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Oily Wastewater Treatment Using Expanded Beds of Activated Carbon and Zeolite

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ABSTRACT

Two types of adsorbents were used to treat oily wastewater, activated carbon and zeolite. The removal efficiencies of these materials were compared to each other. The results showed that activated carbon performed some better properties in removal of oil. The experimental methods which were employed in this investigation included batch and column studies. The former was used to evaluate the rate and equilibrium of carbon and zeolie adsorption, while the latter was used to determine treatment efficiencies and performance characteristics. Expanded bed adsorber was constructed in the column studies. In this study, the adsorption behavior of vegetable oil (corn oil) onto activated carbon and zeolite was examined as a function of the concentration of the adsorbate, contact time, adsorbent dosage and amount of coagulant salt(calcium sulphate) added . The adsorption data was modeled with Freundlich and Langmuir adsorption isotherms. and it was found that the adsorption process on activated carbon and zeolite fit the Freundlich isotherm model. The amount of oil adsorbed increased with increasing the contact time, but longer mixing duration did not increase residual oil removal from wastewater due to the coverage of the adsorbent surface with oil molecules. It was found that as the dosage of adsorbent increased, the percentage of residual oil removal also increased. The effects of adsorbent type and amount of coagulant salt(calcium sulphate) added on the breakthrough curve were studied in details in the column studies. Expanded bed behavior was modeled using the Richardson-Zaki correlation between the superficial velocity of the feed stream and the void fraction of the bed at moderate Reynolds number.

Keywords: Oil removal; adsorption; expanded beds; wastewater treatment; zeolite, activated carbon.

INTRODUCTION

One of the most challenging problems today is the removal of oil from wastewater. large amounts of wastewater are generated by industrial companies that produce or handel oil and other organic compounds, both immiscible and miscible in water. Oily wastewater discharged into the environment causes serious pollution problems since the biodegradability of oil is very low and oily wastewater hinders biological processing at sewage treatment plants.

Petroleum and petrochemical plants are potential oil sources for pollution inland water caused by runoff from oil fields, refineries and process effluent [1].

Removal of dissolved and emulsified oils is achieved by using activated carbon or membrane filtration. The effluent from those operations contains almost no oil. Several types of sorbents have been studied for the removal of oil from water by a packed bed filter such as sawdust, activated carbon, peat, bentonite, and organoclay [2].

Current technologies for oil removal include filtration, gravity separation, induced floatation, ultrafiltration, adsorption, and biological treatment. An oil and water mixture can be classified as free oil for oil droplets larger than 150 μm, dispersed oil with oil droplets in the range of 20-150 μm, and emulsified oil with oil droplets smaller than 20 μm. A wastewater, where the oil in the oil-water mixture is not present in the form of droplets is said to be soluble [3].

The principles of liquid-solid fluidization have been extensively studied. A key work in the field was presented by Richardson and Zaki [3] more than 50 years ago. The equation predicts a linear correlation between the logarithms of superficial fluid velocity (V_0) and the void fraction of the bed ($(1-\phi_s)$ for fluidized bed [4].

$$\log V_0 = n\log(1-\phi_s)+\log V_t \quad \ldots\ldots\ldots \quad (1)$$

where ϕ_s and V_t are the solid fraction of the expanded bed and the terminal settling velocity of the particle at infinite dilution $(\phi_s = 0)$, respectively.

The superficial velocity V_0 is determined by dividing the volumetric flow rate of the feed stream by the cross sectional area of the column.

The solid fraction ϕ_s of the expanded bed at height *H* can be obtained by:

$$\phi_s = \phi_0 \frac{H_0}{H} \quad \ldots\ldots\ldots\ldots \quad (2)$$

Where ϕ_0, and H_0, are the solid fraction and height of the bed at zero flow stream, respectively.

Wen and Yu [5] estimated the terminal velocity at moderate Reynolds number using the following equation:

$$V_t = \left[\frac{4}{225}\frac{(\rho_p-\rho_l)^2 g^2}{\rho_l \mu_l}\right]^{1/3} d_p \quad \ldots\ldots\ldots\ldots \quad (3) \text{ for } 0.4<Re<500$$

The main objective of this research is to remove oil from water using activated carbon and zeoilte as the adsorbents. The effect of process variables such as adsorbent dosage, contact time, and amount of coagulant salt(calcium sulphate) added on the removal efficiency of oil was studied in order to determine the optimum process conditions. The adsorption equilibrium data were obtained to investigate which isotherm model provided the best fit for the adsorption process.

EXPERIMENTAL PROCEDURE

The adsorbents used in this study were granular activated carbon and zeolite. The characteristics of adsorbents are reported in table (1).

Table (1): Major characteristics of adsorbents.

Property	Activated carbon	Zeolite
Density, kg/m^3	1350	1545
BET surface area, m^2/g	1100	630
Bed porosity	0.45	0.25
particle diameter (d_p), mm	0.8	0.25

Adsorption Isotherm Measurements

Oil in water emulsion samples were prepared by mixing corn oil in distilled water with initial concentrations (C_0) ranged 5000-24000 ppm. Equilibrium studies were conducted at room temperatures by employing the batch adsorption technique. Weighed amounts of adsorbent (2-8 g) were taken in conical flasks containing 100 ml of oily water of known concentration (ρ_l=977 kg/m^3 for the highest concentration). The solutions were agitated at 150 rpm using a Teflon coated half-inch bar on a Corning magnetic stirrer for a specified period of contact time ranged 5-25 min. upon equilibrium, the solutions were filtered and the concentration of residual oil was measured using a UV spectrometer (Shimadzu model 160A) with an absorbance wavelength of 450 nm.

Column Studies

The schematic representation of experimental set-up is shown in Fig.(1); it consists of a glass column of 2.45 cm internal diameter and a height of 75 cm. The column was packed with adsorbent to a height of 8 cm. The adsorbent particles are supported by a wire mesh fitted at the column bottom.

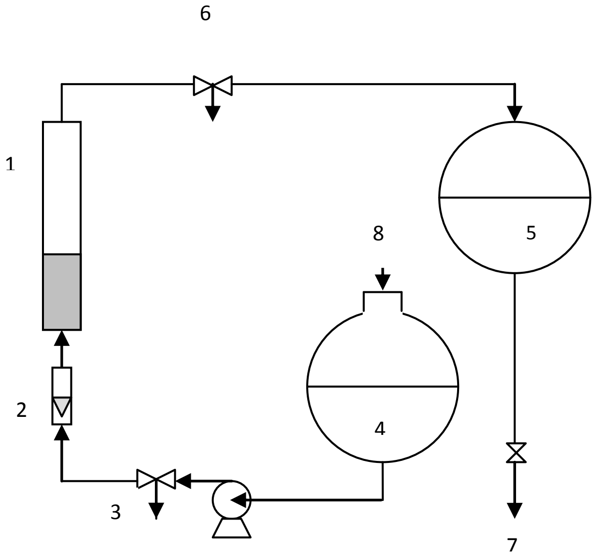

Fig.1: Schematic diagram of expanded bed (1.adsorber, 2 flow meter, 3.pump, 4.feed tank, 5. treated effluent tank, 6.sampling point, 7.to drain, 8.feed.

The flow rate of wastewater was 50 L/h. The effluents from the bed were analyzed for oil content at chosen intervals of time until breakthrough occurs. The minimum fluidized velocity for particles (V_{mf}) had been estimated to be (1.4×10^{-3} m/s) for activated particles and (2.1×10^{-4} m/s) for zeolite using the following equation [6]:

$$V_{mf} = \frac{\mu_l}{d_p\rho_l}\left[\sqrt{(33.7)^2 + 0.0408\frac{d_p^3\rho_l(\rho_p-\rho_l)g}{\mu_l^2}} - 33.7\right] \text{.......} \quad (4)$$

The height of the bed was measured over a certain range of feed velocities.

RESULTS AND DISCUSSION

Adsorption Isotherms

The successful representation of the dynamic adsorptive separation of solute from solution onto an adsorbent depends upon a good description of the equilibrium separation between the two phases.

Adsorption equilibrium is the amount of solute being adsorbed onto the adsorbent. At this point, the equilibrium solution concentration remains constant. By plotting solid phase concentration against liquid phase concentration, it is possible to depict the equilibrium adsorption isotherm. Fig.(2) shows the equilibrium values of oil adsorbed per unit weight of adsorbent q_e versus the liquid phase sorbate concentration at equilibrium C_e. It can be seen that the adsorption capacity increased until an equilibrium concentration was obtained. This confirms a favorable adsorption system.

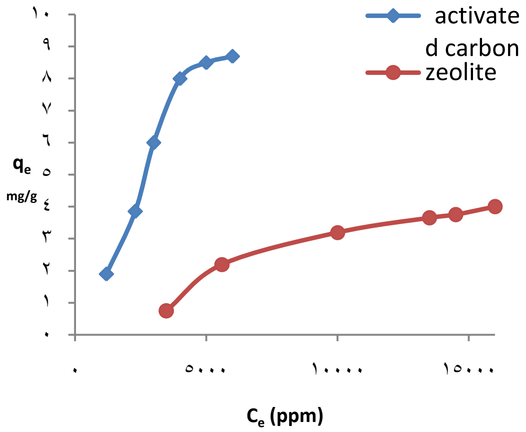

Fig.2 :Equilibrium adsorption of oil on activated carbon and zeolite at 30°C with 2 grams of adsorbent and a mixing time of 20 min.

There are many theories relating to adsorption equilibrium [7],[8],[9].The isotherms of the oil adsorption by activated carbon and zeolite were represented by applying the Freundlich and Langmuir adsorption models.

Langmuir isotherm

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface. Therefore, at equilibrium, upon reaching a saturation point, no further adsorption can occur. In equation (5), q_o is the maximum amount of adsorption corresponding to complete monolayer coverage and K_L is the Langmuir constant .

$$q_e = \frac{q_o C_e}{K_L + C_e} \quad \text{..........} \quad (5)$$

The linea r expression of Eq. (5) can be written in the following form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_o} + \left(\frac{1}{q_o}\right) C_e \quad \ldots\ldots\ldots \ (6)$$

A linearized plot of (C_e/q_e) vs. C_e is shown in Fig. (3).

It was found that in Fig. (3), the Langmuir isotherm did not fit the data with a correlation coefficient much lower than 1.0 throughout the experimental range of oil concentrations studied for both activated carbon and zeolite. The Langmuir equation is applicable to homogeneous sorption where the sorption of each molecule has equal sorption activation energy.

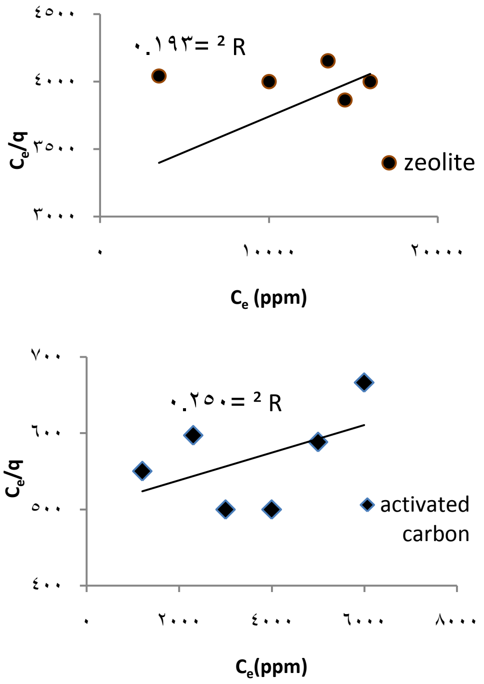

Fig.3: Linearized Langmuir isotherm for oil adsorption by activated carbon and zeolite.

Freundlich isotherm

The Freundlich expression is an exponential equation and therefore, assumes that the amount of adsorbate adsorbed increases infinitely with an increase in concentration.

$$q_e = K_F C_e^{1/n_f} \quad \ldots\ldots\ldots\ (7)$$

In this equation, K_F and $1/n_f$ are the Freundlich constants. This expression is characterized by the heterogeneity factor, $1/n_f$, and thus the Freundlich isotherm may be used to describe heterogeneous system [10],[11].To determine the constant K_F and $1/n_f$, the linear form of the equation as shown below may be used to plot $\ln(q_e)$ against $\ln(C_e)$ as:

$$\ln q_e = \ln K_F + 1/n_f \ln C_e \quad \ldots\ldots\ldots \ (8)$$

Fig. (4) Shows the Freundlich plot and gives a straight line. It is clearly shown that the Freundlich isotherm model fits the analyzed data well for both adsorbents with correlation coefficient (R^2) values of 0.9601 for activated carbon and 0.8949 for zeolite. The isotherm for activated carbon is represented as:

$$q_e = 1.9 \times 10^{-3} C_e^{0.988} \quad \ldots\ldots\ldots\ (9)$$

The Freundlich model assumes that the uptake of any adsorbate occurs on a heterogeneous surface by multilayer adsorption and that the amount of adsorbate adsorbed increases infinitely with an increase in concentration. The heterogeneity factor $1/n_f$ was 0.988 and n_f value was 1.012. it is known that when the n_f value is greater than 1.0, conditions are favorable to adsorption.

Freundlich isotherm for zeolite is represented as:

$$q_e = 3.8 \times 10^{-4} C_e^{0.957} \quad \ldots\ldots\ldots\ (10)$$

Hence it is clearly proved that oil adsorption by activated carbon and zeolite agrees well with the Freundlich adsorption model.

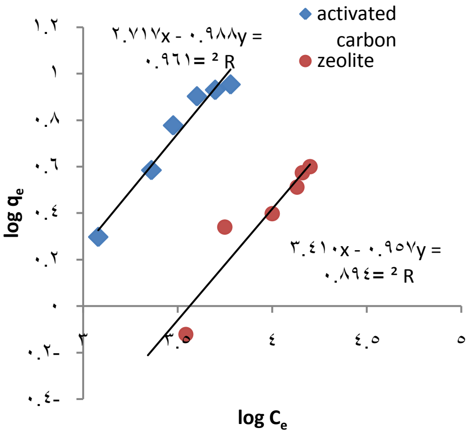

Fig.4: Linearized Freundlich isotherm for oil adsorption by activated carbon and zeolite.

Table (2): Freundlich and Langmuir parameters of adsorption isotherms for the removal of oil by activated carbon and zeolite.

	Freundlich isotherm			Langmuir isotherm		
Adsorbent	n_f (-)	K_F $(g/l)^{1/nf}$	Correlation coeff. (R^2)	q_o(mg/g)	K_L(g/l)	Correlation coeff. (R^2)
Activated carbon	1.012	$1.9*10^{-3}$	0.9617	55.25	$3.6*10^{-5}$	0.2504
Zeolite	1.04	$3.8*10^{-4}$	0.8949	19.01	$1.5*10^{-5}$	0.1934

Effect of Mixing Time

In the adsorption systems contact time plays an important role. In order to study the kinetics and dynamics of adsorption of oil by activated carbon and zeolite, the adsorption experiments were conducted and the extent of oil removal was obtained at various contact time ranged 5-25 min at fixed oil concentration (24000 ppm) with a fixed dosage of adsorbent (2 g) and 150 rpm.

The influence of contact time on residual oil removal using activated carbon and zeolite as adsorbents is shown in Fig.(5) . By increasing contact time, the residual oil molecules have a longer residence time for adsorption on the adsorbent surface area. At equilibrium, the surface of the adsorbent was covered with oil molecules; therefore a longer mixing time does not increase residual oil removal from wastewater. Fig.(5) shows that when the mixing time was increased from 20 min. to 25 min., the reduction value of residual oil was only increased by less than 1000 ppm for activated carbon while the value of residual oil remains unchanged at 10000 ppm for zeoilte. This indicates that zeoilte became saturated faster than activated carbon.

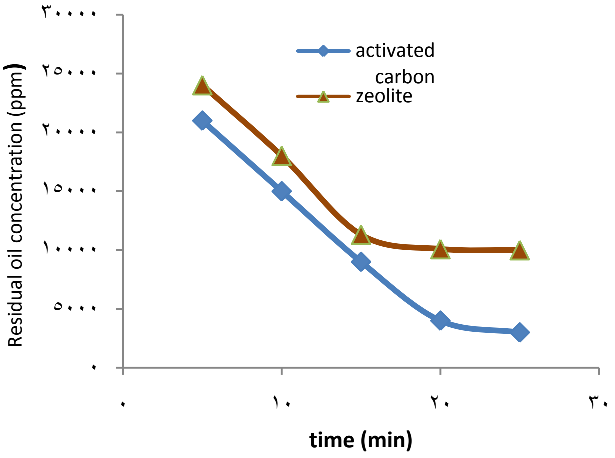

Fig.5: The influence of mixing time on the sorption of residual oil with 2g of adsorbent at 30°C and 150 rpm.

Effect of Adsorbent Loading

Different quantities of adsorbent were added to oily water samples ranged 2-8 g with initial concentration of oil 20000 ppm and contact time 20 min. It was found that as the dosage of adsorbent was increased, the percentage of residual oil removal also increased, as shown in Fig.(6). Adsorption is a surface related phenomenon, at equilibrium most of the oil molecules were adsorbed on the surface and in the intermolecular pores of the adsorbent. It takes about 8 g of activated carbon to reduce the initial residual oil concentration of 20000 ppm to a final concentration of zero ppm while the final concentration is 10000 ppm for the same weight of zeolite. Similar observation has been reported by Ahmed et al [1].

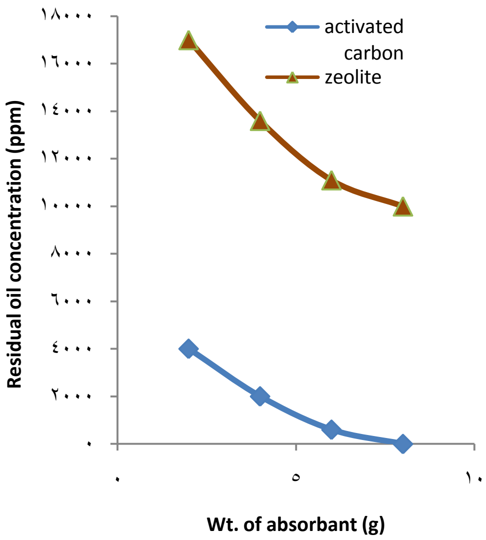

Fig. 6: Effect of dosage of adsorbent on the reduction of residual oil at a mixing time of 20 min. at 30°C.

Expanded Bed Experiments

Break-through Curve

Successful design of a column adsorption process requires prediction of the concentration-time profile or breakthrough curve for the effluent.

Effect of adsorbent type

Based on Fig. (7), activated carbon performed better adsorption properties than zeolite in the removal of oil. Activated carbon differs in their adsorption efficiencies. It is very important to know the nature of pollutants to be removed from contaminated media before deciding what a specific sorbent to select. In many applications, an activated carbon exhibits a sufficient capacity towards existing, especially organic water pollutants, however zeolite may adsorb some metals and ammonia more selectively [12].

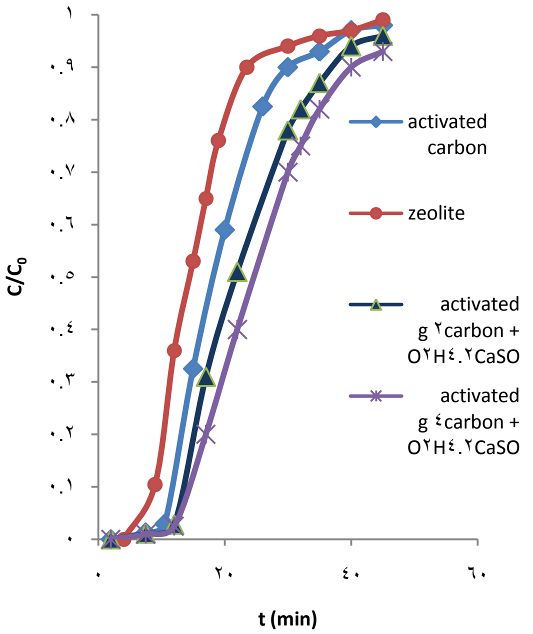

Fig. 7: Effect of adsorbent type and the amount of coagulant salt on breakthrough curve (C_0=24000 ppm, Q=50 L/hr).

Effect of the amount of coagulant salt

Data for the ratio of oil concentration at the outlet of the bed and the concentration of the inlet stream (C/C_0) as a function of time, for beds with varying amounts of coagulant salt are shown in Fig.(7). It is observed that the addition of higher amount of calcium sulphate is essential to achieve larger oil removal. The dissolved salt ions compress the electric double layer around droplets, neutralize repulsive forces among them and between droplets and activated carbon particles and, hence, enhance coalescence of oil droplets. Moreover, the lack of electrostatic repulsion improves the physical adsorption of the oil droplets on the carbon surface. The oil droplet size is increased and its charge neutralized, so that the disperse phase can be retained in the filter media interstices. Furthermore, some authors have pointed out that calcium salts activates the sorption sites of sorbent materials in the removal of different unwanted materials from water [13] , [14].

The Richardson-Zaki exponent constant

The effects of superficial velocity (V_0) of the feed stream on the bed expansion (H/H_0) were measured. The bed expansion factor was limited below 4 as recommended by Reichent et al.[15], for proper performance of expanded beds.

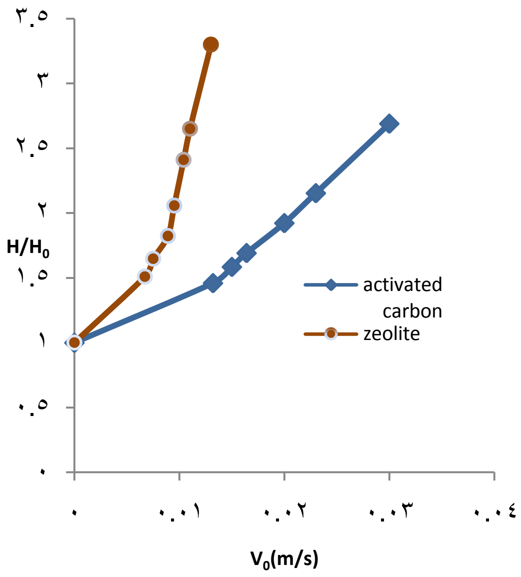

Fig.8:Effect of the superficial velocity of fluid on the bed expansion.

Although Coulson et al.[16], provided $(\phi_s)_0$, values for spherical particles of various sizes, $(\phi_s)_0$ value for the bed was measured as follows. In the column the particles were settled in distilled water. The water contained inside the void fraction of the sedimented bed was drained off. The volume of the drained water was measured and divided by that of the total sedimented bed to determine the void fraction, ε of the bed. Finally, $(\phi_s)_0$ values determined by 1-ε were 0.55 for activated carbon and 0.75 for zeolite [17].

Fig.(9) shows the Richardson – Zaki plot for the experimental data. The line in the figure have a slope (n value) of 3.27 and the terminal velocity is 0.063 m/s for activated carbon and (n) value of 1.311 and the terminal velocity is 0.017 m/s for zeolite.

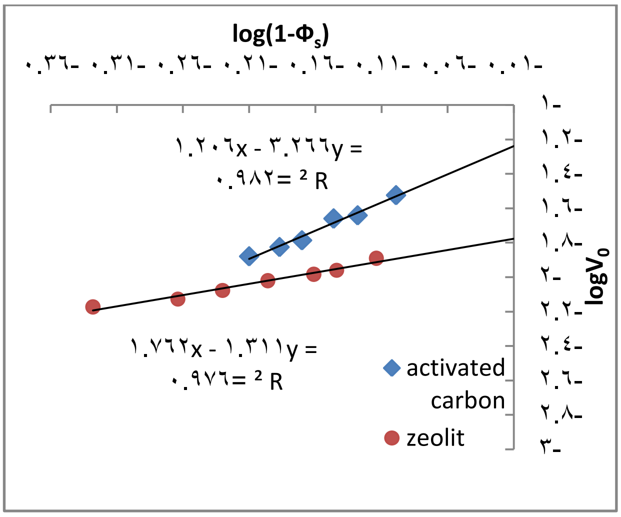

Fig.9: Richardson-Zaki plot for the bed expansion

The exponent n is a function of terminal particle *Re*. Based on bed expansion data, the equation recommended for the range of terminal particle *Re* used is [18],[19]:

$$n = 4.45\mathrm{Re}^{-0.1} \quad \text{for } 1 < \mathrm{Re} < 500 \quad \dots\dots\dots \quad (11)$$

The validity of Richardson- Zaki equation has been confirmed with the experimental data for activated carbon better than for zeolite ($n_{calc.}$= 3.08 for carbon and $n_{calc.}$= 4.88 for zeolite). This allow further investigation of the hydrodynamics for zeolit system such as to predict segregation phenomena in the expanded bed.

Fig. (10) demonstrates that the calculated bed expansion, $(H/H_0)_{\text{cal}}$ using Eqs. (3) and (1) are in good agreement with experimentally measured values of the bed expansion $(H/H_0)_{\text{exp}}$ for activated carbon more than that for zeolite.

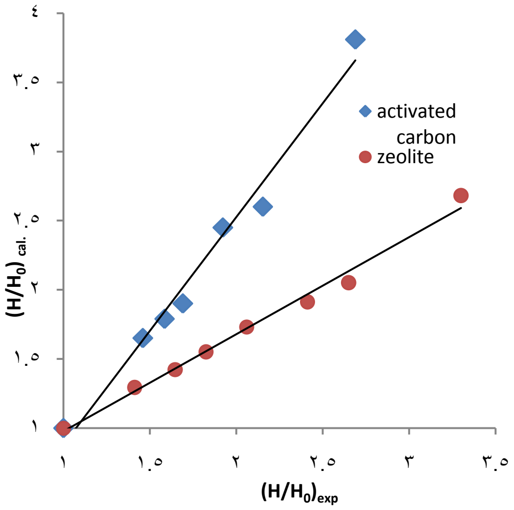

Fig.10: Comparison of bed expansion calculated $(H/H_0)_{\text{cal}}$, with those of experimentally determined values, $(H/H_0)_{\text{exp}}$.

CONCLUSIONS

The following conclusions are drawn from the above-discussed results:

1. The adsorption process of oil on activated carbon and zeolite fits well with Freundlich isotherm.
2. The amount of oil adsorbed increased with the increase in contact time. At equilibrium, the surface of the adsorbent was covered with oil

3. molecules; therefore a longer mixing time does not increase residual oil removal from wastewater.
4. It was found that as the dosage of adsorbent was increased, the percentage of residual oil removal also increased.

For expanded bed experiments

1. Activated carbon performed better adsorption properties than zeolite in the removal of oil

2. It is observed that the addition of higher amount of calcium sulphate is essential to achieve larger oil removal. The break point time is obtained earlier without the addition of the coagulant.

3. The validity of Richardson-Zaki equation has been confirmed with the experimental data for activated carbon better than for zeolite.

NOMENCLATURE

C The concentration of oil at time t (ppm)

C_0 The concentration of oil at time zero (ppm)

C_e Equilibrium concentration of oil (ppm)

d_p Particle diameter (m)

g Acceleration of gravity (m/s^2)

H Height of the expanded bed (m)

H_0 Height of bed at zero flow stream (m)

K_F Freundlich constant$(g/l)^{1/nf}$

K_L Langmuir constant (g/l)

n Richardson- Zaki exponent constant (-)

$1/n_f$ Heterogeneity factor

q_e Amount of oil adsorbed per unit weight of adsorbent (mg/ g)

q_0 Maximum amount of adsorption (mg/g)

V_0 Superficial velocity (m/s)

V_{mf} Particle minimum fluidization velocity (m/s)

V_t Terminal settling velocity (m/s)

Re Particle Reynolds number (-)

Greek letters

ρ_l Density of fluid (kg/m^3)

ρ_s Density of particle (kg/m^3)

μ_l Dynamic viscosity of fluid (kg/m.s)

ϕ_s Solid fraction of the expanded bed (-)

ϕ_0 Solid fraction of the bed at zero flow stream (-)

ε Void fraction of the bed (-)

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معالجة مياه التصريف الزيتية باستخدام اعمدة الامتزاز المتمددة من الكاربون المنشط والزيولايت

الخلاصة:

تم في هذه الدراسة معالجة مياه التصريف الزيتية بواسطة الامتزاز على الكاربون المنشط والزيولايت واستخدمت طريقة الامتزاز ذو الدفعات وباستخدام الاعمدة المتمددة. حيث استخدمت الاولى لايجاد معدل وعلاقة الامتزاز للزيت على الكاربون المنشط والزيولايت بينما استخدمت الثانية لايجاد كفاءة عملية المعاملة وايجاد الاداء. المتغيرات التي تم دراستها هي تركيز المادة الممتزة والزمن وكمية المادة المازة. في هذه الدراسة ، تم فحص سلوك الامتزاز للزيوت النباتية (زيت الذرة) على الكربون المنشط والزيولايت كدالة للتركيز ، وكمية المادة الممتزة وكمية الملح (كبريتات الكالسيوم) المضاف.تم تمثيل النتائج باستخدام علاقات الامتزاز ثابتة درجة الحرارة فروندليتش ولنكمير. ووجد أن معادلة فرويندلش تنطبق على عملية الامتزاز على الكربون المنشط والزيولايت.

ان كمية الزيت الممتز تزداد مع زيادة زمن التماس وكذلك وجد ان زيادة المادة المازة ستزيد من نسبة ازالة الزيت. تم ايضا دراسة تاثير نوع المادة المازة المستخدمة على منحني المقاومة.

تم تمثيل تصرف الاعمدة المتمددة باستخدام معادلة ريتشاردسن – زاكي بين السرعة الفراغية والجزء البيني للعمود في حدود معتدلة من رقم رينولدز.