

Treatment of Industrial Wastewater of Samarra Drugs Factory Using Alum

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Accepted: 26/4/2011, Received: 2010/9/15

Abstract

The aim of the present study is to treat the industrial wastewater of Samarra drugs factory (SDF) by using oven dried alum sludge in fixed bed column with down flow, in performing the present study actual wastewater of (SDF) is taken to perform experimental work. It also involve studying the effect of bed depth [50, 60 and 70] cm, flow rate [2, 4 and 6] L/hr and particle size [2.8 and 5] mm. The dried alum sludge packed in Pyrex column with 2.8mm diameter and 50cm bed depth then increased the bed depth to become 60 and 70cm with different flow rates [2, 4 and 6] L/hr for every bed depth, then used 5mm particle size with 70cm bed depth at different flow rate. The samples were tested by using atomic adsorption apparatus type [shimadzu AA-6200]. The results indicated that the best removal percent of the pollutants [Ca, Zn, Fe, Cu, Cd and pb], at 2.8mm particle size diameter and 70cm bed depth with 2L/hr flow rate. Also the results indicated that the removal percent is directly proportional with bed depth and inversely proportional with flow rate and particle size, and the removal percent different from element to another.

Introduction

Adsorption is the accumulation of a substance at the interface between two phases. The material adsorbed is called the adsorbate or solute and the adsorbing phase is the adsorbent. In water purification, adsorbents are used to remove organic impurities, particularly those that are nonbiodegradable or associated with taste, odor and color. Although adsorption is applied most often as a tertiary treatment for impurities present in low concentrations, recent physical-chemical processes use adsorption as a primary technique to remove soluble organics from wastewater (Donald, 1979). Adsorption from water on a fixed bed of adsorbent is a process of unsteady state mass transfer between the liquid and solid phase. The concentration of adsorbed substance in both phases is the function of both time and location in bed (Wolborska, 1999).

Adsorption is commonly perforated in a packed bed where granular adsorbent is held stationary in a column and the contaminated water is contacted with adsorbent by its continuous passage through the bed. For long passage times, the adsorbent closer to the inlet of the fluid becomes

saturated with the contaminant at the present influent concentration. This give rise to the concentration front that divides the bed into a contaminated region and intact region. This concentration front, also called the mass transfer zone, continues to travel along the bed as more influent is being pushed into the bed. At the time the leading edge of the concentration front has reached the exit end of the bed, breakthrough is said to have been attained and the first emergence of the contaminant (usually at very low concentration) has just taken place. A breakthrough curve represents the effluent concentration history along the course of the adsorption operation. The point at which breakthrough occurs is called break point (Ruthven, 1984).

Adsorption and ion exchange share so many common features in regard to application in batch and fixed-bed processes that they can be grouped together as sorption for a unified treatment. These processes involve the transfer and resulting equilibrium distribution of one or more solute between a fluid phase and particles. The partitioning of a single solute between fluid and sorbed phases or the selectivity of a sorbent towards multiple solutes makes it possible to separate solutes from a bulk fluid phase or from one another. As the processes indicate, fixed-bed operation with the sorbent in granule, bead, or pellet form is the predominant way of conducting sorption separations and purifications. Although the fixed-bed mode is highly useful, its analysis is complex. Therefore, fixed beds including chromatographic separations are given primary attention here with respect to both interpretation and prediction. Adsorption involves, in general, the accumulation (or depletion) of solute molecules at an interface. The accumulation per unit surface area is small; thus, highly porous solids with very large internal area per unit volume are preferred. Adsorbent surfaces are often physically and/or chemically heterogeneous, and bonding energies may vary widely from one site to another. We seek to promote physical adsorption or physisorption, which involves Van der Waals forces (as in vapor condensation), and retard chemical adsorption of chemisorption, which involves chemical bonding (and often dissociation, as in catalysis). The former is well suited for a regenerable process, while the latter generally destroys the capacity of the adsorbent. Adsorbents are natural or synthetic materials of amorphous or microcrystalline structure. Those used on a large scale, in order of sales volume, are activated carbon, molecular sieves, silica gel and activated alumina (Keller, 1987).

For treating large quantities of liquid, columns packed with adsorbent granules are generally used. The liquid is fed to either the top or bottom of the column and flows through the packing. To avoid excessive pressure drop and minimize losses in handling, the particles for packed columns are

usually in the range 0.4 to 2.5 mm diameter. Equilibrium between solid and liquid phases is rarely achieved in practical fixed-bed operations. Under non-equilibrium conditions, concentration gradients exist between the bulk fluid surrounding the particle and the fluid inside the particle.

The steps in an adsorption process are mass transfer through the external boundary layer, internal diffusion through the porous structure, and adsorption on the interior surface. If one step is much slower than the others under a given concentration gradient, it is called the rate-determination step or controlling resistance. The transfer of adsorbate from bulk fluid to outer surface of the particle occurs by molecular and convective diffusion. Transport of material through a boundary layer is often referred to as film diffusion. For a given weight of adsorbent, the external surface area is inversely proportional to the diameter of the particles. If film diffusion is the controlling resistance, the rate of adsorption will be inversely proportional to the particle diameter. The transfer of adsorbate from the external surface to the interior of the particle occurs by diffusion in the void space of the pores or by migration along the pore surface. With fluid-phase pore diffusion, mass transfer precedes the adsorptive phase change whereas, with solid-phase pore diffusion, mass transfer occurs after adsorption on the surface. Since solid and pore diffusion occur in parallel, the over all rate of internal transport is the sum of the two processes. The rate equation for transfer of solute from fluid to solid phase depends upon the nature of the interaction between adsorbate and adsorbent. The relative magnitudes of film and internal diffusion are determined by the particular system and conditions. The external mass transfer resistance decreases with increasing fluid velocity over the solid surface. The internal mass transfer resistance decreases with decreasing particle size since the path length for diffusion is lowered. In packed-bed operations, both external and internal mass transfers are often important (Donald, 1979).

Effect of Flow rate, bed depth and particle size

Flow at low flow rate, the diffusion through the surface film may be the slowest and the rate determining step. If the fluid is agitated, the thickness of the surface layer reduced and the rate of mass transfer will increase. (Weber, 1947) illustrated the effect of flow rate on the solute uptake, based on assumption that film diffusion is rate limiting in early portions of column run. They found that increased flow rate in this region may be expected to result in compression or reduction of surface film, thereby, decreasing external resistance to mass transfer. (Malkoc, 2006) found that when the flow rate was increased the time required for complete

column saturation decreased shallow breakthrough curve is obtained at the highest flow rate tested. This is due to the decrease in contact time between the adsorbate and the adsorbent at higher linear flow rates. Also they found that the increase in adsorption with the bed height in a fixed bed was due to the increase in adsorbent does in larger beds which provide greater surface area (or adsorption sites). (Al-Bahrani & Martine, 1977) showed that the service life of the adsorbent column increase with increasing bed depth and adsorbent capacity at a break point increases with increasing bed depth; this indicates that for deeper bed the contact time will increase. In case of using an adsorbent particles of much smaller size, that will eliminate interparticle mass transfer resistance, so that the rate determining step is diffusion through film around each particle. (Furusawa, 1973) showed that the rate of adsorption by small particles is controlled by the rate of mass transfer from the bulk fluid phase to the solid phase, i.e, the film diffusion. The resistance offered by the solid to mass transfer becomes important as the particle size increased.

Alum Sludge

Alum sludge is an inescapable by-product of the processing of drinking water in water treatment works where aluminum salts is used the coagulant. Aluminum sulphate is arguably the most widely used coagulant in drinking water treatment. When aluminum sulphate is added to raw water, it dissociates into Al^{3+} and SO_4^{2-} . The Al^{3+} ions are immediately surrounded by water molecules and hexaquoaluminum ($[Al(H_2O)_6]^{3+}$) is rapidly formed. Hexaquoaluminum formed then undergoes series of rapid hydrolytic reactions to form charged polymeric or oligomeric hydroxocomplexes of various structures. Such hydrolytic products include $[Al(H_2O)_5(OH)]^{2+}$, $[Al(H_2O)_4(OH)_2]^+$, $[Al_6(OH)_{15}]^{3+}$, $[Al_8(OH)_{20}]^{4+}$ and $Al(OH)_3$, etc. (Bratby, 1980). During coagulation in water treatment process, these complexes adsorb and modify the surface charge of colloidal particles, e.g. natural organic matter such as humic and fulvic acid, microorganisms such as bacteria, protozoa and algae, and inorganic substances such as fine soil particles (Stumm, 1996). Thereafter, in the ensuing treatment units including flocculation, sedimentation and filtration, the colloids in the raw water are removed and transferred to the sludge phase together with the hydrolytic aluminum species. (Razali et al., 2010) Was studied the effectiveness of drinking water treatment sludge in removing different phosphorus species from aqueous solution. They found that the sludge bed remained stable and removed over 80% P in a 30 day period and the bed did not reach saturation point for over 60 days. This proves the potential of the sludge as a filter media in various forms of P

immobilization, thus converting it from wastewater to useful material in pollutant control. (Yang *et al.*, 2008) studied the influence of ageing on the structure and phosphate adsorption capacity of dewatering alum sludge. They found that the ageing time has insignificant effect on the structure and properties of the dewatered alum sludge and therefore, the phosphate adsorption capacity of the alum sludge shows insignificant change during the ageing process. (Zhao *et al.*, 2006) studied characteristics and mechanisms of phosphate adsorption on dewatering alum sludge. They found that the adsorption capacity decreased from 3.5 to 0.7 mgP/g sludge when the solution pH was increased from 4.3 to 9.0, indicating that adsorption capacity is largely dependent upon the pH of the system. The results of competitive adsorption between phosphate and typical anions found in wastewater, such as SO_4^{2-} and Cl^- , onto alum sludge reveal that alum sludge can selectively adsorb phosphate ions. The insignificant effect of SO_4^{2-} and Cl^- on P-adsorption capacity indicates that phosphate adsorption is through a kind of inner-sphere complex reaction. During the adsorption process, the decrease of phosphate concentration in solution accompanied with an increase in pH values and concentrations SO_4^{2-} , Cl^- and TOC (total organic carbon) suggests that phosphate replaced the functional groups from the surface of alum sludge which infers that ligand exchange is the dominating mechanism for phosphate removal. At the same time, the simultaneous increase in PO_4^{3-} and total aluminum concentration indicate that chemical reaction and precipitation are other mechanisms of phosphate removal. The cost of waste water treatment in this process is very small in comparison with other processes or insensitively because every day, huge amounts of alum sludge are generated from waste water treatment plants all over the world (Wei, 1999).

In the present study, the effect of various operating variables flow rate, bed height and particle size on the process of fixed bed down flow adsorption by using alum sludge as adsorbent in samara drugs industrial wastewater treatment are studied.

Experimental Work

Experimental Equipment

A laboratory-scale fixed-bed down flow system as shown in figure below was set up using 2cm diameter Pyrex column 1m long, the dried alum sludge was confined in the column by fine perforated Pyrex screen at the top and the bottom of the bed to ensure a uniform distribution of influent through the alum sludge and to prevent any loss of sludge. It also consists of a feed tank to supply the feed pump in waste water, centrifugal pump type marquee of 10-30L/min capacity it was used to feed the influent waste water from feed

tank to the adsorption column. Apart of waste water was circulated to the feed tank to achieve constant throughput. Rota meter ranged between 2-80 L/hr to measure the influent flow rate. Effluent container is to accumulate the effluent.

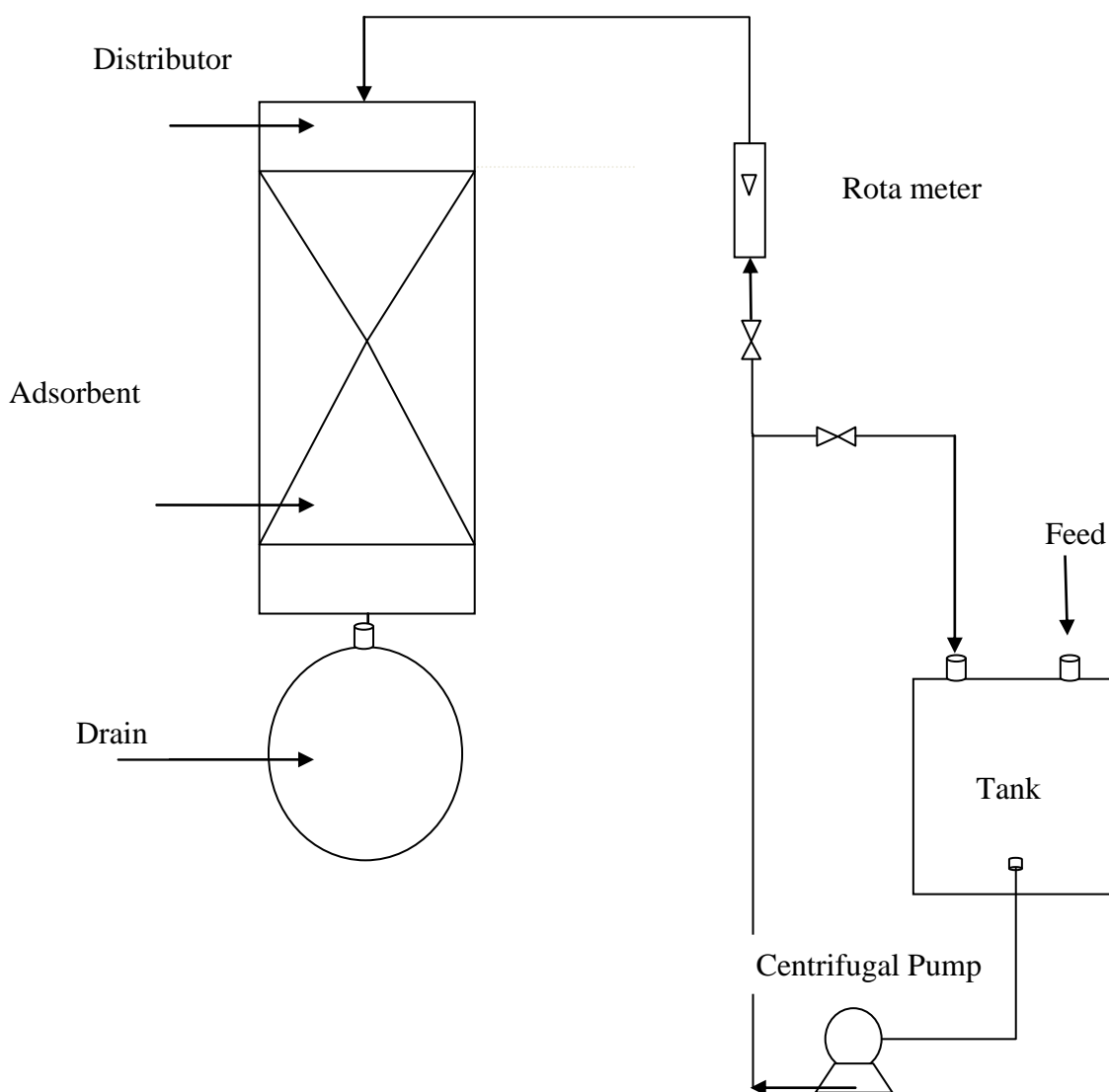


Fig: Schematic Representation of experimental equipment

Materials

Alum sludge was collected from Tikirit University Water treatment plant; inorganic materials in alum sludge are presented in table 1. It was dried in an oven type (pick stone ovens, Thetford England) at 120C° for 24 hr. The dried sludge was then cooled at room temperature. The sludge was

then crushed used mill type (Retsch BBz/A Masch.Nr.30507 Germany) to produce a particle size of (2.8-5) mm these particles are sieved by used shaker type (ELE International model 80-0445/01) to get different uniform particle size. Waste water analysis listed in table2.

Table1: The chemical composition of Alum sludge.

Organic%	CaSO ₄ %	CL ⁻ %	HCO ₃ %	TSS%	SO ₄ %	Al%	pH
0.34	2.41	6.34	4.89	16.7	11.9	9.98	8.6

Table2: The analysis of SDF wastewater in ppm unit.

Zn	Fe	Pb	Cu	Cd	Ca	pH
11.371	5.994	1.074	6.347	1.112	240	8.3

The experimental

The experiments were carried out at various bed depth and various flow rate as shown in table3, this flow rates are not actually used in drugs factory but its experimentally values and particle size [2.8 and 5] mm. The oven dried alum sludge was placed in the adsorption column for the desired bed length and particle size. The wastewater was pumped to the adsorption column through the calibrated Rota meter at the desired flow rate. The samples taken at every desired variable flow rate, bed depth and particle size then tested the concentrations of following elements [Ca, Zn, Fe, Cu, Cd and pb], using atomic absorption apparatus type (Schimatzu AA-6200).All the results are summarized in table 3and 4.

Results and discussion

- 1- The results shown in table 3 are to illustrate the relation between the flow rate and concentrations of pollutants that effluent from adsorption column at 2.8mm particle size with three beds of depth (50, 60 and 70) cm. This results indicated that the effluent concentration pollutants from the adsorption column is directly proportional with flow rate this mean that the rate of adsorption decrease with flow rate increasing ,lead to increase effluent concentration, also the table guide us to observe that the concentrations decrease with increasing bed depth and .The results also indicated that the maximum removal of pollutants was when the particle size is 2.8mm and 70cm bed depth

with 2L/hr flow rate, and these results are within the permissible level, thus the minimum removal of pollutants was when the bed depth is 50cm and 6L/hr flow rate, which give result within the upper permissible level. The results indicated that the increased of bed depth and decreased of flow rate led to increasing of pollutants removal

2- The increase in bed depth will increase the rate competitive and displacement of weak adsorbed component, due to the increase in contact time between the pollutants and the adsorbent particles. Also when the flow rate increases the pollutants adsorption will decrease due to decrease in contact time between the pollutants and the adsorbent particles.

3- The Alum sludge capacity adsorption is the order $Ca > Cu > Zn > Pb > Cd > Fe$.

Table (3): The concentrations (ppm) of pollutants at 2.8mm particle size and various bed depth and flow rate.

pollutants	Initial conc.	Permissible level	concentration at 50cm bed depth and various flow rate			concentration at 60cm bed depth and various flow rate			concentration at 70cm bed depth and various flow rate		
			2L/hr	4L/hr	6L/hr	2L/hr	4L/hr	6L/hr	2L/hr	4L/hr	6L/hr
Zn	11.371	5	5.381	6.014	6.512	4.44	4.782	5.213	1.971	3.37	4.67
Fe	5.994	0.3	0.587	0.631	0.682	0.377	0.521	0.653	0.283	0.368	0.497
Pb	1.074	0.05	0.0542	0.0598	0.0631	0.0487	0.0512	0.0612	0.0033	0.00382	0.00424
Cu	6.347	1	1.19	1.53	2.022	0.767	0.948	1.35	0.187	0.372	0.666
Cd	1.112	0.01	0.0188	0.0217	0.0241	0.0103	0.0168	0.0197	0.0075	0.0096	0.011
Ca	240	50	48.6	54.32	59.86	45.21	48.36	52.13	39.5	42.76	47.48

4- The results shown in table4 are to illustrate the effect of big particle size with different flow rate on the pollutants removal comparison with small particles. The results indicated that when we used 5mm particle size diameter and 70cm bed depth with different flow rate 2, 4 and 6 l/hr lead to decreasing in pollutants removal and will not achieved to the permissible level (except Ca and Cu) due to be formed big channels between adsorbent particles, these channels allow to the fluid passing Quickly through the bed and the contact time between the pollutants and the adsorbent particles will decrease leads to decreasing of pollutants removal.

Table (4): The concentrations (ppm) of pollutants at 5mm particle size and 70cm bed depth with various flow rate.

pollutants	Initial conc.	Permissible level.	2L/hr	4L/hr	6L/hr
Zn	11.371	5	5.11	6.43	8.17
Fe	5.994	0.3	0.876	0.985	1.197
Pb	1.074	0.05	0.0713	0.0903	0.125
Cu	6.347	1	0.876	1.119	1.348
Cd	1.112	0.01	0.0520	0.0681	0.0799
Ca	240	50	46.35	54.74	63.92

Conclusion

The results obtained from this study have provided valuable information regarding the pollutants [Zn, Fe, Cu, Pb, Cd and Ca] adsorption by Alum sludge. The maximum adsorption capacity was at 70cm bed depth and 2.8mm particle size with 2 L/hr flow rate. The results indicated that the pollutants are highly adsorption by Alum sludge; it is believed that dependent on the surface characteristics of the alum sludge. The results also indicated that when the flow rate increased the rate of adsorption decreased due to decreasing in contact time between the liquid and adsorbent particles, and the increasing in bed depth lead to increasing rate of adsorption due to increase the contact time between the liquid and adsorbent particles. The results showed that the rate of adsorption decrease with increasing the particle size due to be formed big channels between the particles, and these channels lead to passing the liquid quickly and the contact time will be very small.

References

- Al-Bahrani, K.S., Martine, R.J., (1977): Adsorption studies using gas–liquid chromatography II-competitive adsorption . Water res, vol.11, pp.991- 999.
- Bratby, J.R., (1980): Coagulation and Flocculation. Uplands Press Ltd Crydon, 321p.
- Donald, W.S., (1979): Wastewater treatment. Prentice- Hall Inc, Englewood Cliffs, 176p.
- Furusawa, T.S., Smith, J.M., (1973): Fluid-Particle and intraparticle mass transfer rates in slurries,. Ind.Eng.chem.Fund, vol.12, pp.197-202.
- Keller, H.U., (1987): Adsorption. Rousseau, Handbook of separation process Technology, Wiley-Interscience, New York, 753p.
- Malkoc, M.G., Nuhoglu, H.T., (2006): Fixed bed studies for the adsorption of chromium (VI) onto tea factory waste. Chem. Eng. Science, vol.53, pp.38-47.
- Razali, M.A., Zhao, Y.Q., Bruen, M.T., (2010): Effectiveness of a Drinking –Water Treatment Sludge In Removing Different Phosphorus Species From Aqueous Solution .Bioresource Technology, vol.101, pp.6576-6579.
- Ruthven, D.U., Yashido, H.B., (1984): Principles of adsorption and adsorption Process. Chem. Eng. Sci, London, vol.39, pp.1489-1494.
- Stumm, W.M., (1996): Aquatic Chemistry. A Wiley-Interscience Publication, New York, 433p.
- Weber, W.J., Keinath, T.M., (1947): Chemical engineering program. chm. soc, 197p.
- Wei, C.M., (1999): Lead metal removal by recycled alum sludge. Elsevier science Ltd, vol.33, pp.3019-3025.
- Wolborska, S. A., (1999): External Control of the Fixed Bed Adsorption. Chemical Engineering Journal, vol.73, pp.189-179.
- Yang, Y.Y., Zhao. Y.Q., Kearney, P.F., (2008): Influence of Aging on The Structure and Phosphate Adsorption Capacity of Dewatering Alum sludge. Chemical engineering journal, vol.145, pp.276-284.
- Zhao, Y.Q., Yang, Y.A., Babatunde, A.Q., Wang, L.K., Ren, X.Y., Han, Y.L., (2006): Characteristics and Mechanisms of Phosphate Adsorption on Dewatered Alum Sludge. Separation and purification Technolog, vol.51, pp.193-200.

معالجة مياه الصرف أدوية سامراء باستخدام روبية الشب كمادة

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تاريخ القبول: ٢٦/٤/٢٠١١، تاريخ الاستلام: ١٥/٩/٢٠١٠

الخلاصة

إن الهدف من الدراسة الحالية هو لمعالجة مياه الصرف الصناعي لمعمل سامراء للصناعات الدوائية باستخدام روبية الشب الجافة في عمود الامتزاز ذو الطبقة الثابتة حيث أجريت التجارب العملية باستخدام مياه حقلية حقيقية من مياه الصرف الصناعي لمعمل أدوية سامراء. تضمن هذا البحث أيضا دراسة تأثير ارتفاع طبقة الحشوة (٦٠،٥٠ و ٧٠) سم وبمعدلات جريان مختلفة (٤،٢ و ٦) لتر/ساعة وبإحجام جزيئات (٢،٨ و ٥) ملم . تم حشو عمود من البايوركس بطبقة من روبية الشب الجافة بقطر ٢،٨ ملم وارتفاعها ٥٠ سم وإجراء التجارب ثم إعادة التجارب مع زيادة ارتفاع الوسط ليصبح ٦٠ سم ثم ٧٠ سم وعلى ثلاثة وباستخدام معدلات جريان مختلفة (٤،٢ و ٦) لتر/ساعة مع كل ارتفاع ثم تم استخدام حجم جزيئات بقطر ٥ ملم وبارتفاع حشوه ٧٠ سم وبمعدلات الجريان السابقة نفسها. تم فحص النماذج الخارجه من عمود الامتصاص باستخدام جهاز الامتزاز الذري نوع [shimadzu AA-6200]. بينت النتائج إن أفضل نسبة إزالة للعناصر (Ca,Zn,Cu,Pb,Fe,Cd) عندما يكون حجم الجزيئات هو ٢،٨ ملم وارتفاع طبقة الحشوة ٧٠ سم وبمعدل جريان ٢ لتر/ساعة وبينت النتائج أيضا إن نسبة الإزالة تتناسب طردياً مع ارتفاع طبقة الحشوة وعكسياً مع معدل الجريان وحجم الجزيئات وتبين أيضا إن نسبة الإزالة تختلف من عنصر لآخر.