Removal of Zinc by Bitter Orange Peels Activated Carbon and Commercially Activated Carbon, a Comparison Study.

Asst. Lecturer: Laith Hamdan Hawal
Environment Engineering Department, Al-Mustansiryiah University, Baghdad.
Laith_hamdaen@yahoo.com

Abstract:

In this study, a comparison between using activated carbon prepared from bitter orange peels (BOAC) and a common commercially activated carbon (CAC), which is brought from the market, as adsorbent materials. This study was designed to find out which of these two activated carbons is more effective in the removal of zinc from waste water. This work examines the use of bitter orange peels, which are available as waste in local markets and in household garbage as an alternative presage to prepare an activated carbon by using (H_2SO_4) as activating reagent. The effects of pH, initial zinc concentrations, treatment time, adsorbent media bed height and the flow rate of simulated synthetic aqueous solution (SSAS) on the removal efficiency of zinc were all studied under 24oC

The results indicated that the removal efficiency of zinc increases with decreasing in pH of SSAS. When the initial concentration of zinc increases in SSAS, the removal efficiency of zinc was decreased. The study proved that the increasing of contact time leads to greater removal efficiency. When the height of adsorbent media in fixed column increases, the removal efficiency was increased. The experiments also showed that the removal efficiency of zinc from the SSAS increased, when the flow rate decreased. It could be concluded from this work that (BOAC) is better than (CAC) as an adsorbent materials in the removal of zinc; with a removal efficiency of (90%, 86%), respectively

Keywords: bitter orange peels, activated carbon, zinc, adsorbent, removal, efficiency.

إزالة الزنك بواسطة الكاربون المنشط المصنع من قشور النارنج والكاربون المنشط التجاري, دراسة مقارنة

الخلاصة

في هذه الدراسة تمت المقارنة بين استعمال الكاربون المنشط المصنع من قشور النارنج والكاربون المنشط التجاري الذي تم جلبه من الاسواق كمواد مازة في إزالة الزنك من مياه المخلفات. تعتبر قشور النارنج من المواد المتوفرة بصورة كبيرة في مخلفات الاسواق المحلية وفي النفايات المنزلية . تم دراسة جدوى استعمال قشور الرارنج كمادة بديلة جيدة في صناعة الكاربون المنشط من خلال معاملتها مع حامض الكبريتيك كعامل كيميائي منشط.تم دراسة تأثير الرقم الهيدروجيني للمحلول المائي, التركيز الأولي للزنك في المحلول, وقت المعالجة, أرتفاع الوسط الماز في العمود المملوء بالمادة المازة وكمية التصريف للمحلول المائي على كفاءة الازالة تحت درجة حرارة 24 مئوي. أشارت النتائج الى ان كفاءة الازالة تزداد مع نقصان الرقم الهيدروجيني للمحلول المائي الحاوي على الزنك, وتتناقص عند زيادة التركيز الاولي للزنك في المحلول المائي. أثبتت ألدراسة أيضاً بأن زيادة وقت المعالجة وكذلك ارتفاع المادة داخل العمود المثبت يؤدي ة كفاءة الازالة. أظهرت التجارب أيضاً ان كفاءة أزلة

الزنك من المحلول ازدادت عندما تناقصت كمية التصريف للمحلول المائي. يمكن الاستنتاج من هذا العمل, إن الكاربون المنشط المصنع من قشور النارنج افضل من الكاربون المنشط التجاري كماد مازة في ازالة الزنك, حيث كانت كفاءة الازالة (86%,90%), على التوالي.

Introduction

The activities of human in agriculture, industry, transportation and mining...etc have a significant emission and excessive quantities of toxic metal ions are disposed to the environment (soil, water and air). The resulting effluents from smelting, battery manufacturing, metal plating and mining are the main resource of heavy metals in water. Heavy metals like (Cu, Cd, Hg, Pb, Ni and Zn) are toxic, non-biodegradable and persevere in the environment. Heavy metals may accumulate in water and soil, and then can cause an adverse effect on organisms **[1]**.

Zinc is one of the most portable heavy metal in groundwater and surface water and it is exist as dissoluble compounds at neutral and acidic pH values **[2]**. Zinc is an influential element that is important in human health. When humans absorb so little zinc they can suffer a loss of relish, reduction in the sense of smell and taste, slower flesh-wound healing and skin inflammation. Although people can handle properly large concentration of zinc, excessive zinc cause eminent health problems, like skin irritations, stomach cramps, vomiting and nausea. Too high standard of zinc concentrations can damage the pancreas and trouble the protein metabolism. Multitude exposure to zinc chloride can cause troubles in respiratory system. Zinc can be harmful to unborn and newborn children, when their mothers have uptake large quantities of zinc, the children may be exposed to damage of it through milk of their mothers or blood **[3]**

Membrane filtration, oxidation, damage effects chemical coagulation, solvent extraction and ion exchange have been suggested for the remediation of contaminated water by heavy metals. These operations are efficient in reduction metal contamination risk. Yet, they are costly and restricted to high concentration of heavy metal ions **[4]**. Adsorption is one of the most appropriate mechanism applied for water treatment, at most because it is appropriate for low concentration of metal ions but it is costly. Adsorption is a physicochemical process whereas the substance called adsorbate collects in the interface of solid called adsorbent. Activated carbon is broadly used as an adsorbent for water treatment because of it has large surface area and porous structure **[5]**. In spite of its considerable physical characteristics, using activated carbon is limited to its high cost. So, substitutional adsorbents taken from low cost materials should be introduced to reduce the operating cost particularly in developing countries **[6]**. Low cost adsorbents can be defined as materials plentiful in nature and waste from industries. Many low-cost materials like peanut, fly ash, husk charcoal, used tea leaves, watermelon peels and sunflower leaves have been examined for the removal heavy metals from aqueous solutions **[7]**.

The objective of this study is to manufacture a new alternative activated carbon material (bitter orange peels activated carbon, BOAC) capable of being used as

adsorbent material in removing heavy metals. This includes a comparison between the manufactured BAOC and a common commercially activated carbon (CAC) as adsorbent material in removing zinc from waste water.

Experimental Work
Materials
Bitter Orange peels

Bitter orange peels compounds were investigated by gas chromatography-mass spectrometry (GC-MS) and gas chromatography (GC), while phenolic compounds analyses was executed by invert -phase high performance liquid chromatography (RP-HPLC). The limonene was the main volatile compound of bitter orange peels (90.25%). HPLC analyses of bitter orange peels showed that phenolic acids compose their main phenolic class represent (73.80%), followed by flavonoids (23.02%). Ferulic acids and p-Coumaric were the most plentiful phenolic compounds represent (24.68%) and (23.79%), sequentially in the peels. The antioxidant effectiveness of bitter orange peels have been estimated using four tests in the laboratory, and the results obtained were compared with the typical antioxidants (BHT, BHA, and ascorbic acid).The results showed that Citrus aurantium peels were in possession antioxidant effectiveness which have less efficiency than those of antioxidant standards **[8].**

Preparation of Bitter orange activated carbon (BOAC)

Bitter orange peels activated carbon (BOAC) is prepared in a procedure modified from Roopa's work **[9]**. Bitter orange peels were collected from the waste of a local market in Baghdad. Peels were sun-dried for 7 to 8 days, and then washed two times with distilled water to remove impurities existence. The dried peels were oven-dried to remove additional moisture and then crushed and sieved to obtain particles with size 0.5 mm. After that, the peels were transferred into a melting-pot and concentrated H_2SO_4 was added and heated by an electrical oven under a temperature ranges between (110 to 150ºC). Finally, the peels were put under heat of (500ºC) for (6 to 8) hours until they were transformed into activated carbon. This chemically activated carbon was put in a beaker and cooled to the room temperature and was washed with distilled water many times, to remove the remaining acid content, then it was dried in hot air oven to evaporate moisture.

The (BOAC) characteristics were measured by the State Company of Geological Survey and Mining, Ministry of Industry and Minerals. The characteristics of the bitter orange peels activated carbon (BOAC) are shown in table (1).

Commercially activated Carbon (CAC)

The activated carbon, so called activated charcoal, is a kind of treated carbon that has a large surface area useful in adsorption and other chemical reactions **[10]**. Granular activated carbon was used immediately without treatment. Activated carbon is oscillator material that can be with positive or negative charge relying on the pH of solution. The attractiveness between the activated carbon and cationic or anionic guest materials is fundamentally associated with the surface characteristics. Widely negatively charged surfaces are acquired at high pH values and this favor the uptake of most cationic sets because of decreased electrostatic potential between cations and activated carbon surface and vice versa. An activation grade adequate for beneficial application may be obtained just from high surface area; yet, extra chemical treatment often enhances properties of the adsorption. The characteristics of the commercially activated carbon (CAC) are shown in table (1) **[11]**.

Table (1) Characteristics of Bitter Orange Peels Activated Carbon (BOAC) and Commercially Activated Carbon (CAC)

No.	properties	BOAC	CAC
1	Specific surface area, BET (m^2/g)	1390	990
2	Grain size/mm	2.9	2.2
3	Total pore volume/(cm^3/g)	1.98	0.9
4	Bulk density, g/cm^3	0.58	0.62
5	pH	5	7

Stock solutions

To avoid intervention with other materials in wastewater, the tests in this study were accomplished on a simulated synthetic aqueous solution (SSAS) with different zinc concentrations. A zinc stock solution was prepared by dissolving 4.55 g of $Zn(NO_3)_2.6H_2O$ powder (Hi Media, Mumbai, India) in 1000 ml of deionized water to achieve (1000 mg/l). All solutions used in the tests have been prepared by diluting stock solution with distilled water in order to get the desired concentrations for the experiential work of this study. The zinc concentrations in treated water were measured by using spectrophotometer (model Shimadzu AAS-7000)**.**

Adsorption System

The experiments, of fixed bed column for continuous flow system were conducted in order to examine zinc removal by treating SSAS under many zinc concentration, adsorbent bed depths (bitter orange activated carbon and commercially activated carbon) and various flow rates of SSAS of zinc at various pH. The pH values were modified using 0.2 N NaOH and 0.2 N HNO_3 solutions. Figure (1) shows a

schematic diagram of the sorption system, where the direction of flow is downwards due to gravity. The sorption system composed of (5 liter) plastic container with inlet and another for outlet. Rotameter is a flow meter that measures the flow rate of solution. Glass column has 2.54 cm ID and height 50 cm. The sorption column filled with adsorbent material to height of (5, 15, 25, 35, and 45 cm). The filled bed sorption column was washed by distilled water twice down flow through the column before starting the runs.

The adsorbent media (CAC and BAOC) were packed in the column to the desired depth, and fed to it as slurry by mixing up the sorption media with distilled water to avoid formation of air bubbles in the media. The adsorption process started by allowing the SSAS of required zinc concentration and pH, to flow downwards by gravity through the sorption column at a precise flow rate (1 l/min), as shown in figure (1). To determination the best operational conditions, the tests were executed at a constant temperature (24°C) and different pH values (between 1–9), initial feed concentrations of zinc (between 1–80 mg/l), treatment time (between 15-120 min), adsorbent bed height (between 5-45 cm) and flow rates (between 5-50 ml/min). Water samples, after treatment in each test, were collected every 15 minutes from the bottom of packed column and the adsorbed concentration of zinc ion in SSAS was determined by spectrophotometer. Table (2) shows the conditions of all experiments.

Table (2) Conditions of the experiments

EX. NO.	Initial zinc conc. (mg/l)	pH of SSAS	Treatment time (min)	Adsorbent media bed height (cm)	Flow rate (ml/min)	Purpose of Exp.
EX-1	1–80	1	120	45	5	Effect of initial concentration
EX-2	1	1–9	120	45	5	Effect of SSAS pH
EX-3	1	1	15-120	45	5	Effect of treatment time
EX-4	1	1	120	5-45	5	Effect of the adsorbent media bed height
EX-5	1	1	120	45	5-50	Effect of SSAS flow rate

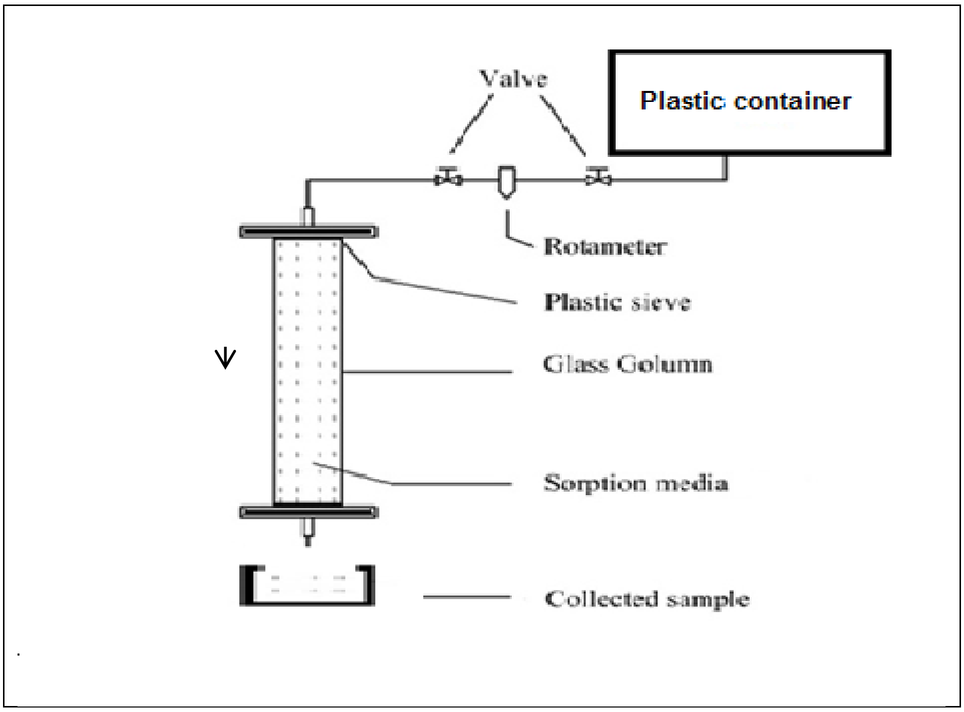

Figure (1) Schematic diagram of the adsorption system

Results and Discussions

The experiments of removing zinc from SSAS is achieved by fixed bed column and executed under continuous system with different parameters, which are initial concentrations (C_o) of zinc in SASS, pH of SSAS, time of treatment (t), bed height of adsorbent media (h) and the flow rate of SSAS (Q). The experiments were executed under a temperature of 24°C ($T_{(feed)}$). The removal efficiency of zinc from SSAS is calculated by the following equation:

$$R\,(\%) = \frac{\text{Initial conc.} - \text{Residual conc.}}{\text{Initial conc.}} * 100$$

Where:

R: Removal Efficiency

Effect of Initial Concentration

Figure (2) shows that the removal efficiency of zinc is decreasing when the initial zinc concentration (C_o) in SSAS increased (at $T_{(feed)}$ of 24°C, h of 45 cm, pH of 1, t of 120 min and Q of 5 ml/min). This can be explained by the reality that the initial concentration of zinc had a limited impact on zinc removal capacity; at the same time, the adsorbent media had a restricted number of active places, which would have become appeased at a definite concentration. This leads to an increase in the number of zinc molecules contending for the available functions places on the surface of adsorbent material. As the solution of lower concentration has a small concentration of zinc than the solution of higher concentration of it, then the zinc removal efficiency was decreased with increasing initial zinc concentration in solution **[12]**. When bitter orange peels activated carbon (BOAC) is used, higher efficiency for zinc removal (reached 90%) at initial concentration of zinc in solution (1 mg/l) under the same other parameters; compared with (86%) removal efficiency when the commercially activated carbon (CAC) was used. This means that (BOAC) was efficient and was better than the commercially activated carbon in removing zinc from SSAS.

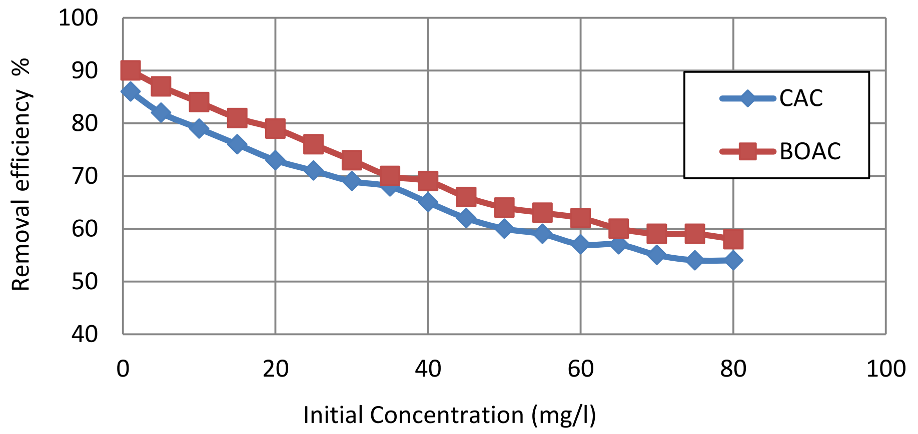

Figure 2. Effect of initial concentration of zinc on the removal efficiency of zinc

Effect of SSAS pH

Figure (3) shows the increasing in the removal efficiency of zinc when the pH of SSAS decreased from 9 to 1 (at C_o of 1 mg/l, Q of 5 ml/min, $T_{(feed)}$ of 24°C, h of 45 cm and t of 120 min). The increasing in removal efficiency can be related to the following: The adsorption of zinc from aqueous solution is dependent on the pH of the solution, which affect the surface charge of the adsorbent, and the degree of ionization and speciation of the adsorbate species. This could be due to the depending of zinc

ionization on the pH value. Zinc may be adsorbed to a lowest extent at higher pH values due to the impulsive force prevalent at higher pH values. In addition and in the higher pH values, zinc might forms salts which readily ionize leaving negative charge on the zinc ion **[12].** Together, the presence of OH- ions on the adsorbent prevents the uptake of zinc ions. pH also effect on the surface properties of the sorbent, i.e., charge of the surface of the cells used as sorbent. At very low pH values, the surface of the sorbent would also be surrounded by the hydronium ions, which reinforce the zinc interaction with binding places of the sorbent by greater attractive forces, thus its intake on polar adsorbent is reduced **[13].** It should be noted however, that BAOC has better (90%) than CAC because it already has less pH than CAC (5 and 7, respectively, table 1.), which may make it more efficient than CAC in zinc removal.

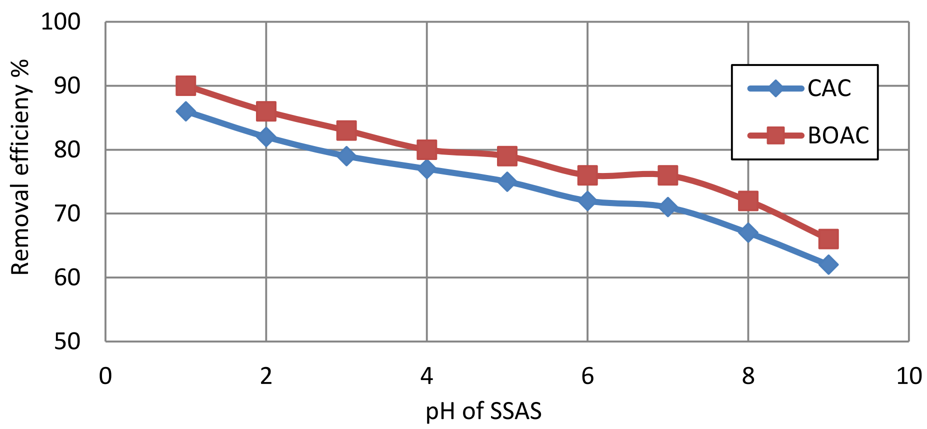

Figure 3. Effect of SSAS pH on the removal efficiency of zinc

Effect of Treatment Time

Figure (4) shows that when the treatment time of SSAS increased, the removal efficiency of zinc was also increased (at C_o of 1 mg/l, Q of 5 ml/min, $T_{(feed)}$ of 24°C, h of 45 cm and pH of 1). This result may be due to the fact that when treatment time is increased, SSAS will take longer time in contact with adsorbent materials (BOAC and CAC). Hence the adsorbent material adsorbs more quantity of zinc and therefore better removal efficiency **[14]**. However, BOAC has shown greater efficiency in removing zinc.

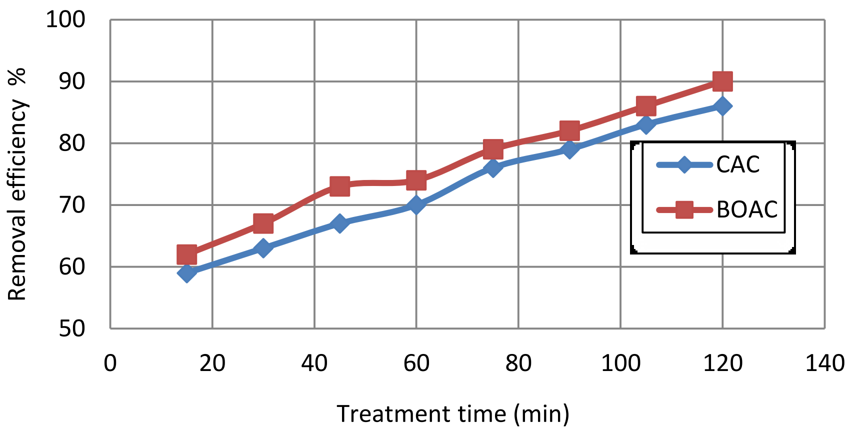

Figure 4 Effect of treatment time (t) on the removal efficiency of zinc

Effect of the Adsorbent Media Bed Height

Figure (5) shows that when the height of adsorbent media bed increased, the removal efficiency of zinc was also increased (at $C_\circ$ of 1 mg/l, Q of 5 ml/min, $T_{(feed)}$ of 24°C, pH of 1, and t of 120 min). The increasing of bed height (h) means increasing in the quantity of adsorbent media and this may increase the surface area, the number of active places on the adsorbent material surface, the availability of binding sites for adsorption and thus increase the capacity of zinc removal on adsorbent media **[14]**. This leads to the capability of the adsorbent media to adsorb largest quantity of zinc from SSAS at low initial concentrations and hence increasing the removal efficiency of zinc. Once again, (BAOC) has shown greater ability in removing zinc than (CAC).

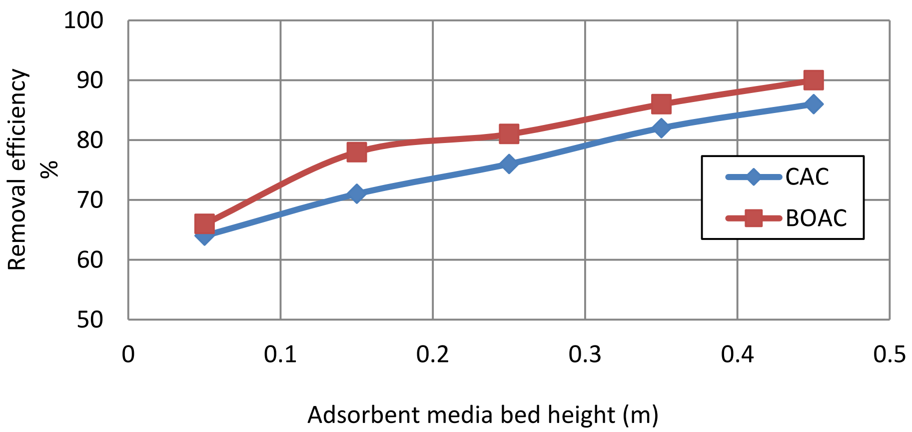

Figure 5. Effect of adsorbent media bed height (m) on the removal efficiency of zinc

Effect of SSAS flow rate

Figure (6) shows the relation between the flow rate SSAS and the removal efficiency of zinc. The results proved that increasing of flow rate means a decreasing in the removal efficiency of zinc from SSAS (at C_o of 1 mg/l, $T_{(feed)}$ of 24°C, pH of 1, and t of 120 min). When the flow rate is increasing, the velocity of SSAS flows in the fixed bed column increasing also. This means that the contact time of SSAS with adsorbent media in the column is decreasing, and then the adsorbent materials may uptake a lower amount of zinc from SSAS. Therefore the removal efficiency of zinc was decreased. While when the flow rate is decreased, the opposite will happen and the removal efficiency of zinc is increased **[14]**. Noticeably, BAOC appears to have greater ability in removing zinc than CAC.

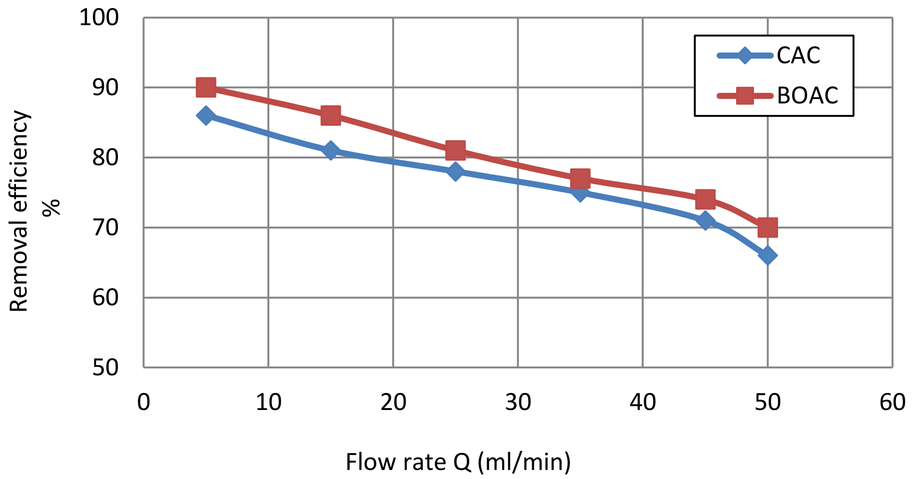

Figure 6. Effect of flow rate (Q) on the removal efficiency of zinc

Conclusions

1. The removal efficiency of zinc by using (BOAC and AACA) was increased with the decreasing of initial concentration of zinc, pH of solution and flow rate. While the removal efficiency was increased with the increasing of both height of adsorbent material and treatment time.
2. The study proved that the prepared bitter orange peels activated carbon (BOAC) is better than the commercially activated carbon (CAC) as an adsorbent material to remove heavy metals from waste water (90% and 86% for BAOC and CAC, respectively); because (BOAC) possesses greater specific surface area, lower pH, superior mechanical resistance and potential to adsorb harmful contaminants than (CAC).

3. The manufactured bitter orange activated carbon (BOAC) showed a good capability in removing zinc from SSAS by using a fixed bed adsorption system. So, (BAOC) is recommended to remove heavy metals from wastewater. In addition, bitter orange peels are available, a low cost and do not cause any damage to the environment. However, (BAOC) is cheaper than CAC, simple in use and has a high capability to adsorb heavy metals.

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