that protons compete with metal ions for carbonate binding sites. The concentration of protons is higher, and thus more groups are bound with protons and therefore less groups are available to metal ions. Moreover, the large part of eggshell sorbent was dissolved.

At pH 8 adsorption removal reached a maximum.
The decrease in the removal efficiency at high pH values more than 8 may be attributed to the fact that the negative species of chromium are not capable of combination with the negative surface of eggshell.

While **Fig.4** shows that adsorption removal of $Cr^{+6}$of modify eggshell that optimum PH 5.8. as the PH increased the carbonate groups in chicken eggshells would be exposed increasing the negative charge on the adsorbent surface, attracting the metal cations and allowing the adsorption onto the adsorbent surface.

3.3 Effect of Adsorbent Dosage on Adsorption.

The effect of non-modify eggshells dosage on remove chromium ion is shown in **Fig. 5**. The removal increased from 30.8%, 41%, and 58% for different concentration (150, 100, 50) mg/L respectively to55%, 60%, and 80% with an increase in adsorbent dosage from0.01 g to 1 g at pH = 8.

However, no more significant removal of Cr^{+6} was observed by addition of more than 0.5 g of non-modify eggshell.

The effect of adsorbent dosage for modify eggshell on the adsorption of chromium (VI) process is shown in **Fig. 6**. Removal of chromium (VI) increases with increase of adsorbent dosage. The percentage removal increases from 56%, 74%, and 80.3% to 88%, 90%, and 99.9% for the concentration (150, 100, 50) mg/L respectively by increasing the adsorbent dosage from 0.005 to 0.05 g. the optimum dosage is (0.01) g.

3.4 Adsorption Isotherm.

A series of solutions containing different initial concentration of Cr^{+6}ions in the range of (50-200) mg/L was prepared and employed for batch adsorption studies at 25 °C and these flasks were placed on a shaker along 24h with 50 ml and 0.3g, pH of 8 of non-modify eggshells and 0.03 g, pH 5.8 of modify eggshells, **Fig.7** and **Fig.8** show the isotherm of non-modify and modify eggshells respectively.

The amount of adsorption at equilibrium qe (mg/g) was calculated as:

$$qe = (C_o - Ce) * v/w \quad (3)$$

where Ce(mg/L)is the concentration of Cr^{+6}solution at equilibrium and C_o is initial concentration of Cr^{+6}. V (L) is the volume of the solution and w (g) is the mass of dry adsorbent used.

The equilibrium study is important for an adsorption process as it shows the capacity of the adsorbent and the adsorption isotherm is normally applied to describe the adsorption mechanism for the interaction of cations on the adsorbent surface.

In the present study, experimental data were analyzed using Langmuir and Freundlic models. The equations for Langmuir and freundlich isotherms are expressed as **eq.4** and **eq.5** respectively.

$$qe = \frac{qm*kl*Ce}{1+kl*Ce} \quad (4)$$

$$qe = kf * Ce^{1/n} \quad (5)$$

Where qe is the adsorption capacity at equilibrium (mg/g), Ce is the adsorbent concentration at equilibrium (mg/L),kl is the adsorption equilibrium constant (L/mg) related to the apparent energy of adsorption, qm is the maximum adsorption capacity of adsorbent(mg/g), n indicates the bond energies between metal ion and adsorbent, and kf(L/g) is related to bond trength [Ghazy S.E.,2008,Zeid,2007].The Langmuir and freundlich equations represent Cr^{+6}adsorption by non-modify and modify eggshells as illustrated in **Fig.9** and **Fig.10**.

The adsorption constants of Langmuir and freundlich equation s and their correlation coefficients (R^2) are presented in **Table1.**

3.5 Analysis of adsorption kinetics

The kinetic study of metal ion adsorption is important to give insight into the adsorption rate, provide information on the contact time required for considerable adsorption to take place and also the factors affecting or controlling the adsorption rate. In order to investigate the mechanism of Cr^{+6}adsorption by non-modify and modify eggshells and potential rate controlling steps one of the most commonly used kinetic model, psedo-fist orderwas employed to evaluate the adsorption of Cr^{+6} . the equation for the pseudo-first order kinetic model can be represented by **eq.5**

$$Log(qe-qt) = Logqe\text{-}\frac{k1}{2.303}t \quad (5)$$

Where qt is the adsorption capacity at time t (mg/g), k1 is the first order reaction rate constant (L/min) [Areej,2012].

First order models illustrated in fig.11. A comparison of reaction rate constants and R^2 values estimated from pseudo first order for non-modify and modify eggshells is presented in**Table2**.

CONCLUSIONS

The removal of $Cr^{+6}$from waste water by using non-modify and modify eggshells has been investigatedl under several condition such as at different pH, different dosage and contact time.the optimum pH of Cr^{+6}adsorption was found at pH of 8 for non-modify eggshells and 5.8 for modify eggshells. The optimum dosage was 0.5g for non-modify eggshells and 0.01g for modify eggshell. The optimum contact time is 60 min and 120 min for modify and non-modify eggshells the modify eggshells is butter than non-modify that the number of active binding sites increased by calcination. Eggshells waste cheap material and thus it would be convenient to use it in industrial waste water treatment plants.

After calcination, most composition of eggshells was transfer med to lime (CaO) as well as enlargement of pore and grain was observed.

These results strongly suggest plausible reuse of calcination eggshell in the treatment of waste water contaminated with heavy metal.

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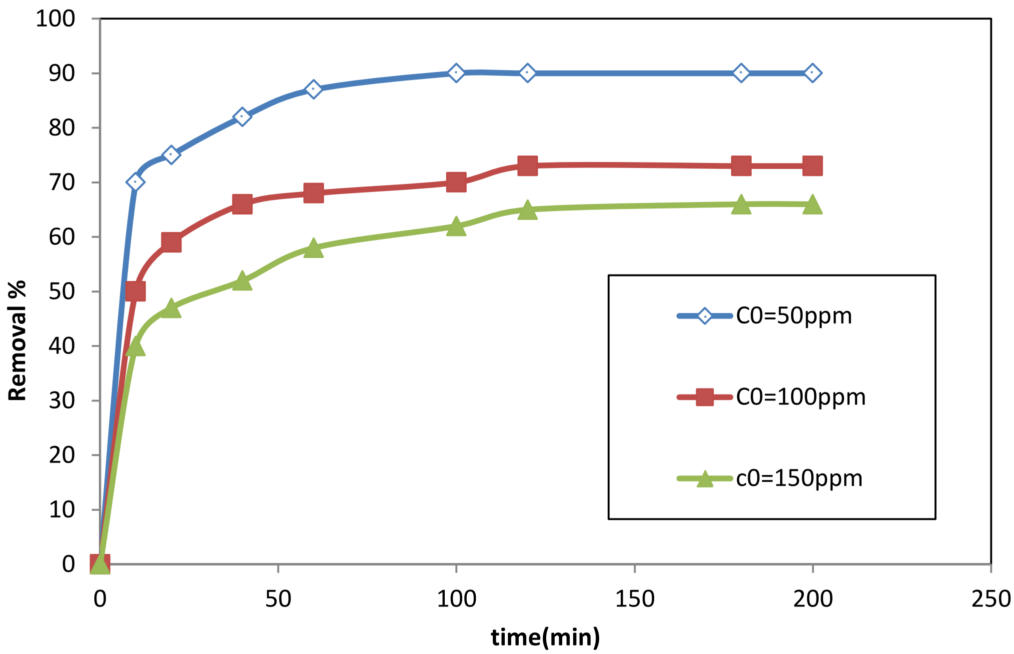

Fig.1 Effect of contact time on adsorption onto non-modify eggshell (w=0.5g, v=50ml, pH=8, T=25°C)

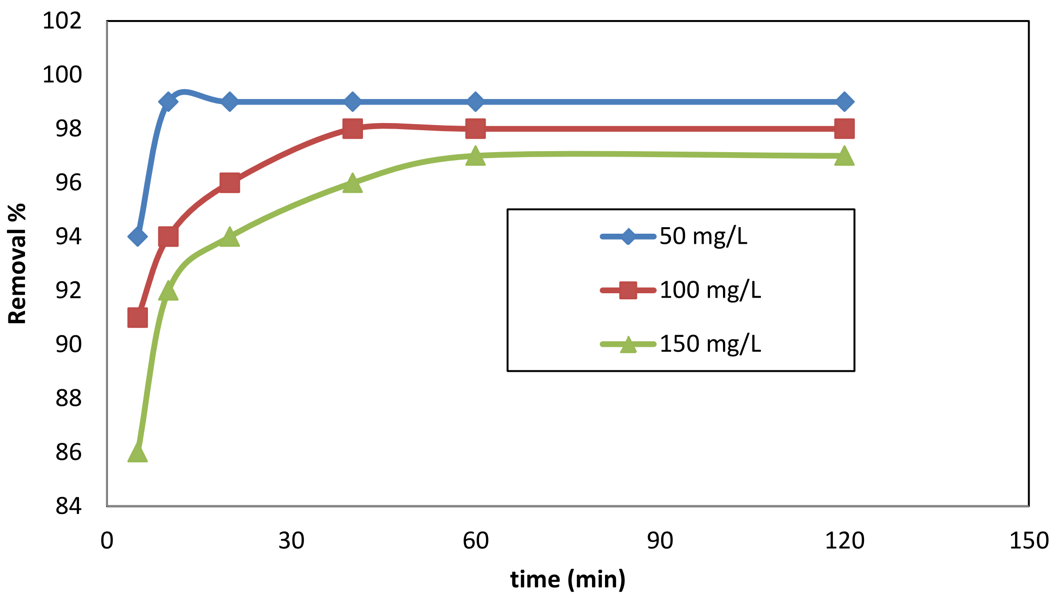

Fig.2 Effect of contact time on adsorption onto modify eggshell (w=0.0.01g, v=50ml, pH=5.8, T=25°C)

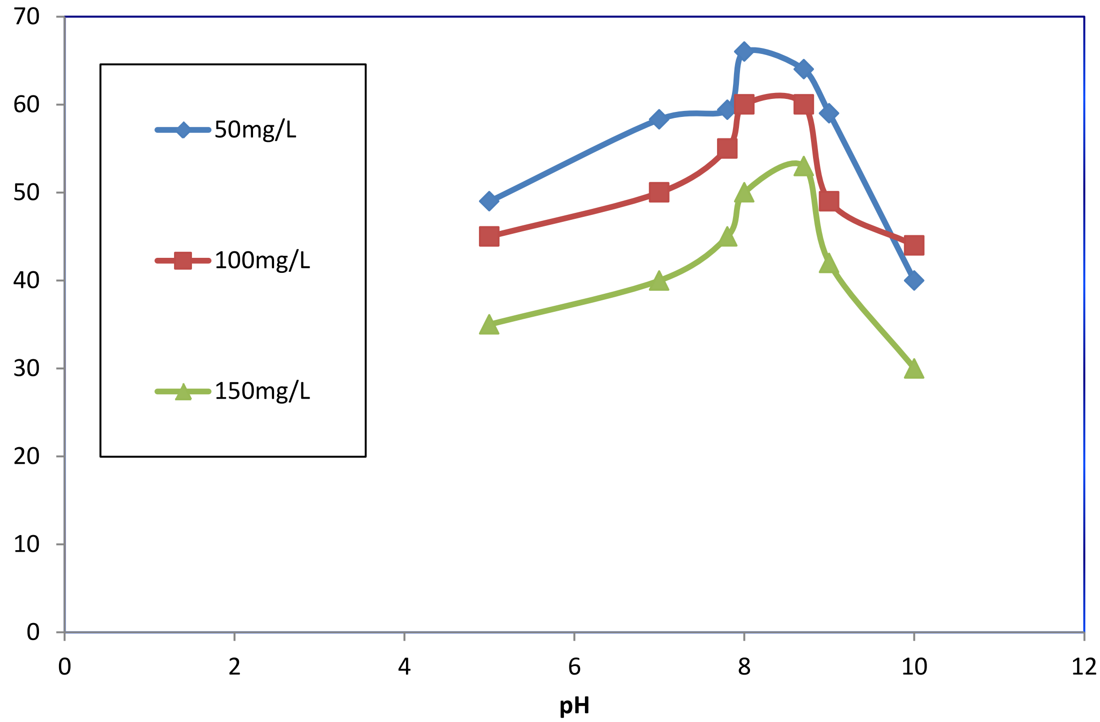

Fig.3 influence of pH on percentage adsorption of Cr^{+6} by non-modify eggshells (w=0.8g, v=50ml, t=120m)

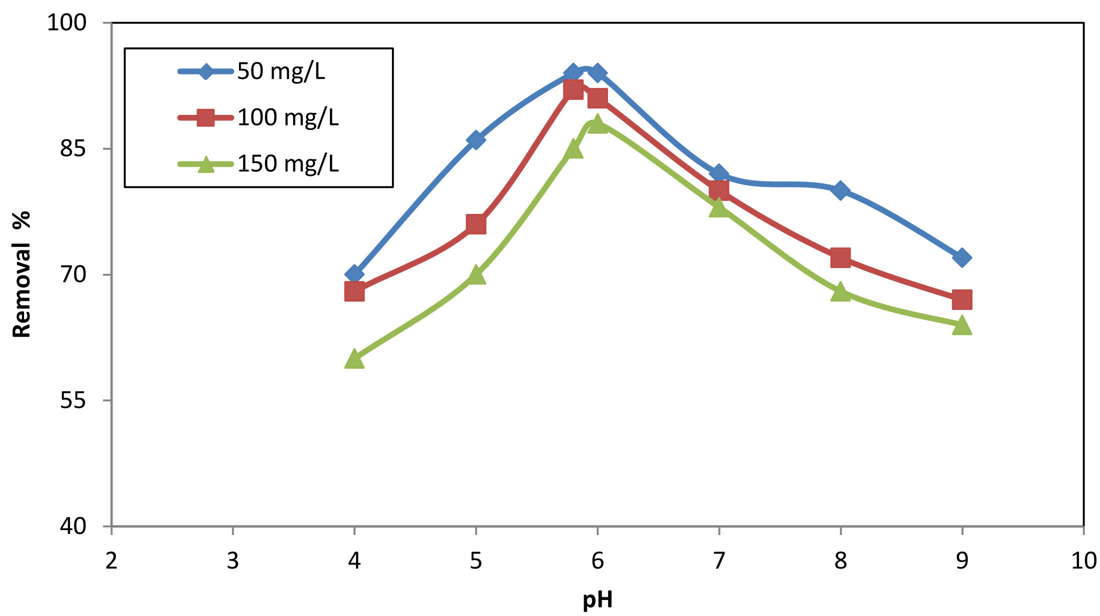

Fig.4 influence of pH on percentage adsorption of Cr^{+6} by modify eggshells (w=0.06g, v=50ml, t=60m)

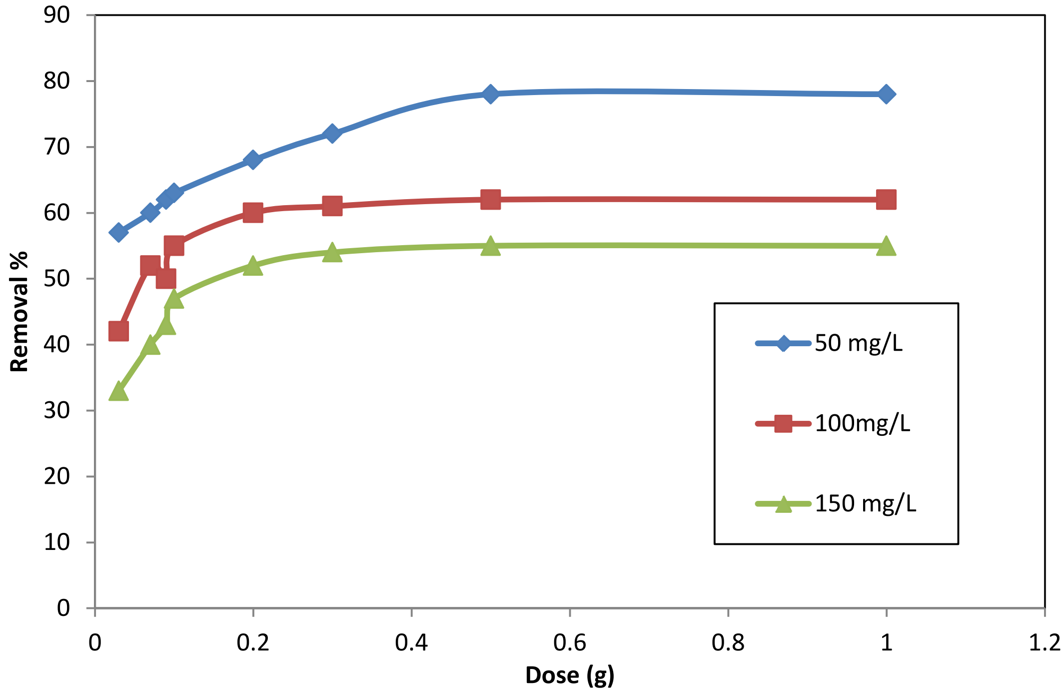

Fig.5 Effect of dosage on adsorption of Cr^{+6}onto non-modify eggshell.

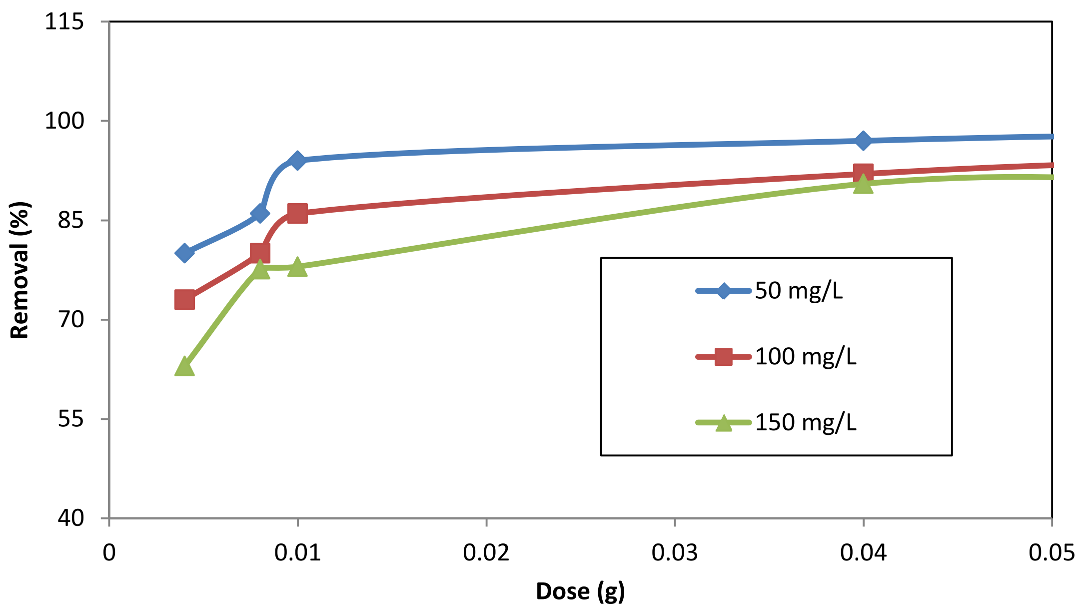

Fig.4 Effect of dosage on adsorption of Cr^{+6}on to modify eggshell.

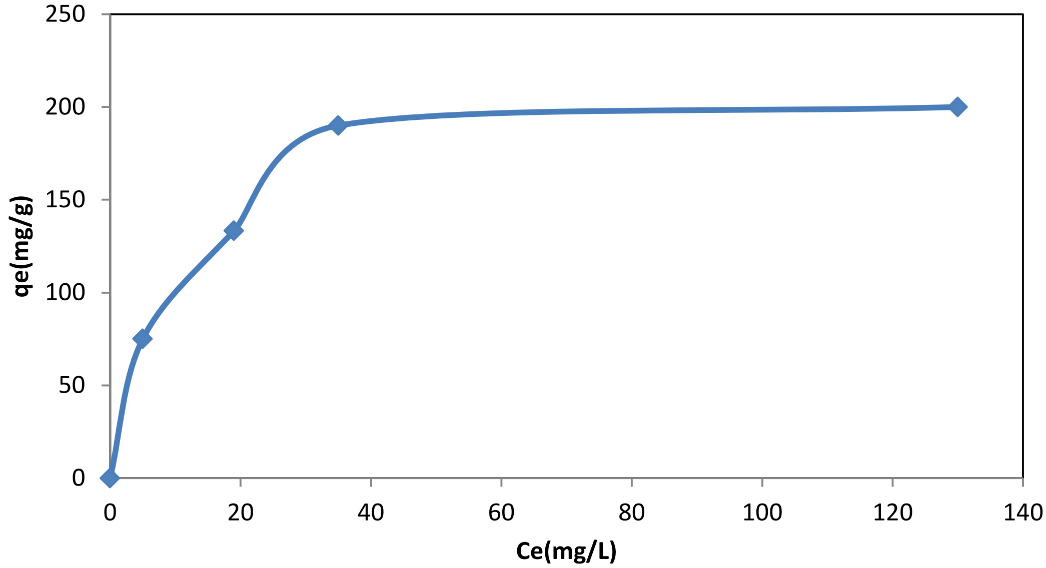

Fig.7 Adsorption isotherm of non-modify eggshell

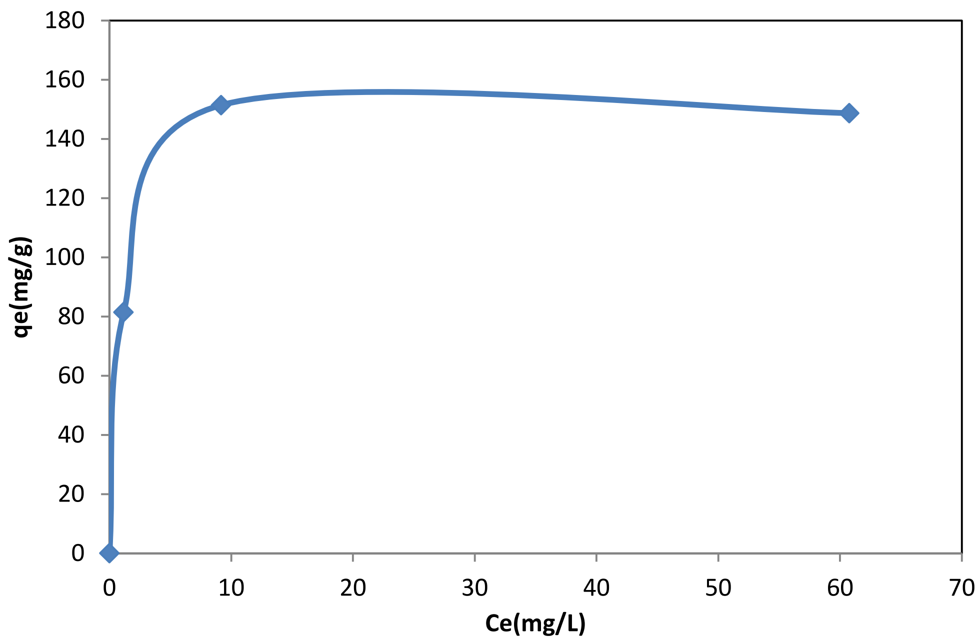

Fig.8 Adsorption isotherm of modify eggshells

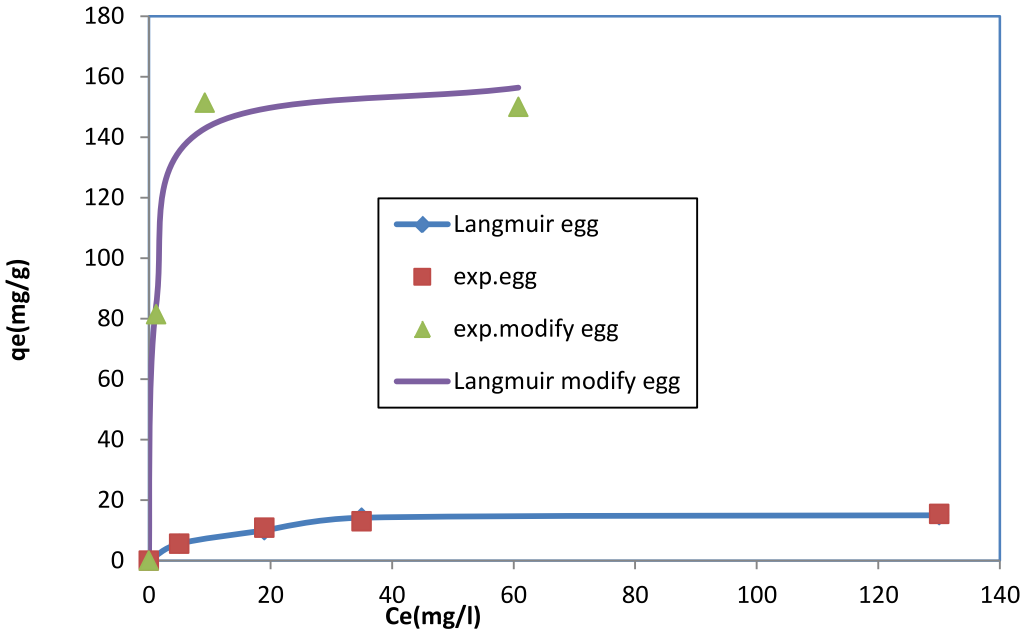

Fig.9 Fitting curve for Langmuir for both modify and non-modify eggshells

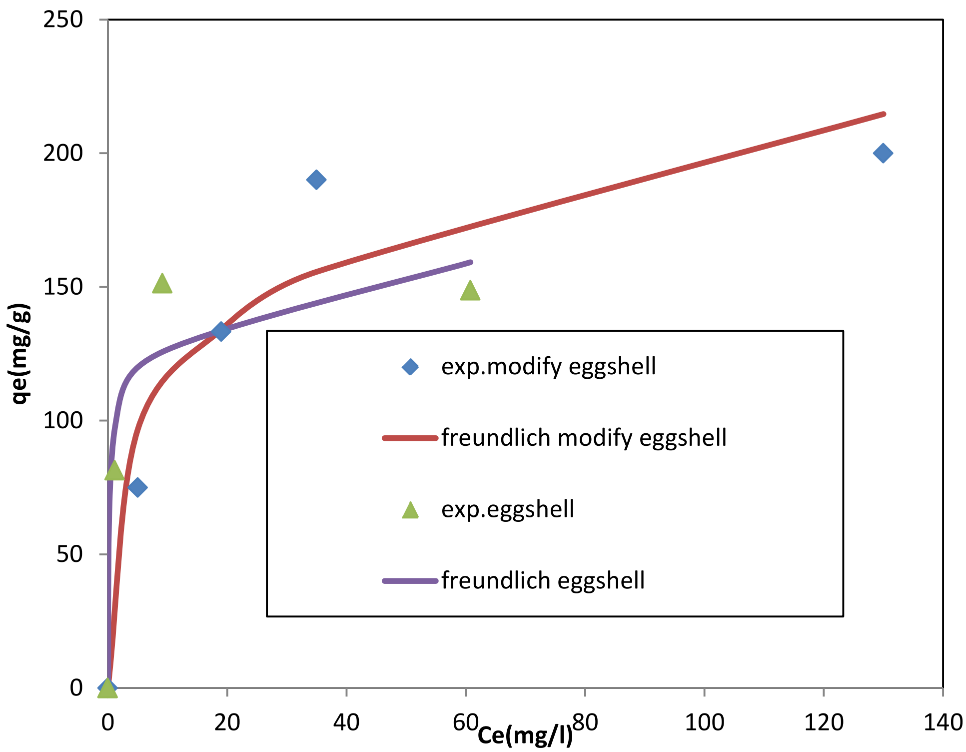

Fig.10 Fitting curve for Freundlich for both modify and non-modify eggshells.

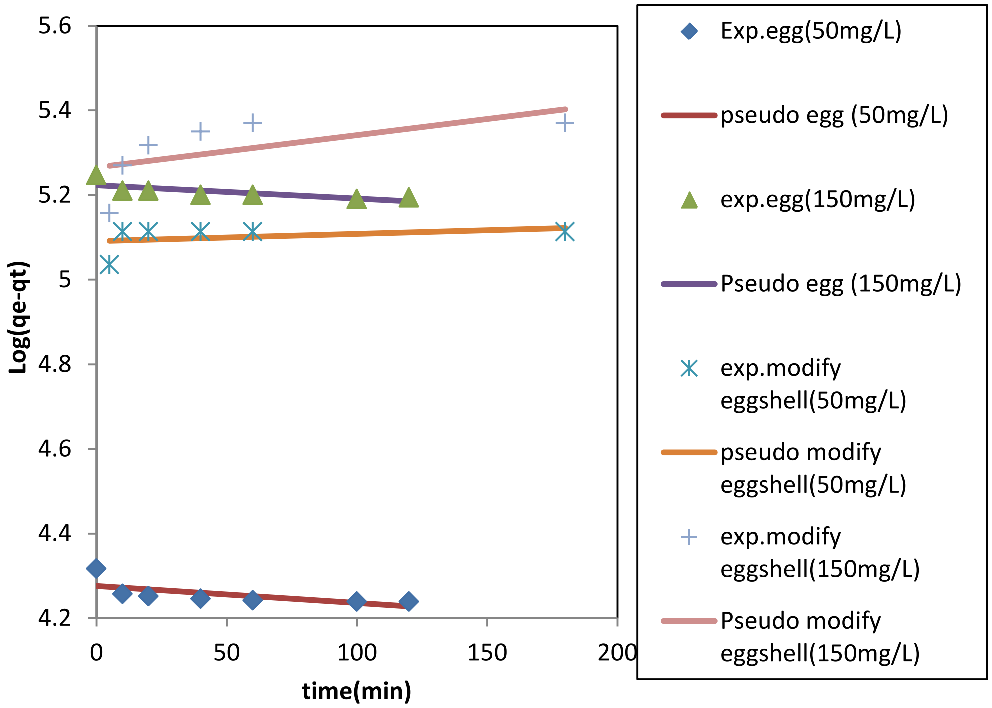

Fig.11 pseudo first order for non-modify and modify eggshells.

Table1. The Langmuir and freundlich isotherm constant

	Langmuir model			Freundlich model		
	R^2	qm (mg/g)	kl(L/mg)	n(g/L)	Kf(g/g)	R^2
Non modify	0.97	16.6	0.099	4.08	65.1	0.8
Modify	0.98	159		8.008	95.3	0.9

Table2.kinetic constant for Cr^{+6} adsorption by non-modify and modify eggshells

	qe(mg/g)	K1	R^2
Non-modify(50mg/g)	6.4027	0.0004	0.96
Non-modify(150mg/g)	9.6593	0.0031	0.94
Modify(50mg/g)	9.12	0.0001	0.99
Modify(150mg/g)	9.838	0.0007	0.99