

Removal Of Methylene Blue From Aqueous Solution By Using Iron Filings Waste Material in Batch and Continuous Experiments

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Abstract

Twenty five experiments for both untreated and treated iron filings were carried out at various initial concentrations of MB , flow rate, bed depth, and different ratios of iron filings .Two types of experiments were carried out, batch experiments and continuous flow (column system) experiments. Batch study showed that equilibrium isotherms for all the adsorbents used in the study are of favorable type. The equilibrium data for methylene blue adsorption on both adsorbent well fitted to the Langmuir equation, with maximum monolayer adsorption capacities of (24.47 mg/g) and (25.03 mg/g) exhibited by untreated iron filings and treated iron filings respectively.

Key Words: (MB) dye, adsorption, iron filings, Batch experiment, continuous experiment.

الخلاصة

أجريت خمسة وعشرون تجربة لكل من برادة الحديد (قبل وبعد المعالجة) والتي تنفذ تحت ظروف مختلفة (التركيز الابتدائي للمادة الممتزة وعمق طبقة المادة ألامازة ومعدل الجريان). تم خلال الدراسة الحالية إجراء نوعين من التجارب تضمنت تجارب دفعية وتجارب النمط المستمر. وقد أظهرت التجارب الدفعية إن علاقة التوازن لكل من المواد ألامازة المستخدمة في البحث هي من النوع المفضل كما أظهرت هذه التجارب إن علاقة التوازن لاممتاز صبغة الميثيلين الزرقاء على كلا المادتين ألامازة تتطابق جيدا مع نموذج لانكمير وقد كانت قيم سعة الامتزاز القصوى (٢٤.٤٧ و ٢٥.٠٣) لكل من برادة الحديد قبل المعالجة وبرادة الحديد بعد المعالجة على التوالي .

1. Introduction

Dyestuff in wastewater from various industries, such as textiles, printing, pulp mills, leather, dyestuffs, and plastics, are stable and resistant to biodegradation because of its complex aromatic molecular structure. (El Qada et al., 2008; Han et al., 2008) Undoubtedly, the removal of dyestuff from waste effluents is of environmental importance. So far, various technologies including biological treatment, coagulation/flocculation, ozone treatment, chemical oxidation, membrane filtration, ion exchange, photocatalysis, and adsorption have been developed for the treatment of dye-containing effluents. Among them, adsorption is a reliable alternative due to its simplicity and high efficiency as well as the availability of a wide range of adsorbents (e.g., activated carbon, clay, biomass, polymer, zeolite, nanomaterials, etc.). In particular, activated carbon offers an attractive option for the efficient removal of various pollutants from waters because of its high surface area and porous structure. (Pelekani and Snoeyink, 2001) Unfortunately, the utilization of activated carbon on a large scale is limited by process engineering difficulties, such as its dispersion problem and regeneration cost ; therefore, many efforts have been made to investigate the use of various low cost organic adsorbents, which are cheap, easily available and disposable without regeneration. These materials are derived from natural resources, agricultural wastes or industrial by-products as peat, wood, barley rice husk, sawdust, biomass. Most of them are cellulose based and can be used without any previous thermal or chemical treatment (Subramani, 2002).

A use of zero-valent iron (Fe^0) as reactive medium for wastewater treatment is one of the most promising techniques because the iron metal is of low-cost, is easy-to-obtain, and has good effectiveness and ability of minimizing contaminants. In addition, iron waste particles from industrial filings can be used as a zero-valent iron (Palaharn and Junyapoon 2004 ; Lee et al., 2003). Reactive barriers containing iron

metals are currently being developed for in situ treatment technology (Puls et al., 1999). As zero-valent iron is a strong reducer, it has been used to remove several contaminants from wastewater such as halogenated hydrocarbon compounds, heavy metals, dyes, pesticides, and herbicides, which represent the main pollutants in wastewater (Sivavec and Horney, 1995).

(Yang, 2005) conducted a study to investigate the key operational parameters of batch and continuous-flow. Zero-Valent Iron (ZVI) decolorization of a reactive anthraquinone dye and Reactive Blue 4 (RB4), batch decolorization kinetics indicates that ZVI decolorization of RB4 is a surface catalyzed, mass transfer-limited process. The results of a long-term continuous-flow ZVI decolorization column demonstrated that continuous-flow ZVI decolorization is feasible. However, column porosity losses and a shift of reaction kinetics occur in long-term column operation, leading to a decrease in column decolorization efficiency. ZVI decolorization of RB4 was successfully described with a pseudo first-order or a site saturation model.

(Omar et al., 2011) the inhibition effect of methylene blue dye (MBD) on the corrosion of mild steel in 0.5 M sulphuric acid solution at 30°C was studied by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. The results show that MBD is an excellent inhibitor even with very low concentration, and the adsorption of methylene blue dye (MBD) on the mild steel surface obeys Langmuir adsorption isotherm. Potentiodynamic polarization curves reveal that MBD behaves as a mixed-type inhibitor. EIS spectra exhibit one capacitive loop and confirm the inhibitive ability. Some thermodynamic functions of dissolution and adsorption processes were also determined. The obtained results indicated that MBD is chemically adsorbed on the steel surface.

2. Materials and Methods

2.1 Adsorbate Material

Methylene blue (MB) dye was chosen in this study because of its known strong adsorption onto solids (Chongrak et al., 1998), and is often serves as a model compound for removing organic contaminants and colored bodies from aqueous solutions. Methylene blue which is the most commonly used material for dyeing cotton, wood, and silk, is a basic cationic dye heterocyclic aromatic chemical compound with (C₁₆H₁₈N₃ClS) as molecular formula and a molecular weight of 373.91 g/mol (Rastogi et al., 2008).

2.2 Adsorbent Material

iron filings used for this study was composed of commercial iron particles obtained from a peerless metal powder and abrasive workshop, where cutlasses and knives are sharpened, and iron materials are made smooth. The mesh size of iron filings used in the study was of (0.5-1.4 mm) .

2.3 Preparation of the Stock Solution

Stock solution of methylene blue (1000 mg/l) and diluted to the required concentration of (100 mg/l) for calibration purposes according to the following equation:

$$(m * v)_1 = (m * v)_2 \quad (1)$$

The pH of the prepared solutions for both batch and column experiments was equal to 5 based on the recommendation of (Noubactep, 2009). Adsorption experiments were carried out at temperature of 25±5 °C.

2.4 Calibration Curve

Table1: Standard samples and absorbency for MB Dye

Concentration (mg/l)	Absorbency
5	0.4905
10	1.1366
15	1.6536
20	2.4948
25	3.1549
30	3.5228

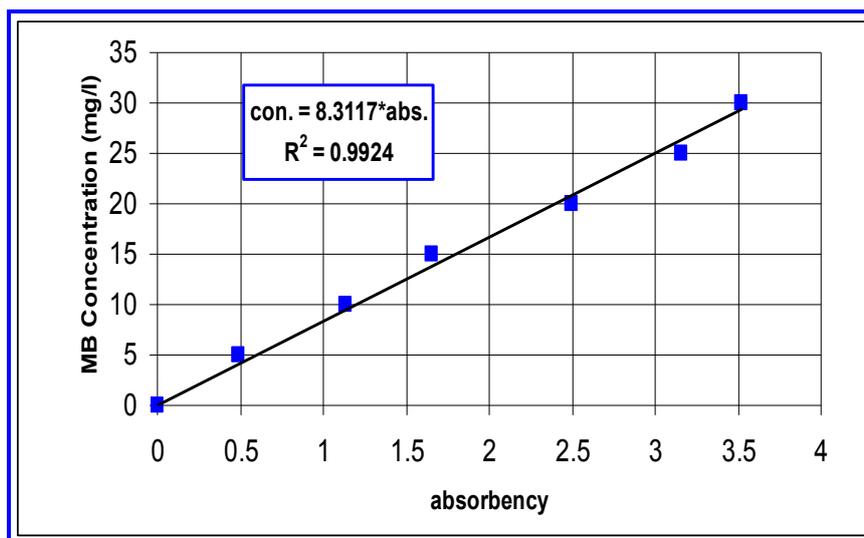


Figure 1: The calibration curve of UV spectrophotometer at ($\lambda_{max}=664nm$).

2.5 Experimental procedure for Batch Experiments

For isotherm studies, accurately different masses (0.3, 0.6, 0.9, 1.2, 1.5, 1.8, and 2.1) gm of adsorbent (treated and untreated iron filings) with the particle size of (0.5-1.4 mm) mixed with 100 ml of MB solution with initial concentration of 100 mg/l. The whole set was then placed on a Wrist shaker at 25°C for 150 min. which is more than sufficient time to reach equilibrium. The pH of the solutions was equal to 5. At the end of the equilibrium period, samples were filtered using Whatmann No.1 filter paper in order to minimize the interference of the iron filings fines with the analysis. Percent removal (R%) was evaluated from the following equation:

$$R\% = \frac{(C_i - C_e)}{C_i} * 100 \quad (2)$$

The concentrations of MB in the solutions before and after adsorption were determined using a double beam UV-visible spectrophotometer (UV 1600 PC Shimadzu) at 664 nm wavelength. The amount of adsorption at equilibrium, q_e (mg/g), was calculated by the following equation (Mahir et al., 2004):

$$q_e = (C_o - C_e)V/W \quad (3)$$

Where C_o and C_e (mg/l) are the liquid phase concentrations of dye at the initial and equilibrium conditions, respectively. V is the volume of the solution (L) and W is the mass of dry adsorbent used (gm).

Equilibrium isotherm treated and untreated iron filings

Table (2) Equilibrium isotherm for untreated iron filings at (Co = 100 mg/l , PH=5, Temp.=25±5°C, Shaking time=150 min., V=0.1L)

W (gm)	Ce (mg/l)	qe (mg/g)	Removal%
0.3	26.6	24.47	73.4
0.6	7.8	15.37	92.2
0.9	2.5	10.83	97.5
1.2	2	8.17	98.00
1.5	1.6	6.56	98.4
1.8	1.19	5.49	98.81
2.1	0.99	4.71	99.01

Table (3) Equilibrium isotherm for treated iron filings at (Co = 100 mg/l , PH=5, Temp.=25±5°C, Shaking time=150 min., V=0.1L)

W (gm)	Ce (mg/l)	qe (mg/g)	Removal%
0.3	24.9	25.03	75.1
0.6	5.5	15.75	94.5
0.9	1.8	10.91	98.2
1.2	1.3	8.23	98.7
1.5	1.01	6.59	98.99
1.8	0.76	5.51	99.24
2.1	0.45	4.74	99.55

3.Results and Discussion

3.1 Estimation of the Adsorption Isotherm Constants for Untreated and Treated Iron Filings System

The Langmuir, Freundlich, and the equilibrium adsorption isotherms of methylene blue adsorption onto iron filings of size (0.5-1.4 mm) at 25°C and pH=5 are shown in Figs.(2), (3) respectively for untreated iron filings and (4), (5) respectively for treated iron filings. The parameters for each model were obtained and presented in Table (2).

3.1.1 Untreated iron filings

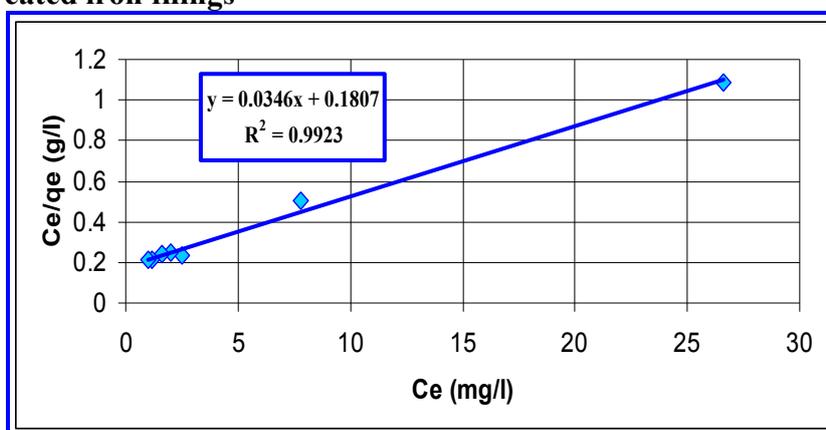


Figure 2: Langmuir adsorption Isotherm of MB onto untreated iron filing at 25°C and pH=5

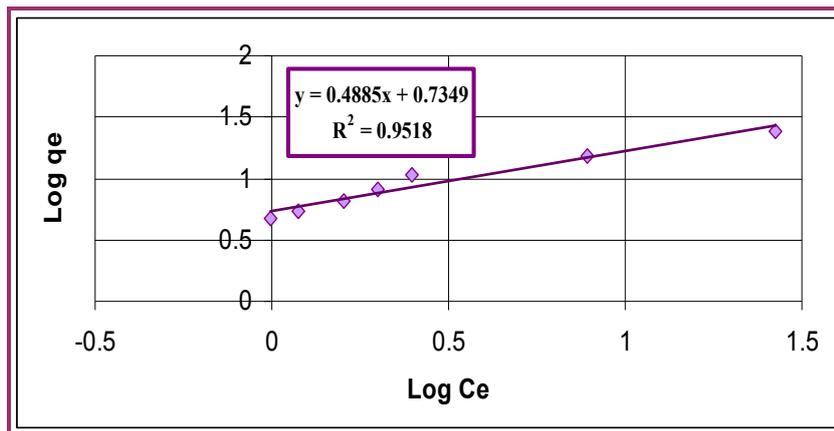


Figure 3: Freundlich adsorption Isotherm of MB onto untreated iron filings at 25°C and pH=5

3.1.2 Treated iron filings

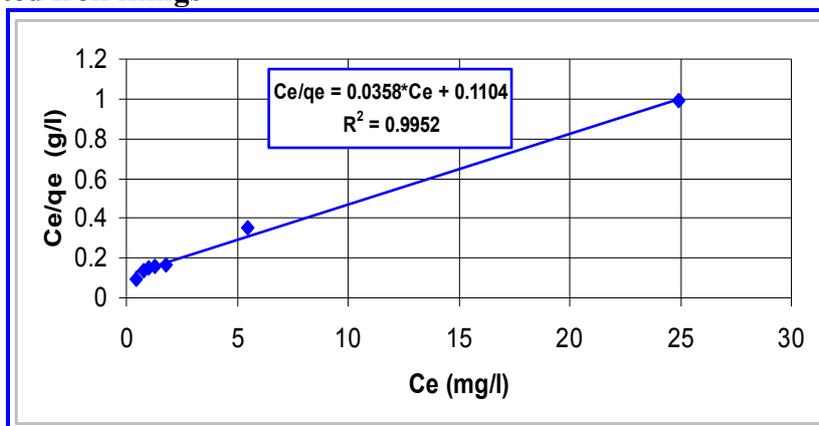


Figure 4: Langmuir adsorption Isotherm of MB onto treated iron filings at 25°C and pH=5

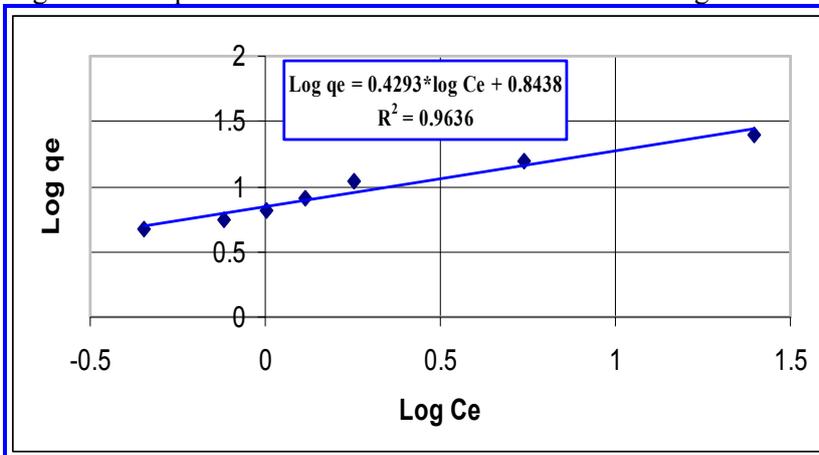


Figure 5: Freundlich adsorption Isotherm of MB onto treated iron filings at 25°C and pH=5

3.2 Adsorption isotherm

Adsorption equilibrium data of MB dye was fitted to the Langmuir and Freundlich isotherm models. These isotherms are expressed by the following equations

$$q_e = (q_0 K_L C_e) / (1 + K_L C_e) \quad (4)$$

$$q_e = K_f C_e^{1/n} \quad (5)$$

where; q_e : Amount adsorbed per unit weight of adsorbent at equilibrium (mg/g), (mol/g)

C_e : Equilibrium concentration of adsorbate in solution after adsorption (mg/g), (mol/L)

K_f : Empirical Freundlich constant or capacity factor (mg/g), (mol/g)

$1/n$: Freundlich exponent

q_0 : Empirical Langmuir constant which represents maximum adsorption capacity (mg/g), (mol/g)

K_L : Empirical Langmuir constant (L/mg), (L/mol)

Eq. (4) and (5) are frequently used in the linear form after rearrangement. The experimental data was also correlated by both linearised Langmuir and Freundlich equations (Eq.4 and Eq.5). For MB dye the Langmuir and Freundlich isotherm constant are summarized in table 1 for both treated and untreated iron filings.

Table 4: Isotherm constants for MB dye Adsorption on treated and untreated iron filings

Model	Adsorbent			
	Untreated iron filings		Treated Iron filings	
	Parameter	Value	Parameter	Value
Langmuir (eq. (3-3))	q_0 (mg/g)	28.90	q_0 (mg/g)	27.933
	K_L (l/mg)	0.1915	K_L (l/mg)	0.324
	R_L	0.049	R_L	0.029
	R^2	0.9923	R^2	0.9952
Freundlich (eq. (3-1))	KF (mg/g(l/mg) ^{1/n})	5.431	KF (mg/g(l/mg) ^{1/n})	6.979
	$1/n$	0.489	$1/n$	0.429
	R^2	0.9518	R^2	0.9636

- In order to assess the different isotherms and their ability to correlate with experimental results, the coefficient of determination (R^2) was employed to ascertain the fit of each isotherm with experimental data. From Table (4), the coefficient of determination values were higher for Langmuir than for Freundlich. This indicates that the Langmuir isotherm is clearly the better fitting isotherm for the experimental data. Conformation of the experimental data with Langmuir isotherm model indicates the homogeneous nature of the surfaces of the adsorbents used.
- The value for the maximum adsorption capacities of (24.47 mg/g) and (25.03 mg/g) and the value of (removal %) of (73.4 %) and (75.1 %) exhibited by untreated iron filings and treated iron filings respectively. It is clear that iron filings is a very comparable material for the commercial activated carbon.
- The values of (R_L) were found to be (0.049) and (0.029) for untreated iron filings and treated iron filings respectively. This gain confirmed that the Langmuir isotherm was favorable for adsorption of MB onto the adsorbents used in this study.

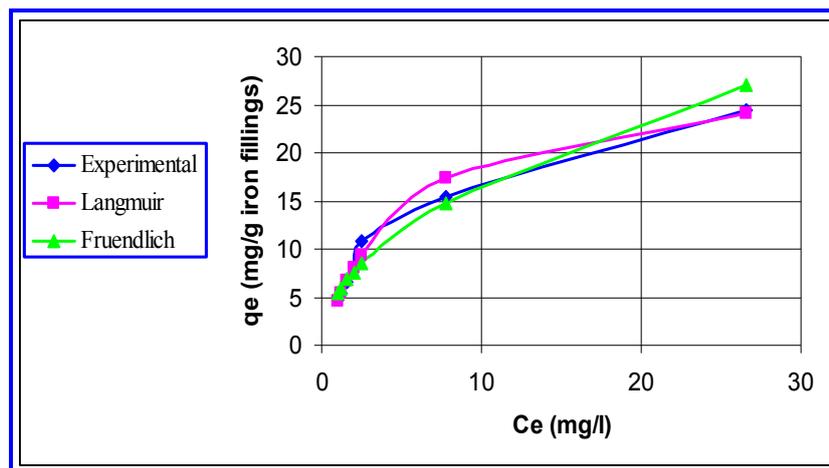


Figure (6) Equilibrium adsorption Isotherm of MB onto untreated iron filings at 25°C and pH=5

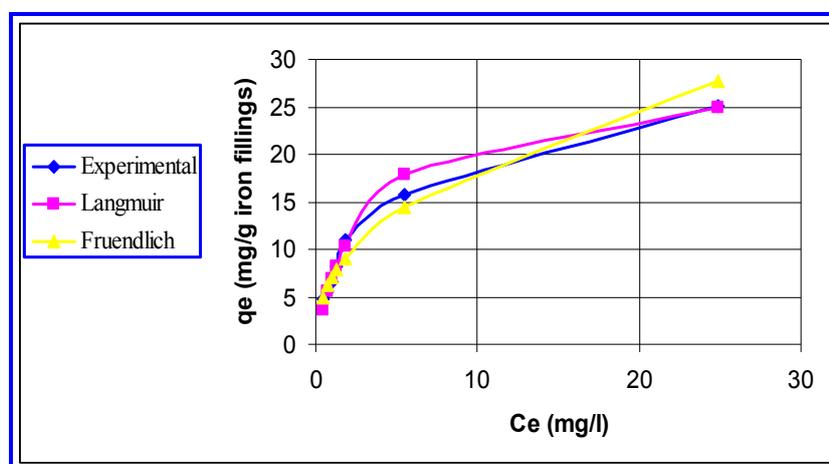


Figure (7) Equilibrium adsorption Isotherm of MB onto treated iron filings at 25°C and pH=5.

3.3 Column Experiments and Breakthrough Curves

The performance of a fixed-bed column was described through the concept of the breakthrough curve. The time for breakthrough appearance and the shape of the breakthrough curve are very important characteristics for determining the operation and the dynamic response of an adsorption column. The loading behavior of MB to be adsorbed from solution in a fixed-bed is usually expressed in term of C/C_0 as a function of time or volume of the effluent for a given bed height, giving a breakthrough curve.

3.3.1 Effect of Initial Dye Concentration

The effect of influent MB concentration on the shape of the breakthrough curves was investigated by varying the initial MB concentration between (15, 30, 40, and 50) mg/l with constant iron filings bed height of 0.1m, solution pH of 5 and flow rate of $3.33 \times 10^{-6} \text{ m}^3/\text{s}$.

The breakthrough curves of the above experiments were plotted in Fig.(8) for untreated iron filings and (9) for treated iron filings . It is clear that the breakthrough time decreased with increasing influent MB concentration. At lower influent MB concentrations, breakthrough curves were dispersed and breakthrough occurred slowly. As influent concentration increased, sharper breakthrough curves were obtained. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time. This can be explained by the fact that more adsorption sites were being covered as the MB concentration increases.

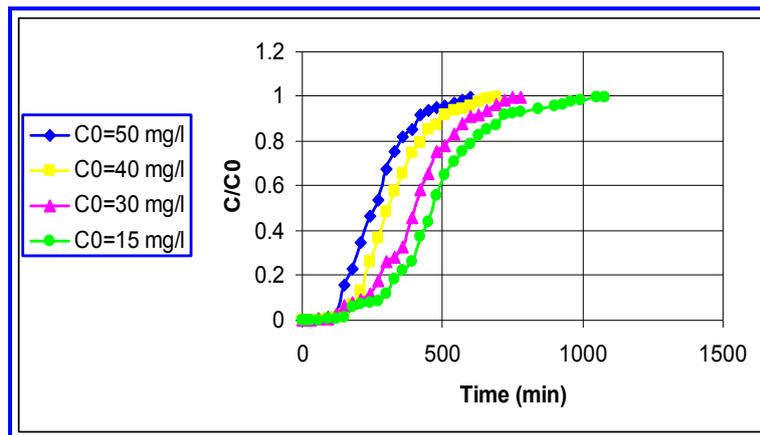


Figure (8) The experimental breakthrough data for adsorption of MB onto untreated iron filings at different initial concentrations, $Q=3.33 \times 10^{-6} \text{ m}^3/\text{s}$, $L=0.1 \text{ m}$, $\text{pH}=5$.

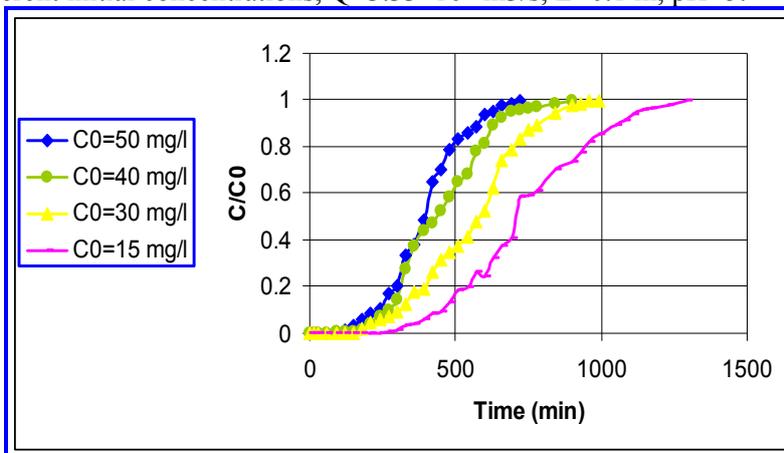


Figure (9) The experimental breakthrough data for adsorption of MB onto treated iron filings at different initial concentrations, $Q=3.33 \times 10^{-6} \text{ m}^3/\text{s}$, $L=0.1 \text{ m}$, $\text{pH}=5$.

3.3.2 Effects of Adsorbent Bed Depth

Figure (10) for untreated iron filings and (11) for treated iron filings shows the breakthrough curves obtained for MB adsorption on the iron filings for four different iron filings bed depths of 0.05, 0.1, 0.15, and 0.2 m, at a constant flow rate of $3.33 \times 10^{-6} \text{ m}^3/\text{sec}$, pH of 5 and MB initial concentration of 50 mg/l.

Both the breakthrough and exhaustion time increased with increasing the bed depth. A higher MB uptake was also expected at a higher bed depth due to the increase in the specific surface area of the iron filings, which provided more binding sites for the dye to adsorb. Since the rate of adsorption is proportional to adsorbent surface area, then total quantity of solute removed from solution at any period of time will increase with increasing bed depth.

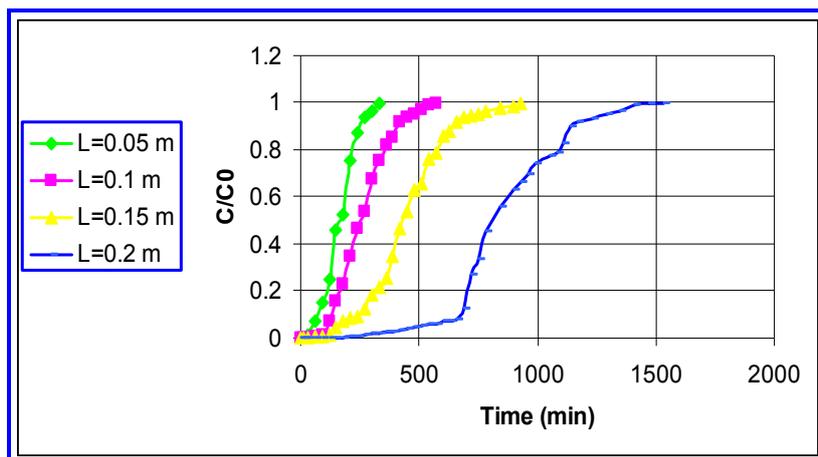


Figure (10) The experimental breakthrough data for adsorption of MB onto untreated iron filings at different bed depths, $Q=3.33 \times 10^{-6} \text{ m}^3/\text{s}$, $C_0=50 \text{ mg/l}$, $\text{pH}=5$

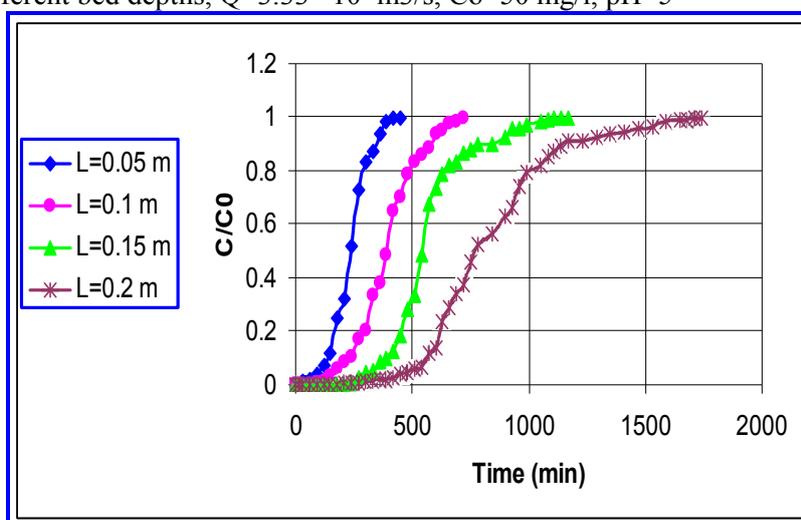


Figure (11) The experimental breakthrough data for adsorption of MB onto treated iron filings at different bed depths, $Q=3.33 \times 10^{-6} \text{ m}^3/\text{s}$, $C_0=50 \text{ mg/l}$, $\text{pH}=5$

3.3.3 Effect of Solution Flow Rate

To investigate the effect of flow rate on the adsorption of MB using iron filings bed, the flow rate of the influent MB solution varied (2.2×10^{-6} , 3.33×10^{-6} , 4.17×10^{-6} , and 5.83×10^{-6}) m^3/sec with constant bed depth of 0.1m, initial methylene blue (MB) concentration of 50 mg/l, and pH solution of 5 as shown by the breakthrough curves in Fig. (12) for untreated iron filings and Fig. (13) for treated iron filings .

It can be seen that the breakthrough generally occurred faster with a higher flow rate. This is due to decreased contact time between the dye and the sorbent at higher flow rate, which results in lower bed utilization. Breakthrough time reaching saturation was increased significantly with a decrease in the flow rate. At a low rate of influent, MB had more time to be in contact with adsorbent, which resulted in a greater removal of MB molecules in column.

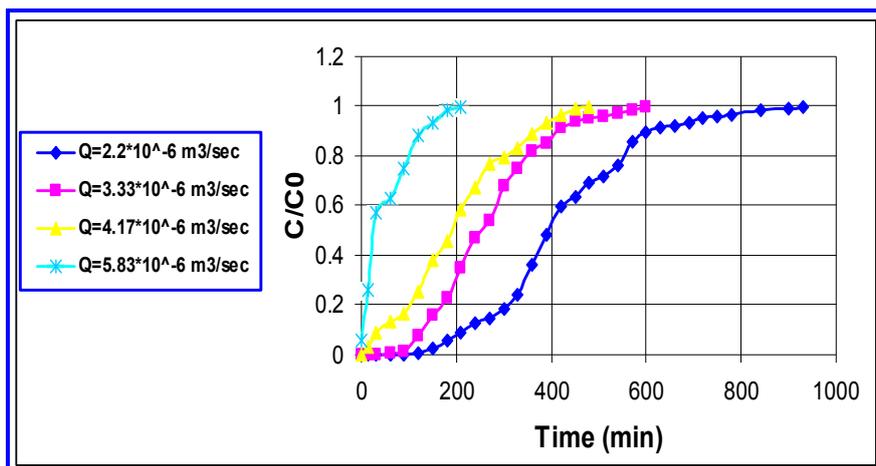


Figure (12) The experimental breakthrough data for adsorption of MB onto untreated iron filings at different flow rates, $L=0.1$ m, $C_0=50$ mg/l, $pH=5$

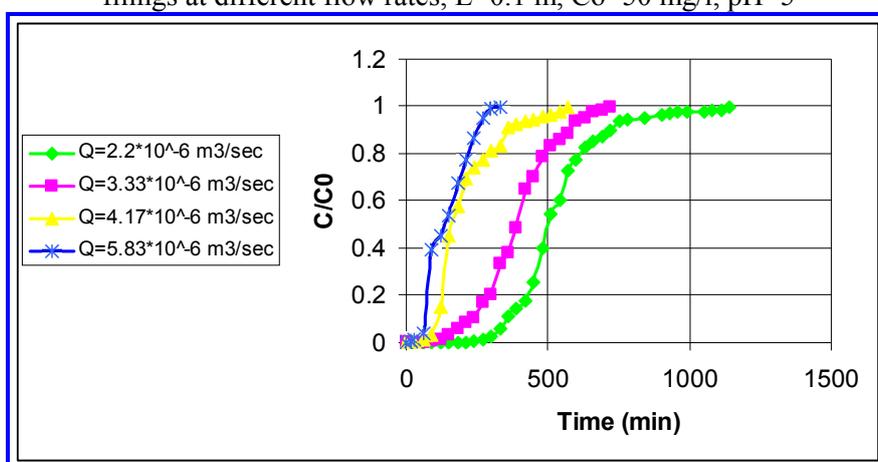


Figure (13) The experimental breakthrough data for adsorption of MB onto treated iron filings at different flow rates, $L=0.1$ m, $C_0=50$ mg/l, $pH=5$

Conclusions

Industrial waste materials (iron filings) appear as effective and cheap adsorbents for removal of MB dye from aqueous solution. Moreover, the materials could also be used for purification of water. The removal of MB dye from effluent is important to many countries of the world both environmentally and for water re-use. Treated and untreated iron filings have a very low economical value, can be an effective adsorbents for MB dye removal from aqueous system for environmental cleaning purposes.

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