Removal of Carmoisine-E112 Using Different Types of Porous Media

Tasnim Fahim
AL- Mustansiriyah University / College of Engineering
Omdema82@gmail.com

Abstract

All over the world the presence of heavy metals in water supply sources has been raising great concern in terms of public health since many epidemiologic studies confirm the potential carcinogenic effect of these pollutants at concentrations above acceptable standards. The purpose of the research is to manufacture porous medium suitable adsorption and remove Carmoisine (E-122).This work includes two tracks; the first track explains the batch model results, while the other track contains continuous flow system.

The results of batch mode experiments have been presented to examine the efficiency of removing carmoisine E112 by activated ceramic. In this system, the effects of pH, activated ceramic amount, initial concentration of the activated ceramic, and agitation speed and equilibrium time on adsorption efficiency are studied.

The continuous flow system experiments, have been carried out during period from April/2014 to May /2014 , to examine the efficiency removal of carmoicine E112 by six types of media one of them is non-uniform which is the activated ceramic and the others are uniform (silty clay, sandy clay, composite porous media, porculinite, gravel and ceramic).

Keywords: carmoisine E112, Adsorption, silty clay, sandy clay, composite porous media, porculinite, gravel and ceramic and the activated ceramic.

خلاصة:

في جميع أنحاء العالم وجود المعادن الثقيلة في مصادر المياه قد سبب قلق كبيرفي مجال الصحة العامة من خلال عدد من الدراسات الوبائية التي تأكد تأثير مسرطن محتمل لهذه الملوثات بتراكيز أعلى من المعايير المقبولة.يتضمن هذا العمل مسارين :المسار الاول يمثل موديل الجريان الدفقي(اونظام الوجبات)بينما المسار الثاني يمثل نظام الجريان المستمر. تم أجراء تجارب الجريان الدفقي لفحص كفاءة ازالة الكارمويسين E112 بأستخدام السيراميك المنشط. وقد تم دراسة تأثير كل من درجة الحامضية، كمية السيراميك المنشط، التركيز الابتدائي للسيراميك المنشط، سرعةالخلط ووقت التوازن على كفاءة الامتزاز.تم أجراء تجارب الجريان المستمر للفترة الواقعة بين نيسان ٢٠١٤ الى آيار ٢٠١٤ لدراسة كفاءة أزالة الكارمويسين E112 بأستخدام ٦ أوساط مختلفة واحد منها غير متجانس وهو السيراميك المنشط او الفعال بينما كانت بقية الاوساط متجانسة وهي(الطين الغريني، الطين الرملي، وسط مسامي مركب، بورسينايت، حصى و سيراميك).

الكلمات المفتاحية: كارمويسينE112 ، الامتزاز ، الطين الغريني ، الطين الرملي، وسط مسامي مركب ، بورسينايت ، الحصى، السيراميك الفعال.

1. Introduction

For treating contaminated effluents many technologies have been developed over the years. Most important of those techniques depend on chemical precipitation, filtration, ion- exchange, reverse osmosis and membrane systems. However, all these techniques have their inherent advantages and limitations in application. In the last few years, adsorption has been shown to be an alternative method for removing dissolved metal ions from liquid wastes (**Bayat, 2002)**.

Adsorption is a mass transfer process in which substances present in a liquid or gas phase are adsorbed or accumulated on a solid and thus removed from the liquid or gas (**Grittenden, 2005)**. Application includes the purification of drinking water, removal of harmful pollutants from waste water. It also has application in air pollution control and many processes in chemical engineering (**Ebrahim, 2008**; **Mckay, 2001).**

A porous solid material of large surface area per unit mass in which adsorption of liquids or gases occurs on its surface is known as "adsorbent". The material to be adsorbed on the adsorbent is known as "adsorbate" **(Ahmed, 2006; Bhatia, 2001**).

There are two general types of adsorption: physical (physisorption) and chemical (chemisorption) adsorption. These kinds depend on the nature of the force between the adsorbate and the adsorbent (**Mckay, 2001).**

The general mechanism attributed to physical attraction is weak bonding processes caused by the attractions of intermolecular forces, such as hydrogen bonding and Van der Waal's forces.(**Israelchvilj,1985)** described physical adsorption in details, classifying physical mechanisms by four types of dipole interaction. Dipole moments are shifts in electron density within molecules that produce a partial separation of charges. The dipole moments can be permanent, as in polar molecules such as acetic acid. Polar molecules can interact with other polar molecules and adsorption can occur through dipole-dipole interactions. In addition, interactions can occur between polar molecules and non-polar molecules (dipole-induced dipole interaction). Still another possibility is the instantaneous dipole-induced dipole, in which a fluctuating electron cloud results in short-term dipole moments that serve as the basis for weak bonding between the adsorbent and adsorbate. The electrostatic attraction is used to describe physical adsorption characterized by electrical attraction between the adsorbate and the adsorbent surface. Ions (usually heavy metals such as Zn^{+2}, Fe^{+2}, Mn^{+2}, Cr^{+3} and Cu^{+2} in the present study), with greater charge are attracted more strongly toward a site of apposite charge than are molecules with lesser charge. Electrostatic attraction considered to be the most important mechanisms for heavy metals **(Graham, 1991**). The physical adsorption is a reversible equilibrium process, it is required a sufficient energy to be added to overcome the attractive forces and is usually predominant at low temperature (**Noit,1999).** It is characterized by a relatively low energy of adsorption and the heat of the physical adsorption is usually less than (40 KJ/mole), that is, the adsorption is not held strongly to the adsorbent. Physical adsorption is a rapid process caused by a non-specific binding mechanism. The physical adsorption is the most common mechanisms by which adsorbate are removed from water and wastewater treatment **(Richardson, 1999)**.

A small particle in close to a solid surface is subjected to either electrical attractions or repulsion, depending on the nature of the surface charge which developed by both the particle and the surface when they are in contact with the fluid and to the attraction caused by Van der Waal's forces. Also, it is subjected to the hydraulic force resulting from the movement of the fluid **.**The mechanisms of chemical adsorption are similar to those of physical adsorption. Yet are often stronger chemical adsorption is produced by the transfer of electrons and the formation of chemical bonds between the adsorbate and the adsorbent. It may be an irreversible reaction and have high adsorption energies. The heat of adsorption is significantly greater than for physical adsorption, ranging from 40 to 400 kJ/mol. It is not unusual for the adsorbate to have chemically changed due to the reaction. Chemical adsorption involves only monolayer coverage, and is a site specific reaction, occurring at specific functional group locations. Functional groups are distinctive arrangements of atoms in organic compounds that give compound its specific chemical and physical properties **(Lin *et. al.*,2000)**. The aim of this study is to remove of Carmoisine-E112 from wastewater by horizontal treatment system instead of vertical treatment system as compare as the other studies.

2. Materials and Methods

2.1. Laboratory Model

The laboratory model has been designed and constructed in environmental fluid laboratory at college of Engineering, Al-Mustansiriya University. The experimental model is consist of two PVC pipes of 150 mm diameter and 6 meters length placed horizontally and contains different porous media without membranes. Each pipe includes one type of porous media. Each pipe contains five points at each of 1.5 m length. At each point there is a one gauge to measure the pressure (water pressure gauge), as well as a one valve for samples collection as shown in Figure (1). The six pipes are entirely separated and connected to the flow measurement system consists of three parallel flow meters to control the inflow discharge. The contaminants are collected inside a 2500 *l* tank, and pumping to the system by electric pumps. The system is built to be used for the measurements of the flow rate, pressure drop and the concentrations of the carmisine E122 in the effluents through the system.

Figure (1): Laboratory model

2.2. Sieve Analysis

The sieving analysis for the suggested six media (silty clay, sandy clay, composite porous media, porculinite, gravel and ceramic and the activated ceramic) was conductive and made in the soil laboratory /College of engineering using standard sieves. The results indicated a good description of the size distribution for selected materials.

Particle-size distribution analysis could be obtained by a mechanical sieve analysis, Particle -size distribution curves for six types of porous media consisting of natural porous media (Sandy clay, Silty clay, Porcilinaite and Crashed Gravel) were obtained and graphed in Figure (1). Samples were classified according to particle size using a standard British Soil Classification System, detailed in BS 5930: Site Investigation.

From the particle -size distribution curves, the samples were classified and the diameters of filters media particles at 10%, 20% and 50% cumulative weight were determined, as well as the coefficients of uniformity.

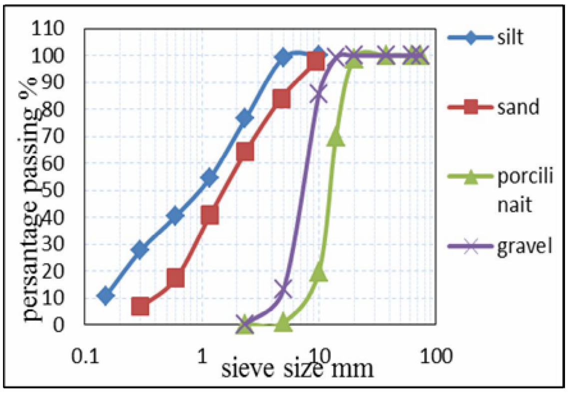


Figure (1): Sieve Size Distribution Curve of the Samples Tested.

2.3. Porous Media

Six types of porous media were test in this study:

2.4. Sandy Clay

The sand sample was carefully washed with distilled water in order to purify it from any chemical impurities. The washed sand was then dried in the oven at105 °C for 48 hours. As shown in Figure (2). Also, physical properties of sandy clay were accomplished in the soil laboratory at college of Engineering, Al-Mustansiriya University, is shown in Table (1).

Figure (2) Sandy clay Porous Media

Table (1): Physical Properties of Sandy Clay

Properties	Test Results
Porosity	0.33
Apparent Specific Gravity	2.65
Bulk Density (kg/m3)	1990
Particle Size Distribution (ASTM) Effective size d_{10} (mm)	0.39

2.5. Silty Clay

A natural formation of Iraqi soil (river sand) was used as a porous media in the experiments conducted in the present study as shown in Figure (3). Also, Table (2) summaries the composition and properties of this soil such as porosity and bulk density.

Figure (3) Silty Clay Porous Media

Table (2): Physical Properties of Silty Clay.

Properties	Test Results
porosity	0.35
Bulk Density (kg/m^3)	1779
Particle Size Distribution (ASTM) Effective size d_{10} (mm)	0.16
Coefficient of permeability (m^2)	2.75e-10

2.6. Porcilinaite

The porcilinaite rocks samples used in this study were supplied from the General Company for Geological Survey and Mineralogy-Ministry of Industry and Minerals (GCGSM).The porcilinaite rocks were prepared for the present work by grinding and sieving to obtain a grain size range (2.5-15) mm and then washed with distilled water and dried in an oven at 105^{o}C for 4hr, as shown in Figure (4).

Figure (4) Porcilinaite Porous Media

Table (3): Physicochemical Characteristic of the Porcilinaite.

Constituent	(%)
Porosity (n)	0.55
Bulk density(kg/m^3)	1325
Particle Size Distribution (ASTM) Effective size d_{10}(mm)	8

2.7. Crashed Gravel

Crashed gravel is used in this research to produce higher surface area and smaller sizes suitable to be used, as shown in Figure (5). The porosity, hydraulic conductivity and bulk density were measured for crashed gravel. Physical properties of crashed gravel are show in Table (4).

Figure (5) Crashed Gravel Porous Media

Table (4): Physical Properties of Crashed Gravel.

Properties	Test Results
porosity	0.42
Bulk Density (kg/m^3)	1928
Particle Size Distribution (ASTM) Effective size d_{10}(mm)	4.8

2.8. Activated Ceramic

Activated Ceramic is a modified structural adsorptive material which had been manufactured for high adsorption process, characterized by a high porosity and a large surface area and made of mega pores interconnected by filaments, as shown in Figure (6). This results in a structure with low resistance to fluid flow, making them appropriate for use as a biofilter. Powder of bentonite, kaolin and crashed coal by volume ratio 1:6:4 respectively were mixed with water by volume ratio 1:1 and formed thermally at different vacuum furnace temperatures. The mixture had been exposed to ozone for 30 minute before using for activation. The effect of ozonation period and thermal treatment on physical and chemical properties of Activated Ceramic under temperature 300,500,700,900 and 1100 C^O were studied. Particle-size distribution curves for Activated Ceramic of porous medias consisted was obtained and graphed in Figure (2). Physical properties of Activated ceramic are shown in Table (5).

Figure (6) Activated Ceramic Porous Media

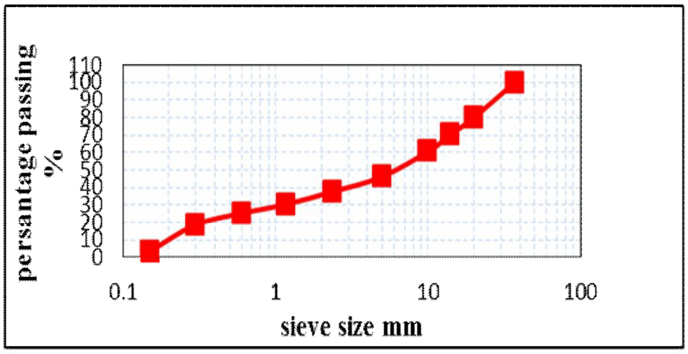


Figure (2) Grain Size Distribution Curve of the Activated Ceramic of Porous Media.

Table (5): Physical Properties of Activated Ceramic Porous Media.

Properties	Test Results
porosity	0.37
Bulk Density (kg/m^3)	1661
Particle Size Distribution (ASTM) Effective size d_{10} (mm)	0.2

2.9. Composite porous media

Four uniform porous media (sand, Gravel, Silt and Porcilinaite) were composed by mixing them. A complex character in non- uniform media arises from irregular pore-size distribution, as shown in Figure (7).Particle-size distribution curves for composite porous media were obtained and graphed in Figure (3). Physical properties of activated ceramic are shown in Table (6).

Figure (7): Composed Porous Media.

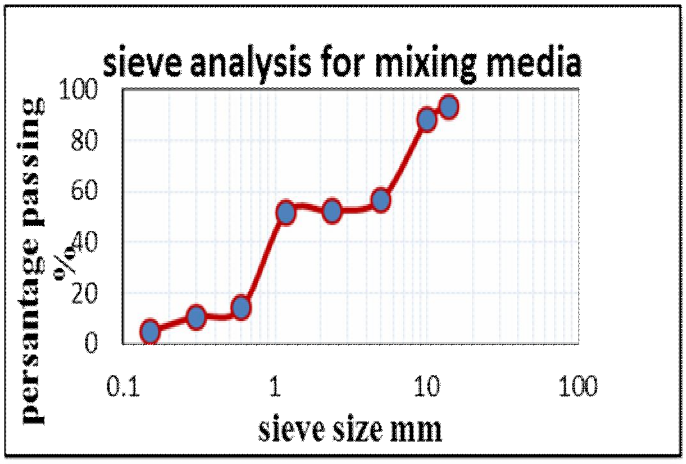


Figure (3): Grain Size Distribution Curve of Composed Porous Media.

Table (6): Physical Properties of Composed Porous Media.

Properties	Test Results
porosity	0.43
Bulk Density (kg/m^3)	1687
Particle Size Distribution (ASTM) Effective size d_{10} (mm)	0.28

2.10. Carmoisine (E-122)

Carmoisine (E-122) commercial synthetic dye food India production was used as tracer (indicator of color, the molecular formula $C_{20}H_{12}N_2Na_2O_7S_2$ and molecular weight (502.44), it has solubility in water reach to (120 g/L), it is red to maroon powder. It was cheap (5 US$/Kg) sufficient to (2778 L) when using (360 mg/L) as initial concentration. Compared with Rhodamine B (34 US$/Kg). It tests in many phases for color characteristics stability such as alkalinity, oxidation, color decay in time, total dissolved inorganic solid, and temperature as shown in table (7).

1- The pH values were measured with a HANNA instruments HI-9811 digital pH-meter .Dye was tested in constant concentration (250mg/L) with pH range (7.0–10.0) alkalinity by $NaOH$. It hasn't affected for this pH range.

2- Dye has been tested for oxidation by ozone producer instrument by exposure constant concentration (250mg/L) with time. The color was converted from red maroon to bright red then to green then be without color.

3- Electrical conductivity: The dye has tested by HANNA instruments HI-9811 digital EC-meter with range of (0.5-50 g/L) of KCl . The increases in spectrophotometer reading produce neither from interface neither of KCl solution nor from chemical reaction.

5- Temperature: The dye has made hot (warm) with range (0-70^oC) in constant concentration (250mg/L). It has not effect on increase temperature.

Table (7): Carmoisine Dye Characteristics for Color Stability (250mg/l)

reading pH	6.8	8.2	8.9	9.2	9.5	10.1
Optical Density	0.674	0.675	0.676	0.68	0.684	0.689
mS/cm ($E.C$)	0.9	5.57	8.83	11.5	13.8	14.4
Temp.(^{0}C)	0	10	25	40	50	60

3. Results and Discussion

3.1. Batch Experiments

3.1.1. Equilibrium Time

The equilibrium time should be fixed at value ensure reaching equilibrium concentrations. Figure (5) shows the effect of contact time on carmoisene E112 colour removal using 20 g of activated ceramic added to 100 ml of colour solution for batch tests at 25ºC. This figure demonstrates that removal percentage of this colour significantly increased with an increase in contact time. The sorption rate was rapid at the initial stage and gradually slowed down afterwards. The slower sorption was likely due to the decrease in sorption sites on the surface of the activated ceramic. The kinetic data show that 60% colour was removed mainly at 100 minutes. There was no significant of change in residual concentrations after these times up to 100 min. However, sorption experiments in other batches were conducted with these contact times.

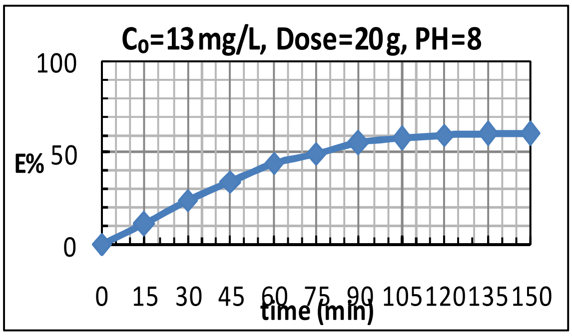


Figure 5: Removal efficiency of carmoisene colour on activated ceramic as a function of contact time.

3.1.2. Initial pH of the Solution

The most important single parameter influencing the sorption capacity is the initial pH of the solution. It is related to the sorption mechanisms onto the sorbent surface from water and reflects the nature of the physicochemical interaction of the species in solution and the sorptive sites of sorbent. The sorption of color on activated ceramic was examined at different pH values ranging from 2 to 10 with an initial concentration of 13 mg/L. The pH of the solutions was adjusted to the required value with 0.1 M H_2SO_4 and NaOH solutions. It is clear that the best initial pH of the sorption was found to be 8 and an increasing or decreasing of the pH from this optimal pH causes reduction in the sorption of these contaminants.

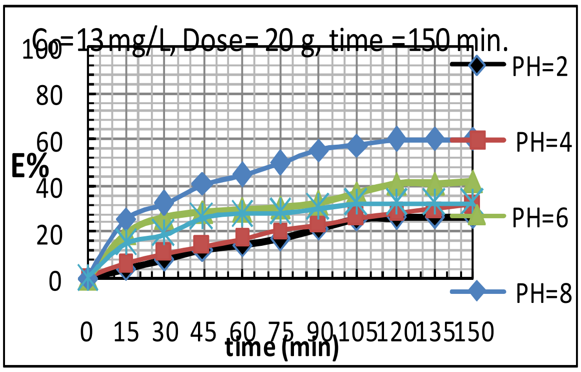


Figure 6: Removal efficien3cy of Colour carmoisene on activated ceramic at different pH solution.

3.1.3. ACR Dose

The dependence of carmoisene E112colour sorption on bio-sorbent dosage has been studied by varying the amount of activated ceramic from 10 to 25 g which was added to 100 ml of contaminated solution for batch tests at 25ºC, while keeping other parameters as follows; C_o= 13 mg/L, pH=8, and contact time 150 minutes.

It is clear that the removal efficiencies of color improved with increasing sorbent dosage from 15 g to 25 g and they are remained approximately constant afterwards as illustrated in Figure (7). This was expected due to the fact that the higher dose of sorbents in the solution, the greater availability of sorption sites. Also, this suggested that after a certain dose of sorbent, the maximum sorption sets in and hence the amount of carmoisene colour bound to the sorbent and the amount of these contaminants in solution remains constant even with further addition of the sorbent dosage.

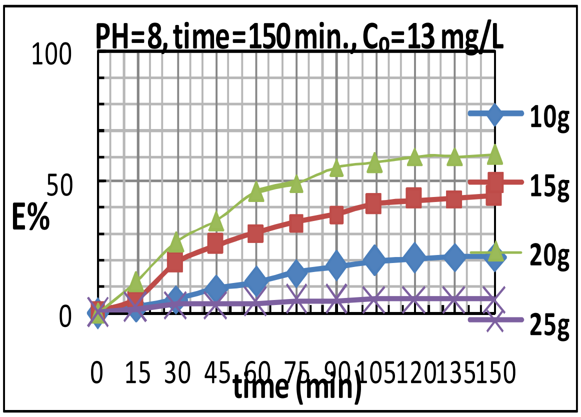


Figure 7: Effect of ACR dosage on removal efficiencies of carmoisene colour.

3.1.4. Initial Concentration of carmoisene colour

The amount of carmoicine E112 colour sorbed per unit mass of sorbent increased with the increase in initial concentration as shown in Figure (8).

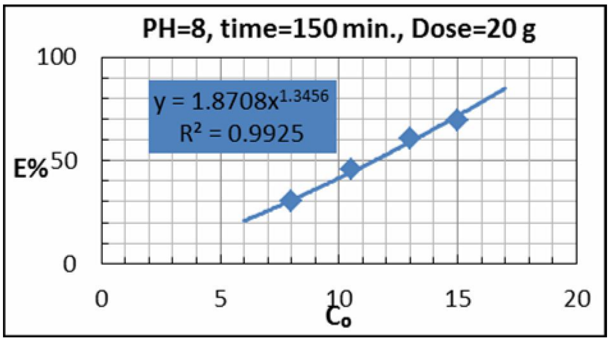


Figure 8: Effect of initial concentration on removal efficiency of carmoisene E112 colour on activated ceramic.

3.2. Continuous Flow Experiments

3.2.1. Pressure variation

The pressure in this system increases gradually, this rise in pressure indicates to increase the amounts of contaminated particles on the surface of the porous medias , this leads to a decrease the efficiency of these medias in removing the contaminant, so the increase of pressure in this study leads to degrease of removal efficiency of the porous media.

Figure (9), (10), (11), (12), (13) and (14) present the effect of pressure on removal efficiency of activated ceramic, sandy clay, silty clay, composite porous media, porcilinaite and Gravel respectively.

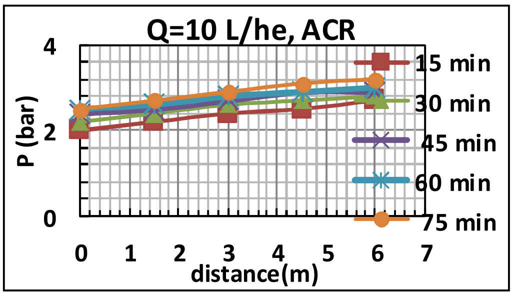


Figure 9: Effect of pressure on removal efficiencies of carmoisene colour in activated ceramic.

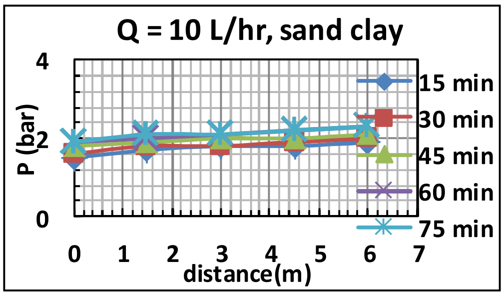


Figure 10: Effect of pressure on removal efficiencies of carmoisene colour in sandy clay.

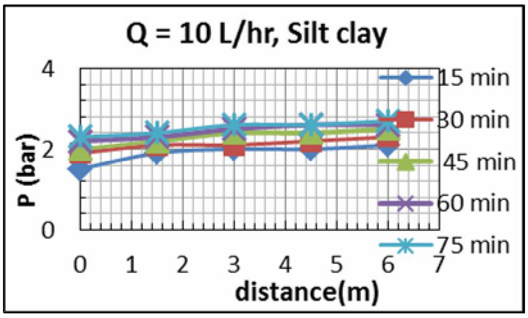


Figure 11: Effect of pressure on removal efficiencies of carmoisene colour in silty clay.

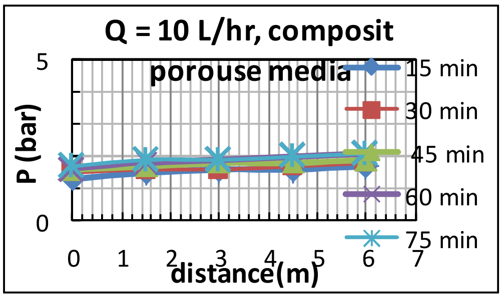


Figure 12: Effect of pressure on removal efficiencies of carmoisene colour in composit porous media.

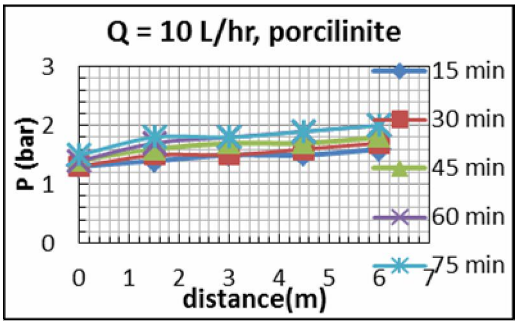


Figure 13: Effect of pressure on removal efficiencies of carmoisene colour in porcilinaite.

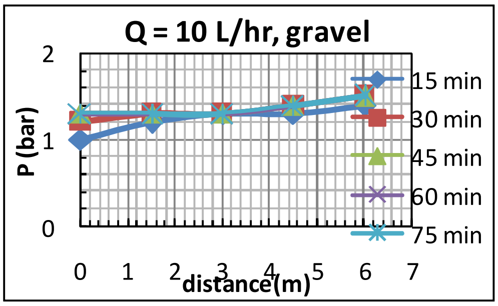


Figure 14: Effect of pressure on removal efficiencies of carmoisene colour in Gravel.

3.3.2. Distance effect

As previously stated that the pipeline is divided into five points each point a distance away from the other 3.5 meters. We note in this system during the flow of contaminated in pipeline the removal efficiency will be degrease cause that is increase the amounts of contaminated particles on the surface of the porous medias, that's mean the increase of the distance leads to degrease of removal efficiency of medias.

Figure (15), (16), (17), (18), (19) and (20) present the effect of distance on removal efficiency of the porous media.

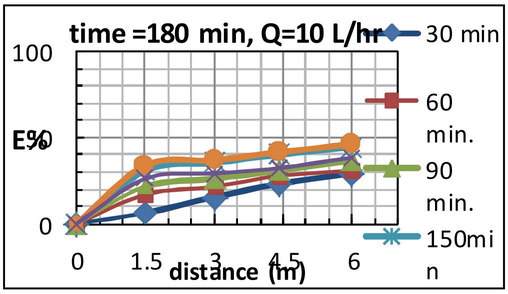


Figure 15: Effect of distance on removal efficiencies of carmoisene colour in activated ceramic.

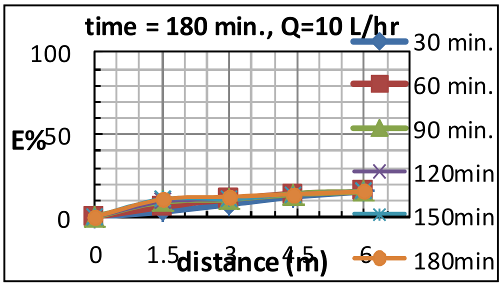


Figure 16: Effect of distance on removal efficiencies of carmoisene colour in sand.

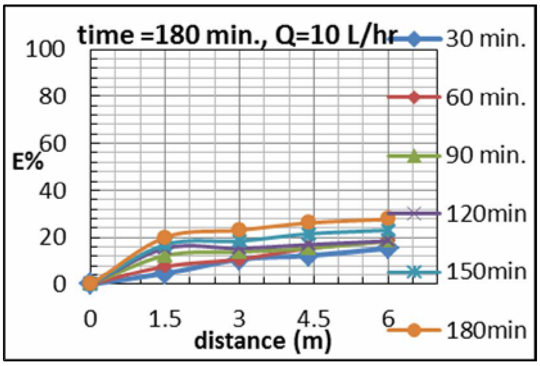


Figure 17: Effect of distance on removal efficiencies of carmoisene colour in silt.

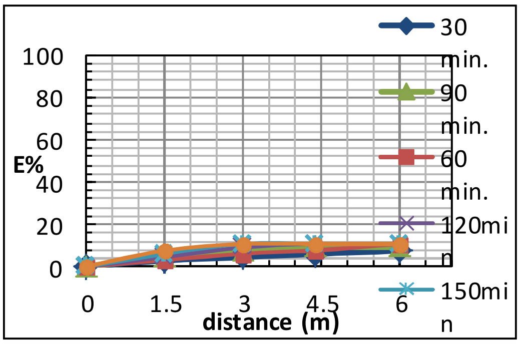
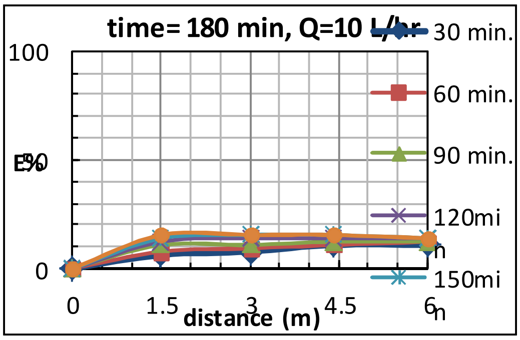


Figure 18: Effect of distance on removal efficiencies of carmoisene colour in composit porous media.



4.

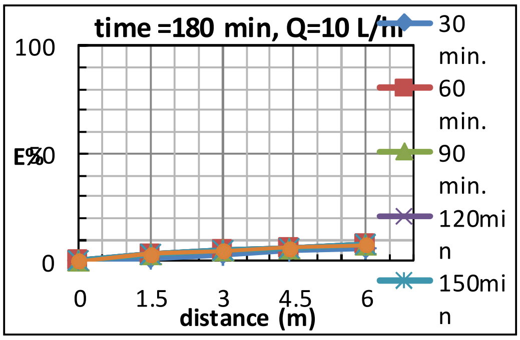


Figure 19: Effect of distance on removal efficiencies of carmoisene colour in porcilinaite.

Figure 20: Effect of distance on removal efficiencies of carmoisene colour in Gravel.

Conclusions

The sorption process and kinetics of Carmoisine-E112 removal on to two tracks; The batch system was:

- Removal efficiency of carmoicine E112 by activated ceramic improved with increasing sorbent dosage, at constant initial concentration, from 10, 15 and 20 g with efficiency of 22, 25and 60% respectively and they remained approximately constant after this amount.
- Removal efficiency of carmoicine E112 increases with an increasing of initial concentration.
- The best removal efficiency of carmoicine E112 at pH=8.

The continuous system was:

- Removal efficiency of the carmoicine E112 by activated ceramic increases with an increasing in detention time, length of the pipe and the pressure.
- Experimental data show that the adsorption capacities of activated ceramic for the carmoicine E112 are greater than that of using the others media.
- Removal efficiency of carmoicine E112 by the activated ceramic, silty clay, sandy clay, composite porous media, porculinite and gravel were: 46, 28, 15, 14, 11 and 8% respectively.

5. References

Ahmed, K.W., 2006,"***Removal of multi-pollutants from wastewater by adsorption method***", Ph.D. Thesis, University of Baghdad, College of Engineering.

Bayat, B., 2002,"***Comparative Study of Adsorption Properties of Turkish Fly Ashes: I. The Case of Nickel (II), Copper (II) and Zinc (II)***", Journal of Hazardous Materials, Vol. 95, pp: 251-273.

Bhatia, G., A., 2001,"***Environment Pollution and Control in Chemical Process Industries***", Khanna publisher, pp: 250-260.

Crittenden, J.C., Trussell, R.R., Hand, D.W., Howe, K. J. and Tchobanoglous, G., 2005,"***Water treatment principles and design***", 2nd edition, John Wiley and Sons, New Jersey, pp: 664-691.

Ebrahim, S.E., 2008,"***Evaluation of mixture adsorbent and glass bed for the removal of Phenol and Methylene Blue from water***", Ph.D. Thesis, University of Baghdad, College of Engineering.

Graham, B. I., 1991,"***Activated Carbon Manufacturing from Natural Resources***", Alberta-Edisson Press, Montreal.

Israelchvilj, J.N., 1985,"***Intermolecular and Surface Forces***", Academic Press, London.

Lin, S.H., Lai, S.L. and Leu, H.G., 2000,"***Removal of Heavy Metals from Aqueous Solution by Chelating Resin in a Multistage Adsorption Process***". *Journal of Hazardous Materials*, B76:139-153.

Mckay, G., 2001,"***Solutions to homogenous surface diffusions model for batch adsorption system using orthogonal collocation***", Chemical Engineering Journal, Vol. 81, pp: 213-221.

Noit, R. T., 1999,"***Industrial Wastewater Treatment Technology***", John Wiley publishing.

Richardson, J.T., 1999,"***Principle of Catalyst Development***", Plenum press, New York.