Journal of Engineering
journal homepage: www.joe.uobaghdad.edu.iq
Number 10 Volume 25 October 2019

Chemical, Petroleum and Environmental Engineering

Removal of Dissolved Organic Compounds and Contaminants from Wastewater of a Petroleum Refinery by Ion Exchange

Dr. Najwa Sabir Majeed
Chemical Engineering Dept./College of Engineering/University of Baghdad
Baghdad, Iraq
Email: majeednajwa@gmail.com

Samira Najem Abdullah*
Chemical Engineering Dept./College of Engineering/University of Baghdad
Baghdad, Iraq
Email: samira.njm@gmail.com

ABSTRACT

The efficient removal of dissolved organic compounds (DOC) from wastewater has become a major environmental concern because of its high toxicity even at low concentrations. Therefore, a technique was needed to reduce these pollutants. Ion exchange technology (IE) was used with Amberlite^{TM} IR120 Na, Amberlite^{TM} IR96RF, and Amberlite^{TM} IR402, firstly by using anion and mixed bed system, where the following variables are investigated for the process of adsorption: The height of the bed in column (8,10 and 14 cm), different concentrations of (DOC) content at constant flow rate. The use of an ion exchanger unit (continuous system) with three columns (cation, anion, and mixed bed) was studied. The effect of the following variables, such as a change in temperatures (23,30 and 40 C^{o}) and the change in flow rate (2,4,6 L/min) was studied. The results showed that the adsorption capacity decreased with increasing the flow rate. The linear equation models of (Langmuir, Freundlich, Timken, and Dubinin-Radushkevich) were used. The results were analyzed using three known models for equilibrium and temperature constant. Graphically, the Langmuir model was the most consistent with the adsorption results because it has the highest adsorption capacity and the highest correlation value of $R^2 = 0.97$. The ion exchange column dynamics were studied using models such as (Thomas model). The results showed that the experimental results were well correlated with the model equations. While the tests showed that the removal rate of pollutants was up to 90% for organic compounds.

Keywords: wastewater treatment of a petroleum refinery; ion exchange; removal oil and phenol.

ازالة المركبات العضوية الذائبة والملوثات من مياه الصرف لتصفية النفط باستخدام تقنية التبادل الايوني

الخلاصة

اصبحت كفاءة ازالة المركبات العضوية الذائبة (DOC) من مياه الصرف الصحي مصدر قلق بيئي كبير بسبب سميتها العالية حتى عند التركيزات المنخفضة . لذلك دعت الحاجة الى ايجاد تقنية جديدة لغرض تقليل هذه الملوثات باستخدام تقنية التبادل الايوني (Ion Exchange) . تضمن هذا البحث امكانية دمج ثلاثة اعمدة لوحدة التبادل الايوني Amberlite^{TM} (Amberlite^{TM} IR96RF, Amberlite^{TM} IR402, IR120 Na) اولا يتم استخدام (نظام الدفعات)ذو حشوة ثابتة(Anion & mixed bed). حيث يتم دراسة تأثير المتغيرات التالية على عملية الامتزاز المبادلات: مثل تغير ارتفاع الحشوة داخل العمود(8,10,14 cm) وباستخدام تراكيز مختلفة للمحتوى المواد العضوية وبثبوت معدل الجريان. ثانيا استخدام وحدة مبادل ايوني(نظام مستمر) بثلاثة اعمدة (Cation,Anion & mixed bed)وتم دراسة تاثير المتغيرات التالية مثل تغير درجة الحرارة(23,30,40 C^{o}) وتغير معدل الجريان (2,4,6 L/min). واظهرت النتائج ان سعة الامتزاز تقل مع زيادة معدل الجريان وزيادة درجة الحرارة ولكنها تزداد مع زيادة ارتفاع الحشوة. تم وصف عملية امتزاز (DOC)على مادة الرزن

---

*Corresponding author

Peer review under the responsibility of University of Baghdad.
https://doi.org/10.31026/j.eng.2019.10.3

Article received: 6/11/2018
Article accepted: 23/12/2018

باستخدام ثلاث موديلات معروفة للتوازن وبثبوت درجة الحرارة. حيث استخدمت المعادلات الخطية لهذه الموديلات (Langmuir, Freundlich, Timken and Dubinin-Radushkevich) وبعد تحليل النتائج بيانيا تبين ان موديل (Langmuir model) هو الاكثر تطابقا مع النتائج التجريبية لعملية الامتزاز لأنه يملك اعلى سعة للامتزاز واعلى قيمة لمعامل الارتباط تصل قيمته الى ($R^2=0.97$).تم دراسة حركية عمود التبادل الايوني باستخدام موديلات مثل (Thomas model) بيانيا اظهرت النتائج هناك تطابق بين النتائج العملية ومعادلات الموديل. حيث اظهرت الفحوصات ان نسبة الازالة الملوثات تصل الى 90% للمركبات العضوية

الكلمات الرئيسية: معالجة مياه الصرف الصحي من مصانع التكرير، التبادل الآيوني ، إزالة الزيوت والفينولات .

1. INTRODUCTION

One of the major problems of the petrochemical industry is the great amount of wastewater produced and the high investment needed for the treatment of this effluent before it is released to the environment.

Phenolic compounds exist in wastewaters from the olive mill, oil refineries, plastics, leather, paint, pharmaceutical, and steel industries, and it must be removed to satisfy the actual environmental regulations**, Metcalf and Eddy, 2003**.

Different techniques have been applied to remove or eliminate phenolic compounds from wastewater, including chemical oxidation, chemical coagulation, solvent extraction, membrane techniques, and adsorption. **Kulkarni and Kaware , 2013.** studied the phenol removal from polluted wastewaters by using the resin Purolite A-510 in the chloride form and found that the phenol removal increased sharply with increasing pH. They described the isotherms by either Langmuir or Freundlich models, **Langmuir, 1916, and Freundlich, 1906**.

Among many water treatment technologies, IE has emerged as one of the most promising technologies for water treatment. The process in which an ion is exchanged from a solution with a similarly charged ion is found on fixed solid particles, called IE resin, occur in a reversible chemical reaction called IE. IE is a more interesting technology from an economic point of view compared with other wastewater treatment processes such as membrane technology. On the other hand, this technology gives high treatment capacity and high removal efficiency. It presents fast kinetics, **Metcalf and Eddy, 1991, and Do 1997**.

IE reaction occurs by replacing ionic impurities in water with releasing ions by an IE resin. The uptake of ions by IE resins is affected to some extent by variables such as pH, temperature, flow rate, ionic charge, the concentration of the initial pollutant and time of contact**, Caetano and Valderrama, 2009**. Resins must be periodically regenerated to restore their original ionic form. IE technology has been widely used for diverse applications on a commercial scale with successful success. The combination of cation-and anion–exchange resins is useful in water purification. IE resins, which have been used for water treatment, are prepared from synthetic polymers such as styrene-divinylbenzene, whether sulfonated or aminated to target contaminants, **Helfferich, 1962, and Anderson, 1997.**

In this work, a strong-base anion exchanger (Amberlite IRA-420) and mixed bed (strong-base anion and weak base anion) were used to eliminate (phenol and oils) from wastewater.

1.1 Langmuir Isotherm Model

In Langmuir isotherm model, the theoretical adsorptive capacity is equal to the adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites**.** ,**Vermeulan, et al., 1966**. The general non-linear form of this model is performed by Langmuir,1916:

$$q_e = \frac{q_{max}\, K_L C_e}{1+K_L\, C_e} \qquad (1)$$

Where: q_e is the adsorption capacity $\left(\frac{\text{mg}}{\text{L}}\right)$, C_e is the concentration of ion at equilibrium in ppm , q_{max} is the maximum adsorption capacity in (mg/L), K_L constant of langmuir, related to the adsorption energy (L/mg).
For this model, the linear form can be written as followed:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \tag{2}$$

The values of q_{max} and K_L were computed from the slope and intercept of the Langmuir plot of $\frac{1}{q_e}$ versus $\frac{1}{C_e}$ (Langmuir,1916).
The dimensionless constant called equilibrium parameter can express the essential characteristic of the Langmuir isotherm R_L defined by **,Webber and Chakravarti, 1974.**

$$R_L = \frac{1}{1+K_L C_\circ} \tag{3}$$

The separation factor R_L values indicate the type of the isotherm to be irreversible (R_L= 0), favorable (0< $R_L > 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$).

1.2 Freundlich Adsorption Isotherm

This is commonly used to describe the adsorption properties of the heterogeneous surface **Tan, et al., 2011,** and **Hutson and Yang, 2000**. The model applies to adsorption on the non-homogenous surfaces. The non-linear expression of Freundlich model can be used to describe the heterogeneous system and is expressed as follows, **Saien, 2007,** and **Freundlich, 1906**.

$$q_e = K_F {C_e}^{1/n} \tag{4}$$

Where K_F is the Freundlich constant related to the bonding energy. 1/n is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption **,Voudrias and Bozani, 2002,** and **Guadalupe, et al., 2008**. The value of (n) determines the degree of non-linearity between solution concentration and adsorption as follows:
when n=1; the adsorption process is linear.
$n < 1$; the adsorption process is chemical.
$n > 1$, the adsorption is a physical process, **Mohan and Karthikeyan, 1997**. Conversely, $n < 1$ and $n > 1$ indicate a normal Langmuir and cooperative adsorption, respectively **Goldberg, 2005**.
Eq. (4) can be linearized, to give the logarithmic form and the constants of Freundlich isotherm can be determined from slope and intercept.

$$\text{Log}(q_e) = \log(K_F) + \frac{\log(C_e)}{n} \tag{5}$$

1.3 The Temkin Isotherm Model

This model contains a factor that takes into account the adsorbent-adsorbate interactions. This model assumes the following, **Tempkin, 1940,** and **Aharoni, 1977**.

1- The heat of adsorption (a function of temperature) of the molecules in the layer decreases linearly with coverage because of the adsorbate-adsorbate interactions**, Gurses, et al., 2014,** and **Zheng, et al., 2008**.
2- Adsorption is characterized by a uniform distribution of binding energies, reaching some maximum binding energy. The Temkin isotherm derivation assumes that the fall in the heat of sorption is linear rather than logarithmic, as given in the Freundlich equation.

Temkin Isotherm model is usually applied in the following form :

$$q_e = \frac{RT}{b} \ln(K_T\, C_e) \tag{6}$$

$$q_e = \frac{RT}{b_T} \ln K_T + \left(\frac{RT}{b_T}\right) \ln C_e \tag{7}$$

Where R is the universal gas constant 8.314 J/(mol. K), T is the absolute temperature in Kelvin. The constant b_T is related to the heat of adsorption. K_T constant of the Temkin isotherm (L/g).

1.4 Dubinin-Radushkevich isotherm model

For isothermal analysis was suggested by another equation used for this model, to assess the porosity apparent free energy and adsorption properties, this model is applied **,Gunay, 2007,** and **Dabrowski, 2001**. This isotherm model is not presumed to be a homogeneous surface or constant sorption potential. The linear form of this model is given in ,**Khaled, et al., 2009,** and **Foo and Hameed, 2010**.

$$q_e = (q_{max}) \exp(-K\, \varepsilon^2) \tag{8}$$

$$lnq_e = lnq_{max} - K\, \varepsilon^2 \tag{9}$$

Where

q_{max} = saturation capacity, theoretical isotherm (mg/g).

q_e = amount of adsorbate ,at equilibrium, in the adsorbent,(mg/g),

K = constant isotherm of Dubinin-Radushkevich (mol^2/KJ^2)

ε = Polanyi potential, can be calculated from.

$$\varepsilon = RT \ln(1 + \frac{1}{C_e}) \tag{10}$$

The plots slope of lnq_e versus ε^2 gives the constant K and the intercept yields to adsorption capacity, q_{max} , K, used to calculate (E) is the mean free energy of adsorption per molecule of the sorbate, can be computed by the relationship ,**Aarfane, et al., 2014, Khaled, et al., 2009, Dubinin, 1960,** and **Hobson, 1969**.

$$E = \frac{1}{\sqrt{2k}} \tag{11}$$

For estimating the type of adsorption process, the magnitude of E is useful, **Silva, et al., 2004**.

2.EXPERIMENTAL

2.1 Materials

The wastewater investigated was obtained from the industrial wastewater collected from AL-Daura petroleum refinery. The wastewater samples were treated by IE.

Two types of commercial ion exchange resins are used in this work. These are Cation exchanger (Strong Acid Cation, SAC), hydrogen form of type Amberlite^{TM} IRA120, Anion exchange (Strong Base Anionic, SBA), hydroxyl form of type Amberlite^{TM} IRA402 CL, and Mixed Bed

(Weak base anion+ Strong Base Anionic), (Amberlite^{TM} IRA96RF, Amberlite^{TM} IRA402), (© 2000 Rohm and Hass / Ion Exchange Company), **Crittenden, et al., 2004 and Zagorodni, 2007.**

2.2 Analytical Methods

All experiments and analyses were carried out in Laboratory of the Chemical Engineering/ University of Baghdad. The samples collected during the experiments were analyzed by several methods.

Parameters of wastewater including, pH, temperature, total dissolved solids (TDS) and turbidity were also measured depending on the standard methods to check up water and wastewater.

Ultraviolet (UV) absorbance at 270 nm and total organic content (TOC) are commonly used to describe the wastewater samples of (DOC), **Table 1**.

Effect of the initial concentration of pollutants, contact time, pH, flow rate, temperature, and height of the bed was studied.

2.3 IE Experiments (batch and continuous)

The IE batch experiments, for the removal of pollutants (oils, phenols, TDS, COD, BOD, and turbidity) were completed in an ion exchange, fixed bed (anion + mixed bed) operating on a closed loop system, glass column of (internal diameter, 7 cm) of the (length 30 cm). The column was filled with the resin to get the desired heights of the bed (8, 10 and 14 cm) with a stratum of glass wool at the bottom. To remove impurities from the adsorbent (resin), distilled water was passed across the column. Wastewater was pumped at three flow rates (4,6 and 8 mL/min) to the top of the IE column by using a peristaltic pump with various initial concentrations (50-800 mg/L) of dissolved organic matters (oil and phenol). **Fig. 8a** shows ion exchange bench-scale equipment. In this process, the input volume of wastewater =225 mL, flow rate (2-10)mL/min, and operation time (10-30) min.

In both batch and continuous experiments, oil, phenols, COD, BOD, TDS, pH, and turbidity were tested in the outlet current at different contact times throughout the entire experiments. The treated amount have been monitored as a function of contact time by removing 75 ml in batch ion exchange and 1-6 L in continuous ion exchange aliquot of solution for the ions concentration measurements. Also, the performance of IE process has been studied at different values of temperature by tuning values at 296 K, 308 K, and 313 K.

For ion exchange experiments (continuous-mode), the amount of wastewater was treated, at different values of inlet flow rates (2, 4, and 6 L/min) for 2h. The samples of the product from (mixed bed) column were taken at uniform time intervals, and concentration of phenols was measured using an UV-visible spectrophotometer at a wavelength of 270 nm. The concentration of oil in wastewater was measured by a simple device TD500-D^{TM} Handheld Oil in water meter. This meter uses an easy solvent extraction procedure with high accuracy.

2.4 IE resins conditioning and regeneration

Ion Exchange resins (anion and mixed bed) were initially washed many times with distilled water. After each playback cycle, the anion and mixed bed exchange resins were regenerated by using an aqueous solution of (NaOH, 4% and NaOH 2%). Similarly, the cation exchange resin was fully washed with an aqueous solution(2% HCl). Lastly, the adsorbent (resins) were washed with distilled water to dislodge all surplus of base and acid, respectively, **Table 1**.

Table 1. The main equipment and apparatus used in the experiments.

Equipment name	**Model**
pH.Ion selective pH and Ion Meter	WTW, Type GLP 22, Germany
Conductivity /TDS Meter (hold)	Digital (HM).
Turbidity Meter(0.01-1100 NTU)	Lovibond, NO.09/1261, Germany
COD meter(COD VARIO)	Lovibond, MD 200, RD 125
Oil in Water Meter	TD500D^{TM} , (Turner Design Hydrocarbon Instruments).
Ultrasonic processor(ultrasound)	UP200S, Hielscher, Ultrasound Technology
UV, Ultraviolet and Visible Absorption, Spectrophotometer	Thermo Electron Corporation Model: GENESYS 10 UV CAT :335902A-02 SN :2H2J012006

3.RESULTS AND DISCUSSION

3.1.Effect of flow rate

The results indicated the percentage of removal oil declined with increased flow rates; this is because of the increase of the hydraulical loading on the resin. The effect of flow rate on oil content by continuous ion exchange was investigated at different produced water flow rates (2, 4, and 6 L/min) and keeping other conditions constant, initial concentration of 255.3 mg/L, the height of bed 80 cm and pH =7.3 at room temperature. The experimental breakthrough curves at various flow rates were presented in **Fig. 1** as effluent oil concentration versus time. **Fig. 1**, shows that the breakpoint appears earlier, and the breakthrough curve becomes steeper. The reason is that the residence time of the oil molecules inside the bed was reduced, **Dabrowski, 2001.**

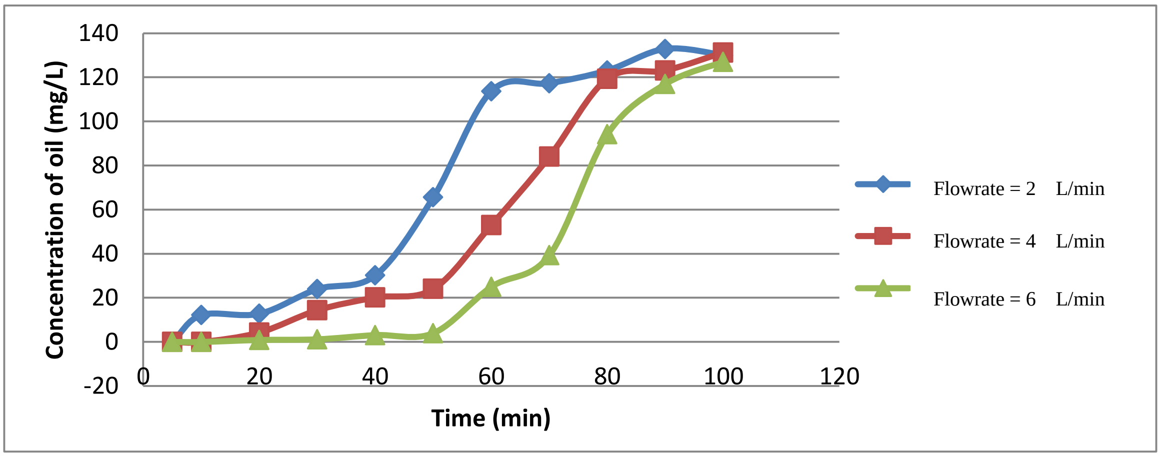
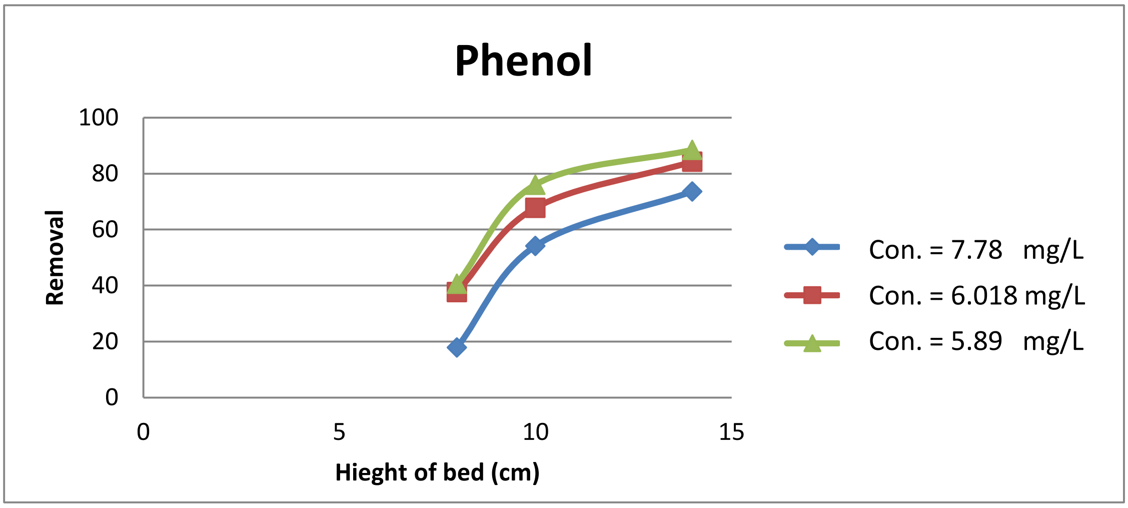


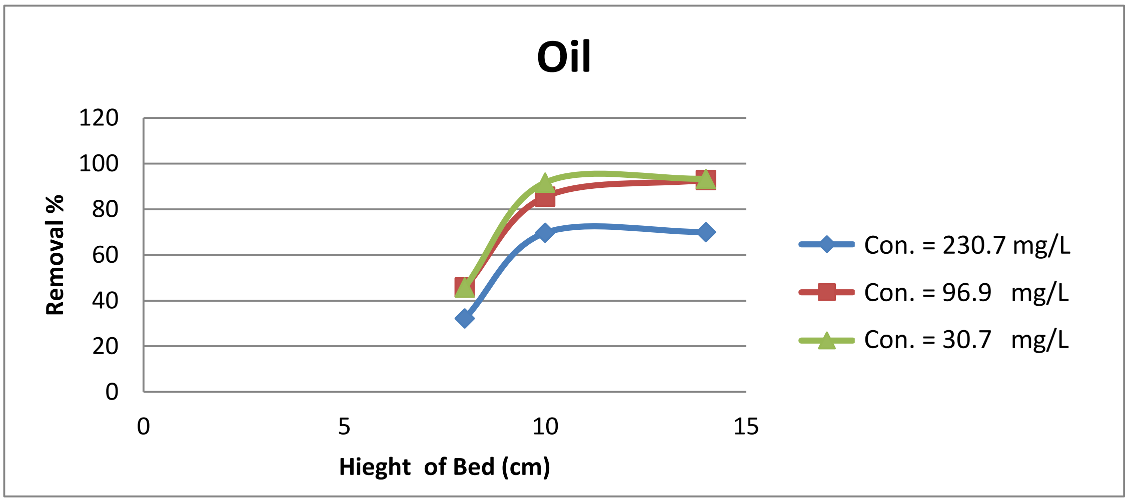
Figure 1. Impact different flow rate on the removal of oil from wastewater, at an initial concentration of oil = 255 (mg/L), by using continuous ion exchange experiments.

3.2.Effect of bed height

The effect of the bed height on (DOC) removal was done at a constant feed concentration of (mg/L) and flow rate (4 mL/min). The percentage removal of oil from wastewater at different heights of bed (8,10,14 cm) was investigated for a constant flow rate, is presented in **Fig. 2**. When the height of bed increases from (8-14) cm, for (batch mode), the percentage removal of (DOC) reaches 90%, and this parameter was chosen for the studies on the breakthrough curve. Since increasing the height of the bed will supply additional surface area and additional particles of resin, there will be an increase in the capacity of the adsorbent. Also, increasing the height of the bed will supply enough time for (DOC) to adsorbed on resin, (**Miyabe and Guiochon, 2000).**



-A-



-B-

Figure 2. A, B. Effect of the height of bed on removal (DOC) from wastewater, at a different initial concentration of (phenol & oil), and constant flow rate (6 ml/min).

3.3 Effect of Temperature

Fig. 3 shows the percentage removal of (DOC) in the output current of the continuous process of ion exchange as a contact time function for the three temperatures studied at (23,30 and 40 ℃). The removal percentage decreased with an increase in temperature, due to the adsorption process with an exothermic decrease of the physical forces responsible for sorption. Higher than (23℃) may be due to the deformation of the surface as well as, at higher temperatures destruction of some active polymeric sites on the surface of adsorbent occurs because of bond rupture. Thus, the study found that the optimum working range was at 23 ℃. The influence of temperature on removal of contaminants (oil and phenol) by ion exchange (anion resin and mixed bed exchange resin), the removal mechanism, provides the opportunity to discuss further the different behaviors of oil and phenol in batch and continuous experiments may be due to different removal mechanisms. The removal efficiencies of (DOC), were around 80% -90%, at the optimal temperature (296 K).

3.4 Isotherm

Four isotherm equations were tested in the adsorption of (DOC) into resin, namely, Langmuir, Freundlich, Temkin, and Dubunin-Radushkevich isotherms. From linear isotherm graphs for each of the isotherm equations tested, the values of the isotherm constants were determined and are given in **Table 2**. The results show that the Langmuir isotherm model fits a good extent with the experimental data, as specified the best correlation for the experimental data with the correlation coefficients, R^2=0.973. Moreover, these results indicate a good property of the Langmuir isotherm with separation factor , R_L<1.00 .

The value of R_L indicates the type of the isotherm. The R_L, which shows that adsorption of (DOC) onto the resin is a favoarable process (linear adsorption), and the experimental data accurately fits with the Langmuir isotherm model.

K_f and n are constants the Freundlich model, and they are related to the sorption capacity and intensity, and it can be calculated from the slope and intercept of the linear form, by plotting log q_e versus log C_e.

The $R^2 = 0.9587$, was found to be lower than the R^2value of Langmuir isotherm. The value of n >1, which highlights the favourability of the adsorption process.

K_T and B_T constants of the Temkin isotherm model, are calculated from the slope and intercept of q_e versus Ln C_e . The linear isotherm constants and coefficients of determination are introduced in **Table 2**. The value of R^2= 0.785 was obtained for Temkin model, which is lower than the value of the Langmuir value and Freundlich value, **Foo and Hameed , 2010 .**

In the D-R model, the plot of Ln (q_e) versus ε^2 gives adsorption capacity, Q_m(mg/g) and the K_{DR}. The constant K_{DR} gives the (E) average free energy of adsorption for each sorbate molecule when it is transferred to solid surface from bulk solution. The value of coefficient of regression D-R isotherm R^2=0.649 is lower than the Langmuir value, Freundlich value, and the Temkin value, in this case, Dubunin-Radushkevich equation represents the poorest fit of experimental data than the other isotherm equations.

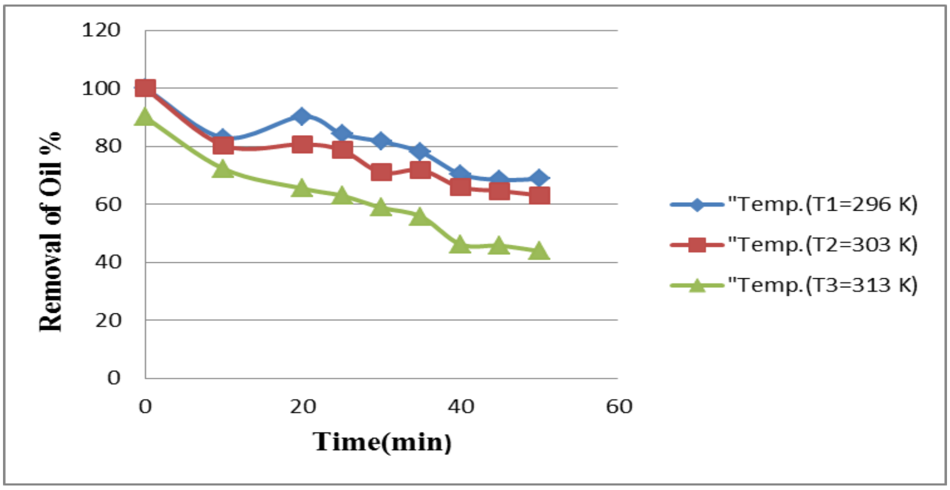


Figure 3. Effect temperature on removal % of Oil in wastewater, Initial Concentration of Oil = 255.3mg/L, at constant of flow rate = 6L/min and height of bad = 80cm.

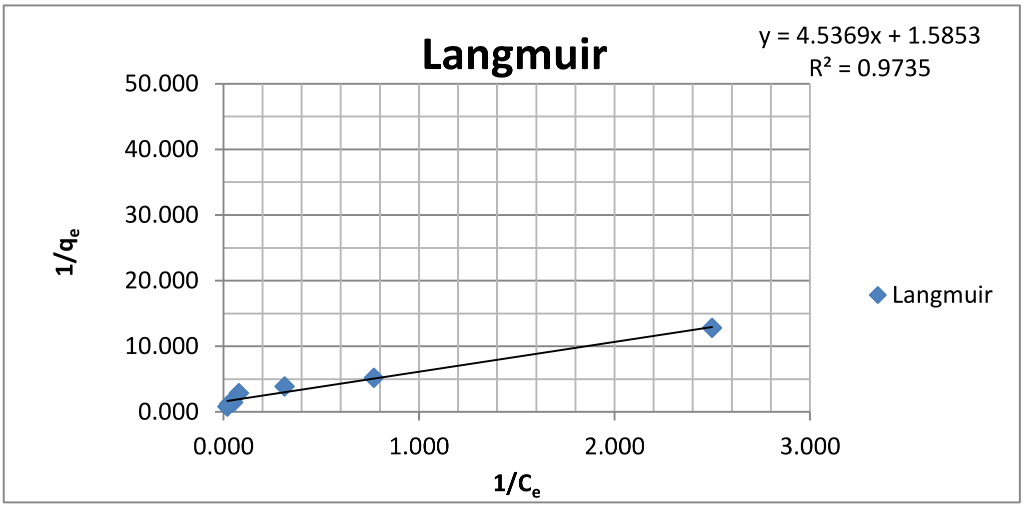


Figure 4,a. Constants of the Langmuir model.

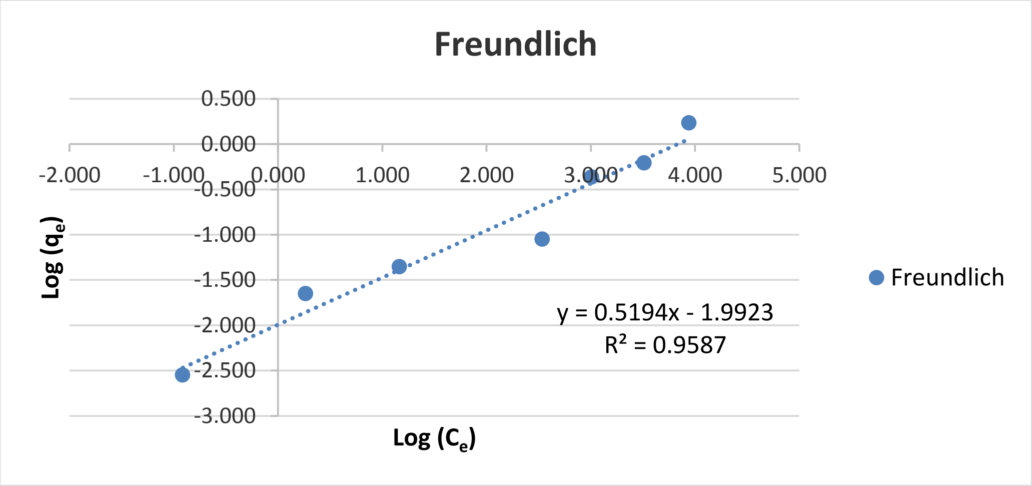


Figure 4,b. Constants of Freundlish model

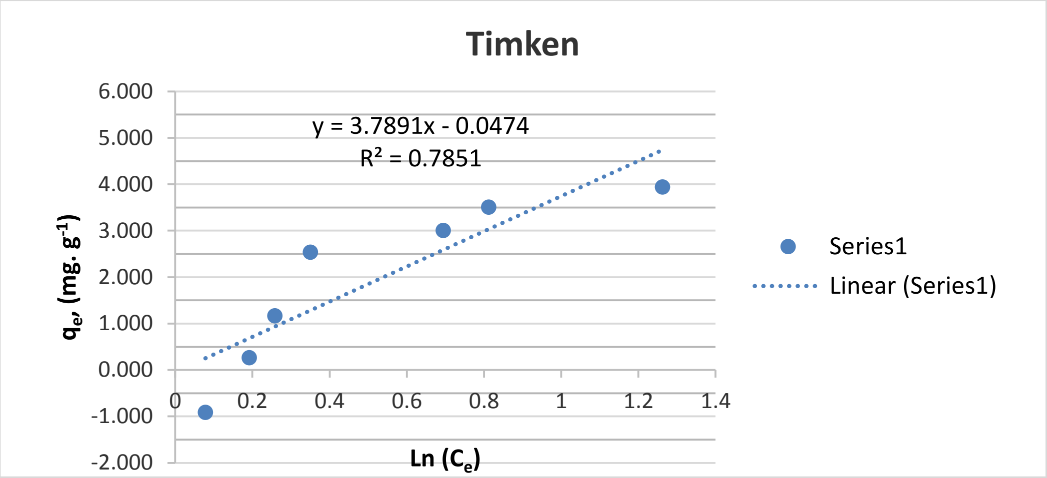


Figure 4,c. Constants of the Timken model.

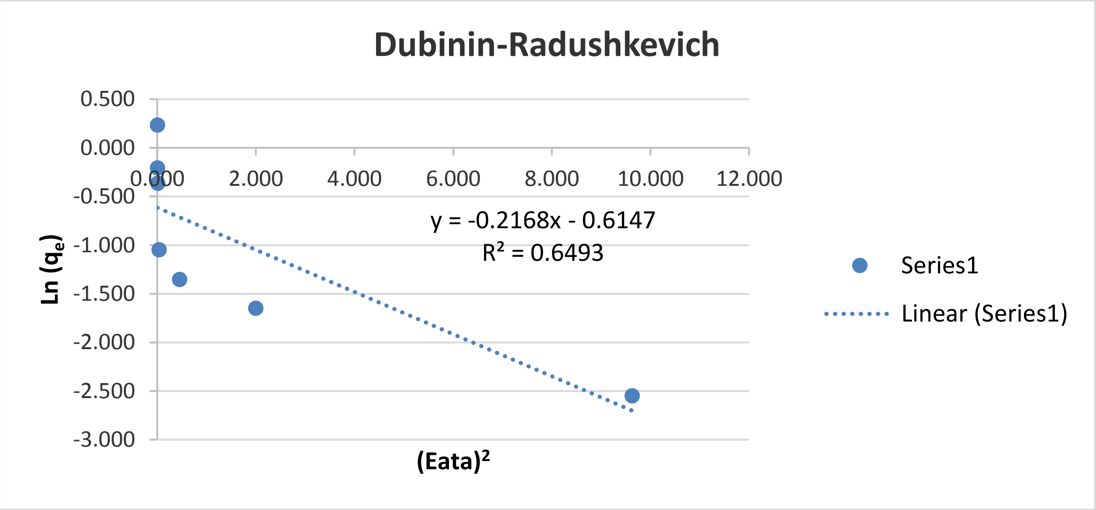


Figure 4,d. Constants of the Dubinin-Radushkevich.

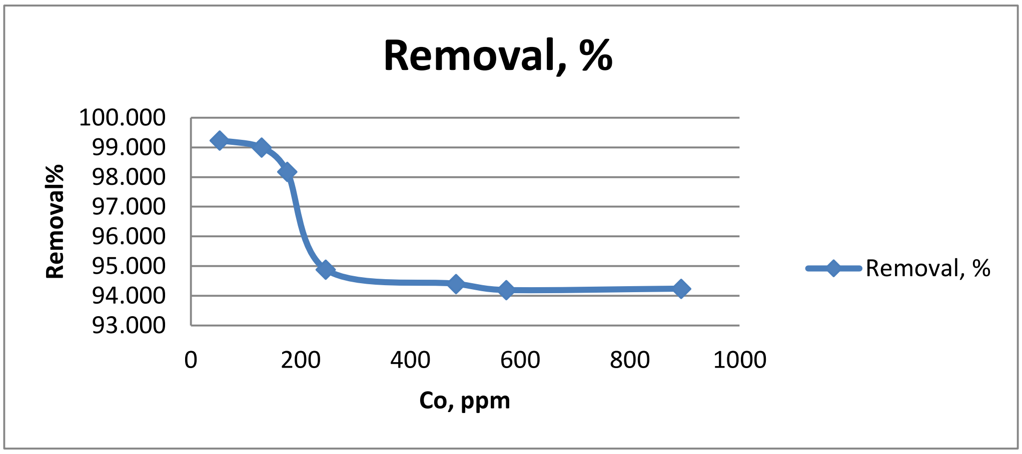


Figure 4,e. Effect of Removal Percentage on initial Concentrations of (DOC).

Table 2. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich Isotherms constants for the Adsorption of DOC ions into Ion Exchange.

	Langmuir Isotherm				*Freundlich Isotherm*			
Oil mg/L	$Q_\circ$(mglg)	K_L(L/mg)	R_L	R^2	$\frac{1}{n}$	n	K_f(mg/g)	R^2
	0.6308	<1.0013	0.01866	0.973	0.5192	<1.92598	7.332	0.9587
	Temkin Isotherm				*Dubinin-RadushkevichIsotherm*			
	A_T(L/mg)	b_T	B	R^2	q_s(mg/g)	$K_{ad}(mol^2/KJ^2)$	E(KJ/mol	R^2
	0.0085	<1.000	=1.00	0.7851	0.5408	<0.216	1.5214	0.649

3.5.Breakthrough curves

To determine the volume and capacity saturation was determined by plotting $c/c_\circ$ versus time (t) at a different initial concentration of (DOC) .

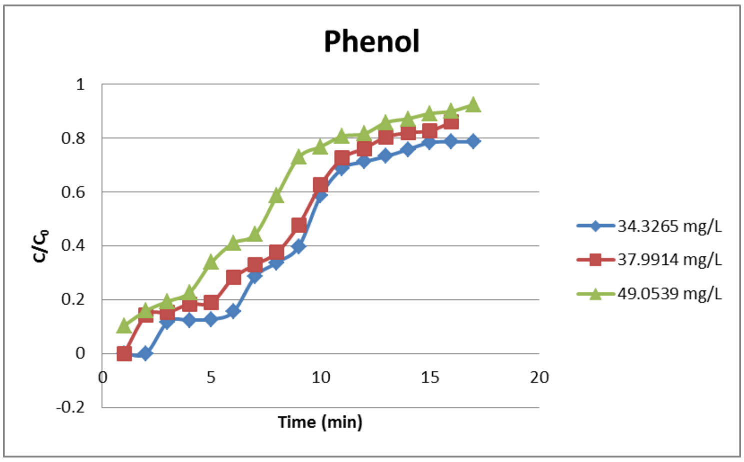


Figure 5,a. Breakthrough curves for phenol content adsorbed onto ion exchange. at a different initial concentration.

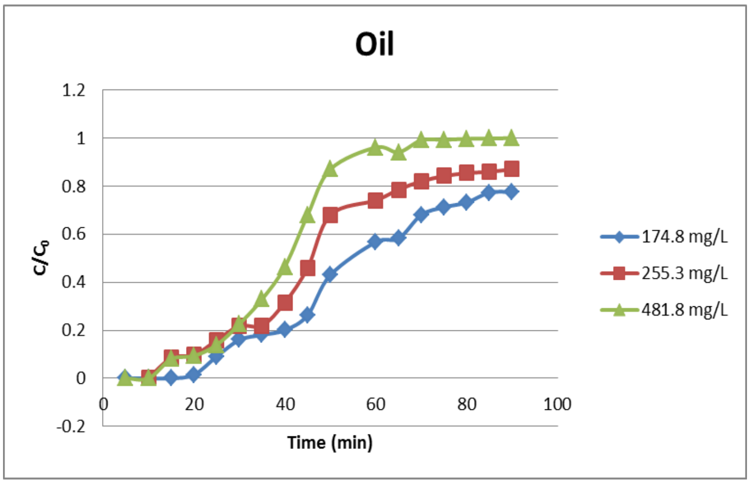


Figure 5,b. Breakthrough curves for oil content adsorbed onto ion exchange. at a different initial concentration

The secondary treatment operation used for wastewater ion exchange process (fixed bed), was addressed as a final purification for the removal of organic compounds from wastewater. For this purpose, the influence of the initial (DOC) concentration on the profiles of the breakthrough curves were studied with continuous mode of ion exchange (anion + mixed bed), under constant flow rate (6 L/min), constant height of bed (80 cm), and different initial concentration of phenol.

3.5.1 Effect of the initial concentration of Oil and Phenol on breakthrough curves

Fig. 6 shows the influence of initial concentration on the breakthrough curves for oil and phenol adsorption onto the resin (anion and mixed bed) in the ion exchange column (continuous mode). The results obtained can be explained by the increase in the IE capacity through the fact that a higher influent (DOC) concentration leads to a higher driving force for the transfer process to overcome the mass transfer resistance, **XiaoFeng, et al., 2014**. Moreover, the highest volume could be treated upon the lowest initial concentration, as a result of the increased diffusion or mass transfer coefficient. A focus on this figure also shows that increasing initial concentration values resulted in an earlier breakthrough curve.

In this figure, S-shaped curves can be observed for all three (DOC) concentration investigated.

3.5.2 Evaluation of Thomas Model Parameters

The Thomas model was applied to the experimental data for $C/C_{\circ}$ ratios ranging from to the initial concentration of DOC. The experimental IE data were fitted to the Thomas model to determine the Thomas maximum sorption capacity of the resin ($q_{e,th}$) and rate constant (K_{th}). The parameters values from the fitting of the experimental IE data to Thomas model are hereafter reported in **Table 3**, including mainly involves the rate constant of the Thomas model K_{Th} and adsorbate equilibrium ,$q_{\circ}$., **Thomas, 1944.**

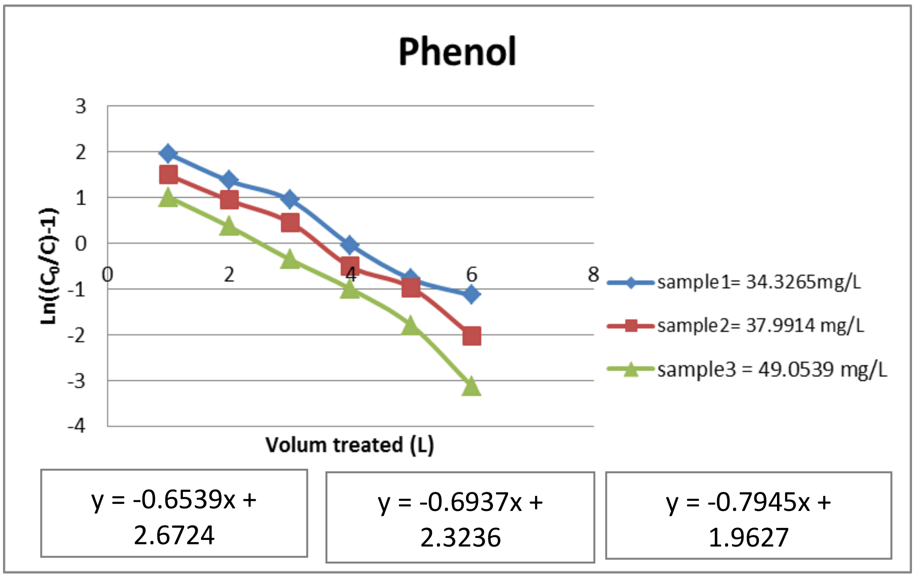


Figure 6. Thomas Model Parameters for different initial concentration of phenol.

Table 3. Thomas Model Parameters for different initial concentration of phenol.

Inlet(DOC) concentration of Phenol (mg/L)	Thomas model parameters			
	K_{Th}(ml/min.mg)	$q_\circ$ (mg/g)	R^2	SE
34.3265 mg/L	0.1143	5.611×10^{-3}	0.9847	1.1122×10^{-5}
37.9914 mg/L	0.10956	5.855×10^{-3}	0.9843	2.0699×10^{-5}
49.0539 mg/L	0.0972	4.847×10^{-3}	0.9796	5.334×10^{-6}

From **Table 3**, it can be noted that when $C_\circ$ is increased, the value of $q_\circ$ increases significantly, but the value of K_{Th} decreased. This is due to the difference in adsorption driving force associated to the concentration gradient**, XiaoFeng, et al., 2014**.

By using the Thomas model, it was found that the estimated values of $q_\circ$ to be very close to the values of $q_\circ$ obtained from experimental results with varying $C_\circ$ conditions. **Table 2** shows a comparision of the R^2 and Square Error (SE) values for different initial concentration of DOC.

Fig. 7 shows a photograph of the ion exchange equipment and a flow-sheet scheme for the ion exchange batch process.

Figure 7, a. Photograph of Ion exchange bench-scale equipment.

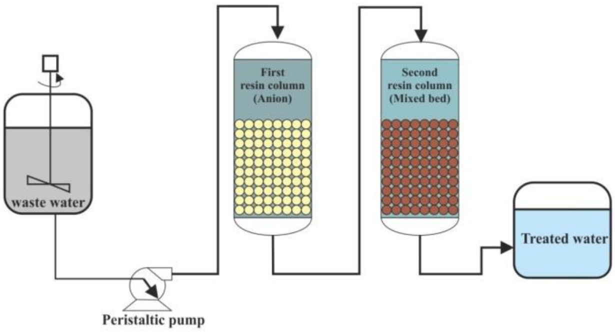


Figure 7, b. Flow-sheet scheme for IE batch process.

Fig. 8 shows a photograph of the ion exchange continuous equipment and a flow-sheet scheme for the ion exchange continuous process.

1

2

3

Figure 8,a. Photograph of Ion exchange continuous equipment.

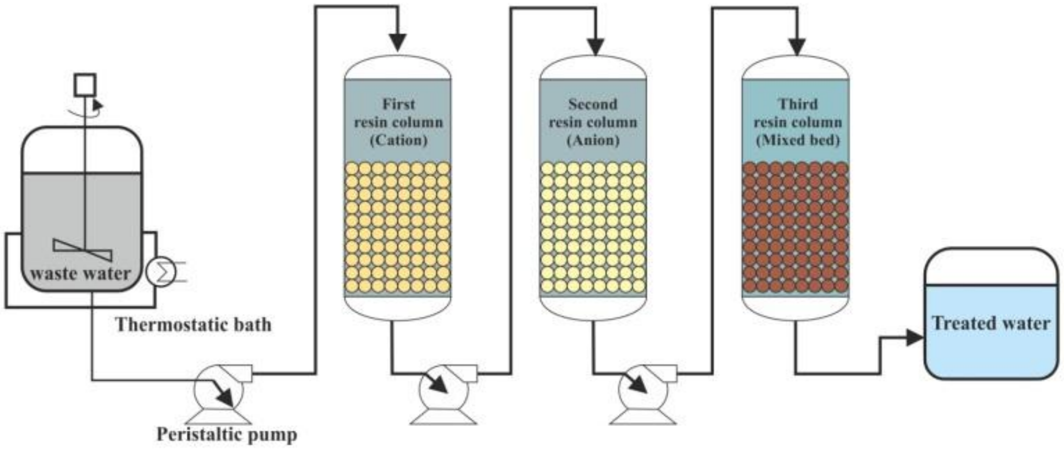


Figure 8,b. Flow-sheet scheme for IE continuous process.

4.CONCLUSIONS

1- Anion exchangers of open structure and high water content were found to be the best resin type for very efficient removal of any charged aquatic DOC, whether hydrophobic or hydrophilic. The water content and performance of resin is influenced by the degree of cross-linking and the presence of polar groups.

2- The parameters from wastewater as measured by pH, COD, and turbidity were drastically reduced after treatment with anion and mixed bed. Thus, the present study suggests that ion exchange; anion+mixed bed (strong base with weak base) is an attractive low-cost for the removal of phenol and other pollutants from wastewaters.

3- The results showed that the adsorption capacity decreases with increasing flow rate and increasing temperature but increases with increasing height of the bed. The process of adsorption of the oil content was described by the matrix using three well-known equations for equilibrium and constant temperature buildup. The linear equations of these models were used; Langmuir, Freundlich, Timken, and Dubinin-Radushkevich. Langmuir model is the most consistent with the adsorption results of the adsorption process because it has the highest adsorption capacity of 0.6308 mg/g and the highest correlation coefficient of 0.973.

4- The analysis of the ion exchange column kinetics using models such as Thomas model graphically showed that there is a correlation between the experimental results and the model equations. Several tests were conducted on the water resulting from the ion exchange process. The tests showed that the percentage of removal of the oil content was 90% and the removal rate of phenol was 95% and the percentage of the removal of the total soluble salts was 98% and the change of color and watercolor or water free from contaminants. The resulting water can be used for agricultural purposes.

REFERENCES

- Aarfane A., Salhi A., EI Krati M., Tahiri S., Monkade M., Lhadi E.K., Bensitel M., J.Mater.Environ. Sci. 5 (2014) 1927-1939.
- Aharoni C., Ungarish M., 1977, Kinetics of activated chemisorptions.” Part 2. Theoretical models, J. Chem.Soc. Faraday Trans. 73, pp. 456-464.
- Anderson, R.E., 1997, *Ion-Exchange Separation in Handbook of Separation Techniques for Chemical Engineers*, P.A. Schweitzer (Ed.), McGraw-Hill, New York.
- Caetano, C., and Valderrama, A. 2009, *Phenol Removal from Aqueous Solution by Adsorption and Ion Exchange Mechanisms onto Polymeric Resins*, J. Colloid Interface Sci., 338: PP. 402-409.
- Crittenden, J. C., Trussell, R. R., Hand, D. W. and Tchobanglouse, G., 2004, *Water Treatment- Principles and Design*, 2nd Ed, John Wily, and Sons.
- Dabrowski, 2001, *Adsorption-from Theory to Practice*, Ady. Colloid Interface Sci.93 PP 135-224.
- Do, D.D., 1997, *Adsorption Analysis: Equilibrium and Kinetics*, Imperial College, London.
- Dubinin, M.M. 1960,” The potential theory of adsorption of gases and vapors for adsorbents with energetically non-uniform surface,” Chem. Rev. 60 ,235-266
- Foo K.Y. and Hameed B.H., 2010, *Insights into The Modeling of Adsorption Isotherm Systems*, Review Chemical Engineering Journal, 156, 2-10.
- Freundlich, H.M.F. 1906, *Over The Adsorption in Solution*,. J. Phys. Chem., 57, PP. 385-471.
- Goldberg. S.,2005, Equations and Models Describing Adsorption Processes in Soils “ Soil Science Society of America, 677 S. Segoe Road, Madison, WI 53711, USA. Chemical Processes in Soils. SSSA Book Series, no.8.
- Guadalupe R., Reynel-Avila H.E, Bonilla-Petriciolet A., Cano-Rodriguez I., Velasco-Santos C., and Martinez-Hernandez A.L., 2008, “Recycling poultry feathers for Pb removal from wastewater; Kinetic and equilibrium studies”. Proceedings of World Academy of Science, Engineering and Technology, Volume 30.
- Gunay, E. Arslankaya, I. Tosun,” Lead removal from aqueous solution by natural and pretreated clinoptilolite”: adsorption equilibrium and kinetics, J. Hazard. Mater. 146 (2007) 362-371.
- Gurses A., Hassani A., Kiransan M., Acisli O., Karaca S.,J. 2014,”WaterProcessEng”. 2, 10-21.
- Helfferich F.1962, *Ion Exchange*, McGraw-Hill, New York, pp.231-240.
- Hobson J.P., 1969,” Physical adsorption isotherms extending from ultra-high vacuum to vapor pressure”, J. Phys. Chem. 73, 2720-2727.
- Hutson N.D. and Yang R.T.,2000, Adsorption”, J. Colloid Interf. Sci., pp 189.
- Khaled A., El Nemr A., EI-Sikaily A., Abdelwahab O., J. 2009, Hazard. Mater”. 165, 100-110.
- Kulkarni S.J., and Kaware J.P., 2013, *Review on Research for Removal of Phenol from Wastewater*. Int. J Sci. Res. Publ.;3: PP. 1–4.

- Langmuir, I., 1916, *The Constitution and Fundamental Properties of Solids and Liquids*, J. Am. Chem. Soc. 38, 2221-2295.
- Metcalf & Eddy, 1991, *Wastewater Engineering: Treatment, Disposal, and Reuse*, McGraw-Hill, New York, pp. 740-741; 756-757.
- Metcalf and Eddy, 2003, *Wastewater Engineering*. 4^{th}ed, McGraw Hill, N. Y. US.
- Miyabe K., and Guiochon G., 2000, *Kinetic Study of The Mass Transfer of Bovine Serum Albumin in Anion-Exchange Chromatography*, Journal of Chromatography, A, 886, pp. 147-171.
- Mohan, S. and Karthikeyan J.,1997, Removal of lignin and tannin color from aqueous solution by adsorption on activated carbon solution by adsorption on to activated charcoal", Environ. Pollut. 97, pp. 183-187.
- Saien, J., Nejati, H., 2007, Enhanced photocatalytic degradation of pollutants in petroleum refinery wastewater under mild condition". Journal of Hazardous Materials, v.148, p.491-495.
- Silva J.P., Sousa S., Rodrigues J., Antunes H., Porter J.J., Goncalves I., Ferreira-Dias S., Sep. Purif. Technol. 2004, 40, 309-315.
- Tan C.Y.,Li M., Lin Y.M., Lu X.Q., Chen Z.L., 2011, Desalin. 266 56-62.
- Tempkin, M.I., Pyzhev, V., 1940," Kinetics of ammonia synthesis on promoted iron catalyst", Acta Phys. Chim. USSR 12, 327-356.
- Thomas, H.C., 1944. *Heterogeneous Ion Exchange in a Flowing System*. J. Am. Chem. Soc. 66, PP. 1664–1666.
- Vermeulan T.H., Vermeulan K.R., and Hall L.C..,1966, Fundamental" Ind.Eng.Chem. 5, p 212-223.
- Voudrias, E., Fytianos, F. and E. Bozani, 2002, Sorption Description isotherms of Dyes from aqueous solutions and wastewaters with Different Sorbent materials", Global Nest. The Int.J., 4(1), PP 75-83.
- Webber T.N. and Chakravarti R.K., 1974, Pore and solid Diffusion Models for fixed bed adsorbers". J.Am.Inst.Chem.Eng. 20, 228-238.
- XiaoFeng, S., Tsuyoshi, I., Masahiko, S., Takaya, H., Koichi, Y., Ariyo, K., and Shiori, N. 2014, *Adsorption of Phosphate Using Calcined Mg3–Fe Layered Double Hydroxides in a Fixed-Bed Column Study*. J. Ind. Eng. Chem. 20, PP. 3623-3630.
- Zagorodni, A.A., 2007 , *Ion Exchange Materials Properties and Applications*, Elsevier BV.
- Zheng W., Li X.M., Wang F.,Yang Q., Deng P., Zeng G.M.,J. 2008, Hazard. Mater". 157, 490-495.