



Comparison between traditional and low cost materials to remove residues of Methylene Blue dye from aqueous solutions

Mounes, H. A. M and Reham, A. A.

Department of Limnology, Central laboratory for Aquaculture Research, Abbassa, Agricultural Research Center, Egypt.

Correspondence: E-mail: HMOANS80@hotmail.com

Received: March. 16, 2020; Accepted: May.20, 2020 published: 2020 Vol.10 (4):39-56

ABSTRACT

Dyes considered harmful pollutants that represent a serious threat to the aquatic environment, which require expensive materials to get rid of. It is consequently producing a critical situation that requires the availability of all efforts to solve, especially in conditions of water scarcity expected in the near future. Hence, the urgent need, to use cheap and eco-friendly adsorbents instead of traditional materials to purify and reuse water several times. It becomes one of the most important motives for conducting this research. This experiment was conducted, to compare the effect of using low cost adsorbent material against a traditional one with various dosages and various contacting periods at an ambient conditions of pH and temperature that are suitable for aquatic animals to remove Methylene Blue (MB) dye residues from water. The highest removal efficiency percentages of 0.1 g chitosan and silica gel toward 100 mg/l of MB dye were 93.1 % and 86.9 % respectively, after 60 minutes of contacting period. The equilibrium adsorption behavior data were fitted well to Langmuir and Freundlich adsorption isotherm models. Based on the achieved results, we recommend that the use of chitosan in purifying the aquatic environment from some organic pollutants such as dyes, which are widely used in many industries, because of the advantages of chitosan, which are low cost, wide availability and completely safe for the environment.

Key words: Methylene Blue, Dye, Chitosan and Silica gel

Introduction

Synthetic dyes are extensively used by many industries including dye houses, pulp and paper printers, textile dyers, color photography, chemicals, metallurgy, leather, paint, and coatings industry, food, packaging, pharmacy, plastics and as additives in petroleum products consume considerable amounts of water, and chemical reagents during processing, dyeing and finishing operations (**Zollinger, 1991; Selvam *et al.*, 2003**). The textile industry (54 %) discharges the largest amount of dye wastewater, contributing to more than half of the existing dye effluents observed in the environment worldwide (**Katheresan *et al.*, 2018**). The effluents of these industries are composed of non-biologically oxidisable organic components because of the molecular size and

structure of the dyestuffs which can cause the disposal of these wastes into the environment can be extremely deleterious, which affect photosynthetic activity in aquatic systems by reducing light penetration (O'Mahony *et al.*, 2002). In Egypt, the problem of dye removal from industries wastewater has been considered of great interest, which requires the use of conventional methods for treating water, to meet the increasing demand for water for various uses. Based on that, a national effort has been launched to deal with this problem using natural, local adsorbents. Due to the low biodegradability of dyes, a conventional biological treatment process is not very effective in treating a dye wastewater. It is usually treated by physical and /or chemical methods (Garg *et al.*, 2003). Although these treatment methods are efficient, they are quite expensive and have operational problems (Garg *et al.*, 2003; Kapdan *et al.*, 2000). In the past three decades, numerous approaches have been studied for the development of cheaper, ecofriendly and more effective biosorbents capable to eliminate pollutants present in synthetic solutions contaminated with a single type of pollutant (Piaskowski *et al.*, 2018). Adsorption is a physico-chemical process which considers an ideal option for de-colorization, which is evidenced of the effectiveness of adsorption for various dye types (Kapdan *et al.*, 2000; Porter *et al.*, 1999) and offers great potential for treating effluents containing undesirable components such as color, phenols, detergents, and other toxic or non-biodegradable and render them safe and reusable (Gupta *et al.*, 1987; 1988a; 1988b; Annadurai and Krishnan 1996 and El-Sherbiny *et al.*, 2009).

Methylene blue, a basic dye, is an important cationic heterocyclic aromatic chemical compound that releases aromatic amines (e.g., benzidine, methylene) and is a potential carcinogen (Boeningo, 1994). It interferes with a diversity of different fields, including the dyeing of silk, leather, paper, wool, and cotton, and the production of ink and copying paper, as well as the quality control test of concrete and mortar (Berneth, 2003). The choice of methylene blue as an adsorbent is due to its known strong adsorption onto solids (Özer and Dursun, 2007). So, it has been used as an effective therapeutic and antibacterial to protect newly laid fish eggs from being infected by fungus or bacteria in the aquaculture industry (Tacon and Forster, 2003). Several workers have examined toxicity of dyes in waters on fish mortality (Rana and Raizada, 1999; Karanjkar *et al.*, 2000) and sensitivity of erythrocytes due to cell membrane permeability which may alter their shape or even destroy them completely (Sharma *et al.*, 2007). Methylene blue has been used extensively as

fungicides in fish culture to treat fungi diseases. It is used to treat fungal infections of fish at the early stages (**Drolet et al., 2004**). It is effective against some external protozoan such as *Chilodonella*, *Costia*, and fungal disease, *Ichthyophthirius* (**Drolet et al., 2004**), this compound as an oxygen transporter, converts methemoglobin to a normal oxygen-carrying component of fish blood, hemoglobin (**Anderson 2002**). In addition, over the past two decades, there have been concerns about the potential toxicity of dyes and of their precursors, which poses a serious risk to aquatic living organisms (**Liu and Liptak 2000; Khalaf 2016; Katheresan et al. 2018**). It has been reported that methylene blue has interference with oxidation reduction processes in fish and other aquatic organisms (**Anderson 2002**). Due to repeated and persistent applications of methylene blue in fish ponds when treating for infections and diseases, large quantities find their ways into the water bodies affect treatment. Many studies have been made on the possibility of adsorbents using mineral absorbents (activated carbon, peat, chitin, rice husk, soy meal hull, and agro wastes). However, the adsorption capacity of the adsorbents is not very effective to improve adsorption performance and new adsorbents are still under development (**Hasan, 2008**). It is well known that chitosan has widely been used in the preparation of various bio-medical products. Chitosan is easily prepared from chitin by deacetylating its acetamide groups with a strongly alkaline solution (**Annadurai et al., 2012**). This is the most abundant biopolymer in nature after cellulose. This biodegradable and biocompatible biopolymer is interesting because of its wide range of applications (**Kumar, 2000**). One of the most important applications is based on its ability to strongly adsorb a wide range of pollutants, including metal ions and organic dyes molecules due to the high proportions of amino functions. The deacetylated amino groups in chitosan can be protonated and the polycationic properties of the polymer are expected to contribute to the charged interactions with a model dye, methylene blue, which is a basic dye.

Among numerous absorbent, silica gel deserves particular attention, considering its high thermal and chemical stability, controlled porosity, swelling resistance, relative rapidity in reaching equilibrium and high surface area (**Donia et al., 2009** and **Cestari et al., 2009**).

The present work aims to investigate the efficiency of Chitosan (as a low cost natural substance) against Silica gel (a traditional material) with water pH and temperature suitable for fish farming for removing

methylene blue dye as an organic pollutant from water which in turn could be used for aquaculture and other purposes.

Materials and Methods

This work was conducted in Limnology Department, Central Laboratory for Aquaculture Research, Abbassa, Abo-Hammad, Sharkia Governorate, Agricultural Research Center, Egypt, to investigate the efficiency of Chitosan (as a low cost natural substance) against Silica gel (as a traditional material) with water pH suitable in fish farming (7.2) for removing methylene blue dye as an organic pollutant from water which in turn could be used in aquaculture.

Methylene blue (MB) Preparation and Determination:

In this experiment, Methylene blue (MB) dye (Central Drug House (P) Ltd. India) was used without further purification (characterization of MB dye present in Table 1). The dye solution was prepared by dissolving MB powder in distilled water (Distilled water prepared by using a double distillation unit) to prevent and minimize possible interference. 1000 mg/l stock solution of the dye was prepared by dissolving 1 g of MB dye in 1000 ml distilled water, where the dye was stirred until it was completely dissolved. Then, the experimental solutions were prepared by diluting definite volumes of the stock solution to get the desired concentrations. A standard curve of the investigated dye was prepared through a series of different prepared dye concentrations while distilled water was used as a blank (0 mg / l). Absorbance against each concentration was determined by using a UV-visible spectrophotometer (Unico UV visible spectrophotometer) at a wavelength of 664 nm, and a standard curve was plotted in linear form. Then the absorbance readings of the blank and each standard were recorded. The residues of the investigated dye in different samples after treating the prepared aqueous solution with the two investigated adsorbents were determined at different contact periods.

Table (1) Properties of Methylene Blue dye Solution:

Chemical formula	$C_{16}H_{18}ClN_3S$
Molecular weight	319.9 g / mol
Melting point	> 190°C
Density	1 g / ml
Lambda Max.	664 nm

Chitosan preparation method:

The Chitosan, which used in this experiment, was excreted from shrimp wastes (heads and scales), which were collected from El-Obour local fish market, Qalyubia Governorate, Egypt. The wastes were packed

in plastic bags and stored at -20°C until use. The shrimp wastes were washed, dried at 70°C overnight, grinded, then sifted to obtain a coarse powder at the required particle size, which is 60 mesh, and stored in a dry place until chitosan was extracted. The chitosan was extracted according to the method reported by **Kurita (2001)**, and then preserved in plastic stoppered bottles, which were kept in desiccators to reduce contact with humidity until use. The chemical structure of Chitosan is shown in Figure (1)

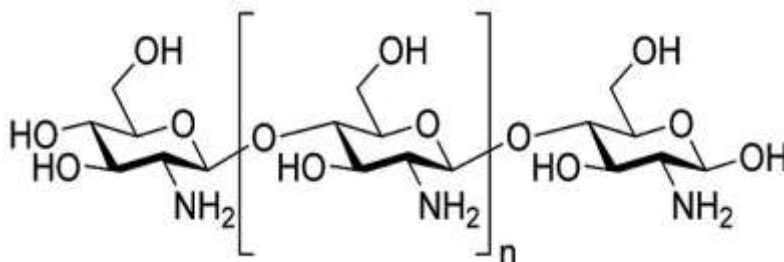


Fig. (1). The structures of Chitosan

Chitosan characterization:

Chitosan powder was characterized according to Molecular weight (Mw), Degree of Deacetylation (% DDA), Solubility (S), Total nitrogen (% TN), and Ash Content (AC) as shown in Table (2).

Table (2). Functional properties of chitosan extracted from shrimp wastes.

Parameters	Chitosan
Molecular weight (M.W)	1.62×10^4 # 16200
Degree of Deacetylation (DDA)	94 %
Solubility	63 %
Total nitrogen (T. N) percentage	2.76 %
Ash content percentage	3.06 %

Effect of Adsorbent dosage and contact period:

To determine the optimum dose of each of the investigated adsorbent materials (CH and SG), different dosages of each of them (0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09 and 0.1 g) were added separately to 100 ml of 100 mg / l MB solutions. The tested solutions were stirred at room temperature for different periods. The samples were taken at different contact periods (2, 5, 10, 20, 40, 60, and 80 minutes) in the case of CH, while in the case of SG the contact periods were (2, 5, and 10

minutes). All samples were taken with two replicates. Samples were filtered and the dye residues in each sample were determined with UV-VIS Spectrophotometer at a wavelength of 664 nm, and then the removal efficiency of each adsorbent substance at different tested contact periods was calculated.

Adsorption isotherm

Isotherm data were analyzed using Langmuir and Freundlich adsorption equations. The two equations contain two adjustable parameters and different constants were generated (**Zubair and AbdelKhader, 2007; Khan, et al., 2005**). The Langmuir and Freundlich parameters were determined and correlation coefficients were calculated.

The Langmuir isotherm in linear form is given as:

$$1/X = 1/X_m \cdot K_l + 1/C + 1/X_m$$

Where:

X = is the amount of the investigated dye adsorbed per gram of the adsorbent.

C = is the equilibrium concentration.

X_m = is a constant which is refer to the monolayer capacity.

K_l = is a constant which is a measure of adsorption binding energy.

The linear form of Freundlich isotherm is:

$$\text{Log } x = \text{Log } K + 1/n \text{ Log } C$$

Where:

K = is a constant which is a measure of adsorptive capacity.

1/n = is a constant refer to adsorption intensity. (**Uddin, et al., 2007; Khan, et al., 2005**). All the constants are specific to test conditions and the adsorbent type. (**Uddin, et al., 2007**).

The plots of 1/x versus 1/C and Log X versus Log C were made to test the Langmuir and Freundlich adsorption models respectively. In each case related respective constants were determined.

Removal efficiency %

Removal efficiency percentage of different investigated adsorbents at different contact periods as well as with different initial dye concentrations had been calculated according to the following equation:

Removal efficiency % = (C_i – C_f / C_i) *100 where:

C_i = initial dye concentration

C_f = dye residue in the solution after treatment.

Statistical analysis:

The statistical analysis was applied according to **Steel and Torrie (1980)** data of the frequent samples were analyzed with repeated statement (**SAS, 2009**). For detecting the significant differences among means, Duncan Multiple range test (**Duncan's, 1955**) was used.

Results and Discussion

Obtained results revealed that both examined adsorbents (Chitosan and Silica gel) have proven ability to remove the investigated dye (methylene blue, as an organic pollutant) from aqueous solutions, with greater preference and efficacy for the less expensive adsorbent (Chitosan) compared to the conventional adsorbent (Silica gel). This effectiveness could be attributed to their chemical composition. Chitosan had attention as an effective biosorbent due to: its (1) high hydrophilicity of the polymer due to hydroxyl groups of glucose units; (2) presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups); (3) the high chemical reactivity of these groups; (4) the flexible structure of the polymer chain (**Crini, 2005** and **Bhatnagar and Sillanpää 2009**).

MB dye residues at different contact periods by different dosages of both adsorbents:

As shown in Tables (3 and 4), MB residues decreased rapidly in the investigated solution within the first 2 minutes; and then decreased gradually with the increase of the contacting period with both investigated adsorbents per 100 ml of the solution; until 80 minutes in case of Chitosan and 10 minutes in case of Silica gel. Silica gel has high surface area, tunable and uniform pores structure, high pore volume, ordered pore structure, and mechanical stability which make it binding fast with dye particles more than chitosan (**Yan et al. 2006a** and **Chen et al. 2012**).

As obtained from Tables (3 and 4), the lowest residue of MB dye in the case of Chitosan adsorbent was 6.9 (mg / l) on dose 0.1 g after 60 and 80 minutes, while the highest one was 43.7 (mg / l) on dose 0.02 g after 2 minutes and the lowest record of Mb dye residue in case of Silica gel adsorbent was 13.1 (mg / l) on dose 0.1g after 10 minutes, while the highest one was 28.6 (mg / l) on dose 0.05 g after 2 minutes of treating.

Table (3). MB residues at different contact periods by different concentrations of Chitosan adsorbent

Adsorbent Conc. (mg / l)	Contact Time (minutes)							
	0	2	5	10	20	40	60	80
0.01	100 ^{NS} ± 0.2	40.2 ^b ± 2.5	32.4 ^a ± 0.5	29.1 ^a ± 1.2	27 ^a ± 0.9	23.6 ^a ± 1.4	17.6 ^a ± 2.8	17.6 ^a ± 2.8
0.02	100 ± 0.2	43.7 ^a ± 1.8	29.2 ^b ± 5.1	26.5 ^b ± 7.3	22.9 ^b ± 8.6	21.3 ^b ± 7.2	13.1 ^b ± 2.5	10.1 ^b ± 0.5
0.03	100 ± 0.2	37.6 ^c ± 5.2	28.2 ^{bc} ± 3.3	23.6 ^c ± 6.4	17.6 ^{cd} ± 7	11 ^c ± 1.7	10 ^c ± 1.3	9.2 ^c ± 0.5
0.04	100 ± 0.2	16.3 ^e ± 0.3	15.1 ^f ± 0.5	12.8 ^f ± 0.2	11.2 ^g ± 0.3	9.3 ^d ± 0.08	7.9 ^e ± 0.4	7.9 ^d ± ±0.4
0.05	100 ± 0.2	29.4 ^f ± 0.9	23.7 ^{de} ± 2.7	20.8 ^d ± 0.4	16.9 ^d ± 1.6	11.6 ^c ± 0.5	9.3 ^c ± 0.3	9.1 ^c ± ±0.2
0.06	100 ± 0.2	30.3 ^{ef} ± 5.3	19.9 ^e ± 2.7	19.3 ^e ± 2.5	12.9 ^{ef} ± 1.1	11.7 ^c ± 0.2	9.9 ^c ± 0.2	8.8 ^{cd} ± 0.08
0.07	100 ± 0.2	31.6 ^c ± 2.6	29.3 ^b ± 0.6	19.3 ^e ± 0.3	12.1 ^f ± 1.2	8.9 ^{de} ± 0.2	8.9 ^d ± 0.2	8.9 ^{cd} ± 0.2
0.08	100 ± 0.2	35.3 ^d ± 1.9	32.2 ^a ± 0.4	20.7 ^d ± 0.6	13.6 ^e ± 1.3	8.3 ^c ± 1.1	7.3 ^c ± 0.6	7.3 ^d ± 0.6
0.09	100 ± 0.2	29.9 ^f ± 1	24.8 ^d ± 0.2	19.3 ^e ± ±0.4	12.7 ^{ef} ± ±0.2	9.3 ^d ± 1.2	9.3 ^c ± 1.2	9.3 ^c ± 1.2
0.1	100 ± 0.2	28.9 ^g ± 1.4	27.2 ^c ± 1.4	20.4 ^d ± 1.5	18.2 ^c ± 0.5	7.6 ^f ± 0.9	6.9 ^f ± 0.9	6.9 ^{de} ± 0.9

Means in the same column having the same superscript letters are not significantly different ($P < 0.05$)

Table (4). MB residues at different contact periods by different concentrations of Silica gel adsorbent

Adsorbent conc. (mg / l)	Contact Time (minutes)			
	0	2	5	10
0.01	100 ^{NS} ± 0.4	20.8 ^c ± 0.2	20.5 ^b ± 0.08	20.5 ^b ± 0.08
0.02	100 ± 0.4	25.2 ^b ± 0.8	23.6 ^a ± 1.5	23.4 ^a ± 1.5
0.03	100 ± 0.4	24.8 ^b ± 0.5	23.02 ^a ± 1.3	22.8 ^{ab} ± 1.4
0.04	100 ± 0.4	24.9 ^b ± 1.9	17.1 ^c ± 0.08	17.02 ± 0.2
0.05	100 ± 0.4	28.6 ^a ± 0.8	20.6 ^b ± 2	19.7 ^{bc} ± 0.8
0.06	100 ± 0.4	19.3 ^d ± 2	17.9 ^c ± 1.2	17.7 ^c ± 1.2
0.07	100 ± 0.4	18.1 ^c ± 0.9	15.2 ^{de} ± 0.5	15.2 ^d ± 0.4
0.08	100 ± 0.4	19.2 ^d ± 0.7	15.8 ^{de} ± 1.1	15.8 ^d ± 0.9
0.09	100 ± 0.4	17.4 ^{ef} ± 0.4	16.3 ^d ± 0.08	14.9 ^{de} ± 0.2
0.1	100 ± 0.4	16.7 ^f ± 4	13.2 ^e ± 1.6	13.1 ^e ± 1.6

Means in the same column having the same superscript letters are not significantly different ($P < 0.05$).

Those results were in accordance with **Ngadi, *et al.* (2013)**, who mentioned that the adsorption efficiency increased with adsorbent dosage to a specific limit because there was plenty of surface area and more adsorption sites available to interact with the dye molecules provided by the increased adsorbent dosage.

The removal efficiency of different concentrations of both adsorbents on MB dye at different contact periods

As shown in Figs (2 and 3), the 0.1 (g / l) of chitosan achieved the highest efficiency (93.1 %) in removing methyl blue dye residues) from the aqueous solution after 60 minutes, while the maximum removal efficiency % of Silica gel towards MB dye at different adsorbents doses were 86.9 % after 5 minutes contacting period, while the lowest removal efficiencies of Chitosan and Silica gel towards MB dye were 56.3 and 71.4 % at dosage 0.02 and 0.05 after 2 minutes, respectively. These results revealed that adsorbent dosage plays a very vital role in the adsorption process for color removal. Similar results obtained by **Shashikala *et al.*, (2013)**, who reported that the maximum color removal, was obtained at a dosage of 0.1 g chitosan after 30 min of treatment. (**Gaikwad and Misal., 2010**) found that, Silica gel removed 93 % of 25 mg/l and 94.6 % of 12.5 mg/l of MB dye solution respectively.

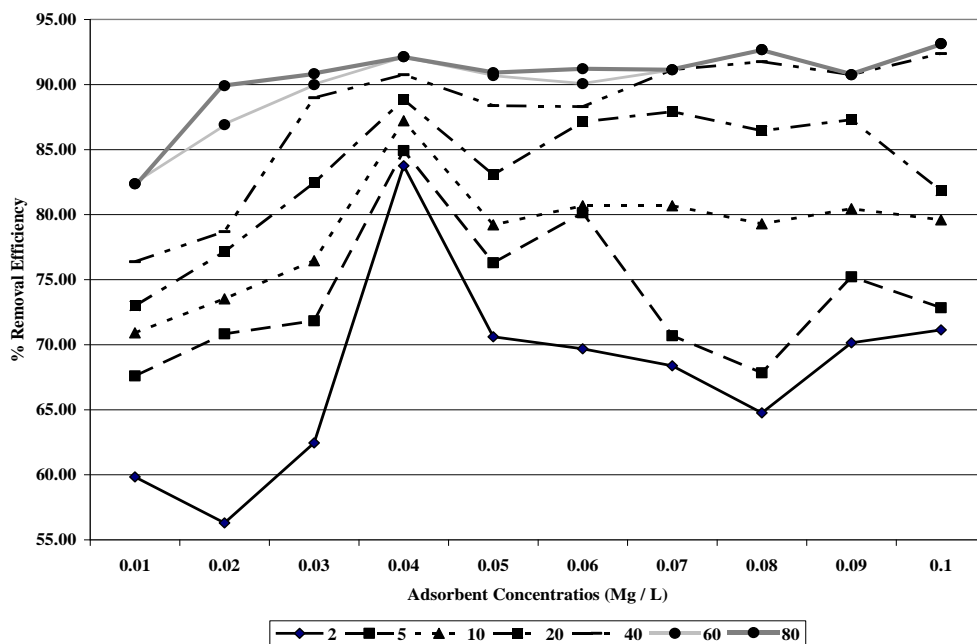


Fig. (2) The effect of Chitosan dosages and contact period on % MB dye removal in water

Several investigations demonstrated that although, increasing adsorbent dosage leads to a corresponding increase of active sites for adsorption, but this phenomenon may not lead to high adsorption capacity and adsorption efficiency of adsorbent due to that the overload of the adsorbent area is decreased (Verma and Mishra, 2010; Lopes *et al.* 2004).

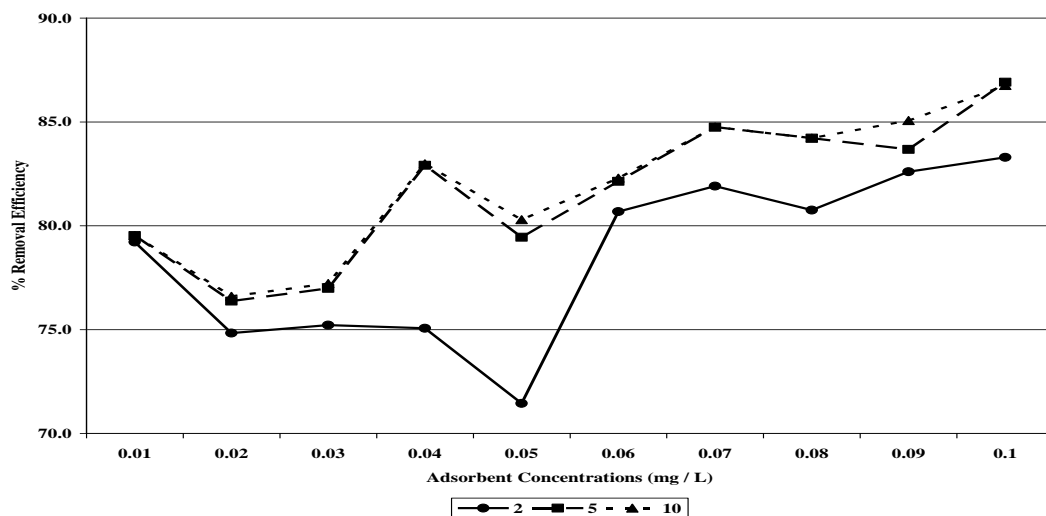


Fig. (3) The effect of Silica gel dosages and contact period on % MB dye removal in water

The adsorption isotherms:

Adsorption isotherm describes how the adsorbate interacts with adsorbents and which are critical and optimizing the use of adsorbents. Thus, the correlation of equilibrium data by either theoretical or empirical equations is essential to the practical design and operation of the adsorptions system. As shown in Tables (5 and 6) the adsorption isotherms data were fitted to both the Langmuir and Freundlich isotherm equations for Chitosan and Silica gel, respectively. The typical graphical representations of the linearized plots are shown in Figures 4 and 5 for adsorption of MB on CH and SG, respectively, according to Langmuir equation; as well as in Figures 6 and 7 for adsorption of MB on CH and SG, respectively, according to Freundlich equation. The correlation coefficient values for CH and SG were 0.9818 and 0.9688 for Langmuir equation, respectively, while values for CH and SG were 0.9145 and 0.8908 for Freundlich equation, respectively. The previous results were in disagreement with those reported by (Shashikala *et al.*, 2013).

Table (5). Isothermal data for Chitosan as an Adsorbent.

C (Dye conc. mg / l)	17.6	10.1	9.2	7.9	9.1	8.8	8.9	7.3	9.3	6.9
Dye removed (mg / l)	82.4	89.9	90.8	92.1	90.9	91.2	91.1	92.7	90.7	93.1
Chitosan dose (g / l)	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1
X (dye removed / g of adsorbent (mg / g))	8240	4495	3026.7	2302.5	1818	1520	1301.4	1158.8	1007.8	931
1/C	0.06	0.09	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2
1/X	0.0001	0.0002	0.0003	0.0004	0.0006	0.0007	0.0008	0.0009	0.001	0.001
Log C	1.25	1	0.96	0.9	0.96	0.94	0.95	0.86	0.97	0.84
Log X	3.92	3.65	3.48	3.36	3.26	3.18	3.11	3.06	3	2.97

Table (6). Isothermal data for Silica gel as an Adsorbent.

C (Dye conc. mg / l)	20.5	23.4	22.8	17.02	19.7	17.7	15.2	15.8	14.9	13.2
Dye removed (mg / l)	79.5	76.6	77.2	82.98	80.3	82.3	84.8	84.2	85.1	86.8
Chitosan dose (g / l)	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.1
X (dye removed / g of adsorbent (mg / g))	7950	3830	2573.3	2074.5	1606	1371.7	1211.4	1052.5	945.6	868
1/C	0.0488	0.0427	0.0439	0.0588	0.0508	0.0565	0.0658	0.0633	0.067	0.076
1/X	0.0001	0.0003	0.0004	0.0005	0.0006	0.0007	0.0008	0.001	0.001	0.001
Log C	1.31	1.37	1.36	1.23	1.29	1.25	1.18	1.2	1.17	1.12
Log X	3.9	3.58	3.41	3.32	3.21	3.14	3.08	3.02	2.98	2.94

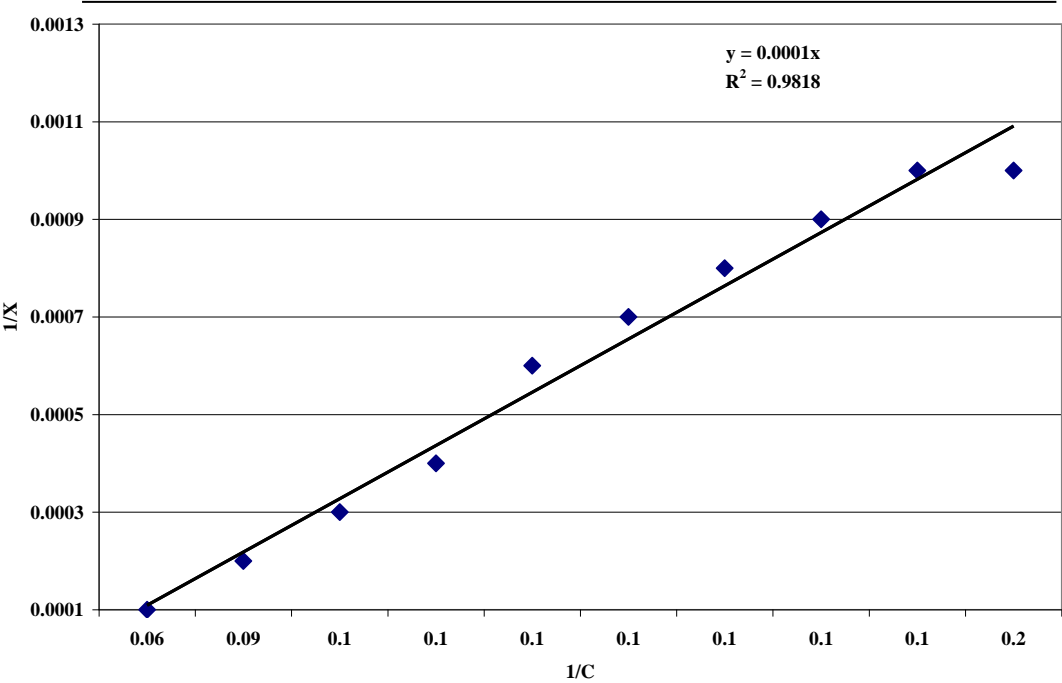


Fig (4). Application of Langmuir equation to the experimental data points determined for the adsorption of MB on Chitosan.

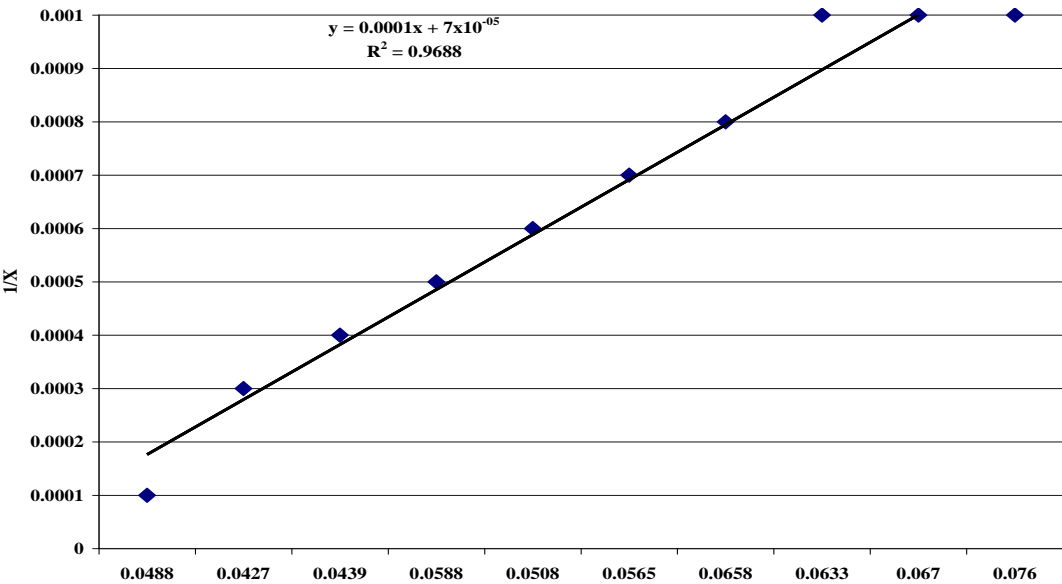


Fig (5). Application of Langmuir equation to the experimental data points determined for the adsorption of MB on Silica gel.

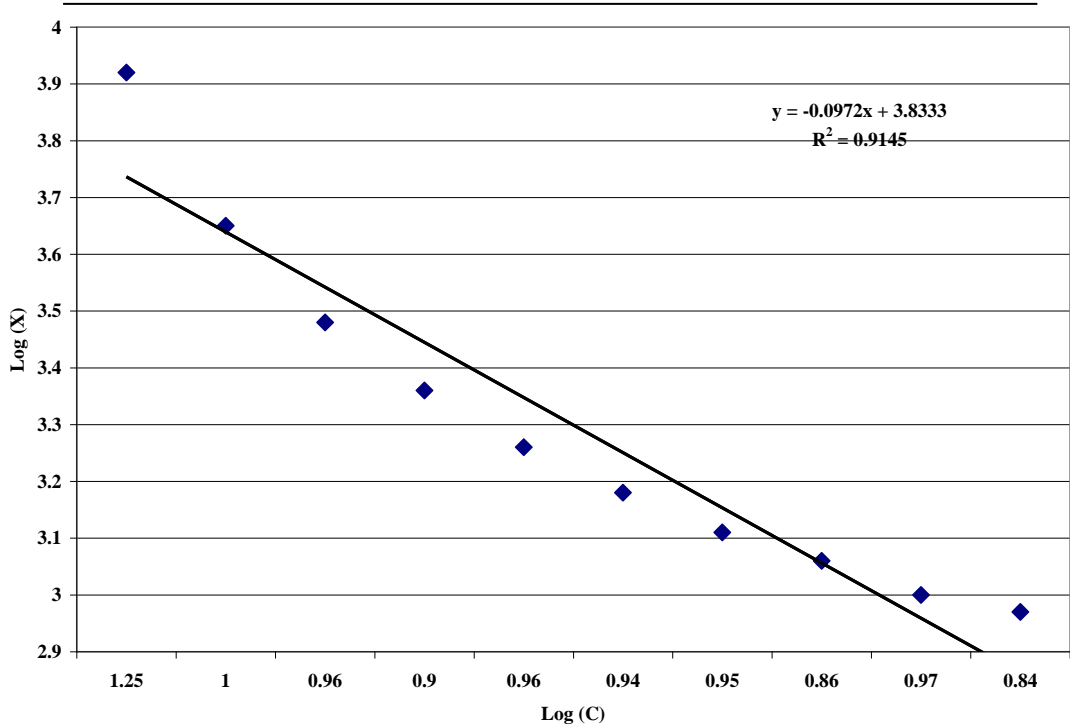


Fig (6). Application of Freundlich equation to the experimental data points determined for the adsorption of MB on Chitosan.

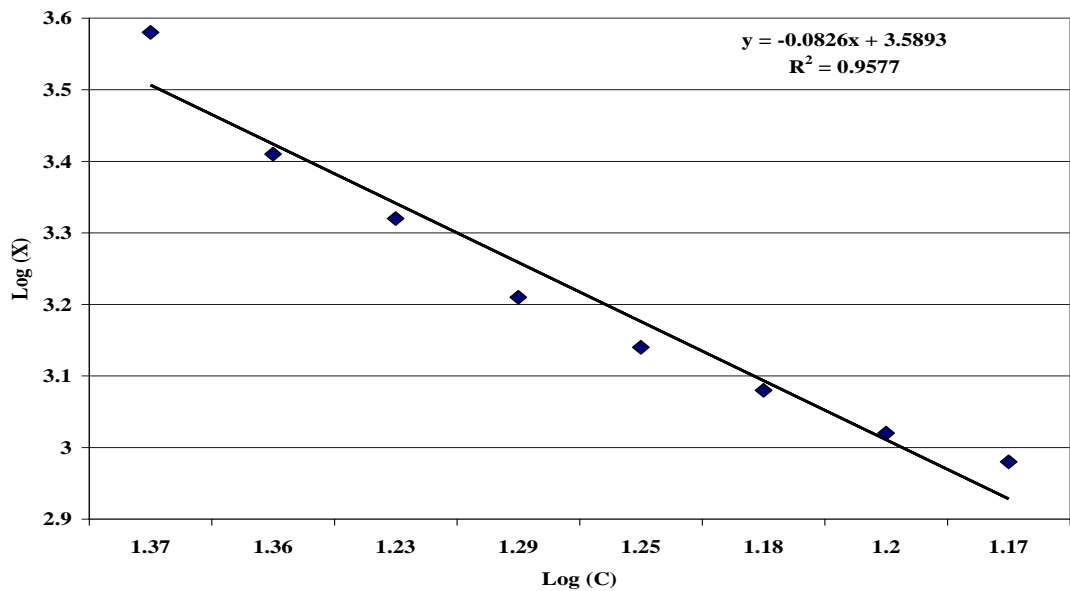


Fig (7). Application of Freundlich equation to the experimental data points determined for the adsorption of MB on Silica gel.

CONCLUSION

From the previous data, we conclude that the use of both the investigated adsorbents contributed to the removing of the methyl blue dye that can be found in the aquatic environment, and cause harmful effect to fish and aquatic organisms and, consequently to humans, with the preference of using chitosan and such natural materials, because of its advantage represented in low cost, wide availability and quite safe for the environment.

REFERENCES

- Anderson, I. G. (2002). The use of chemotherapeutic agents in finfish and shellfish culture in Australia. pp. 493-504. In: Sheriff, M., Subasinghe, R. P., and Arthur, J.R. (eds.). Diseases in Asian Aquaculture I. Fish Health Section, Asian Fisheries Society, Manila, Philippines. 587 pp.
- Annadurai, G. and Krishnan, M. R. V. (1996). "Adsorption of basic dye using chitin," Ind. Jr. of Environ. Protection, 16(6), PN. 444-449.
- Annadurai, G.; Sivakavinesan, M. and Mary-Helen, S. (2012). "Equilibrium Studies on the removal of Methyl Orange from Aqueous Solution by Adsorption on to Biopolymer Drug Invention Today. 4(11), 590-593.
- Berneth, H. (2003). Cationic dyes. In Ullmann's Encyclopedia of Industrial Chemistry. 6th Ed., Wiley-VCH, Weinheim, Germany (6) pp. 585-591.
- Bhatnagar, A. and Sillanpää, M. (2009). Applications of chitin- and chitosan-derivatives for the detoxification of water and wastewater — A short review. Adv. Colloid Interface Sci. 152, 26 – 38.
- Boeningo, M. (1994). "Carcinogenicity and metabolism of azodyes especially derived from benzidine". Washington DC, U.S Gov. Printing Off; DNHS (NIOSH) publication, July 1994, 80-119.
- Cestari, A. R., Vieira, E. F. S., Vieira, G. S., Costa, L. P. da., Tavares, A. M. G., Loh, W. and Airoidi, C. (2009). The removal of reactive dyes from aqueous solutions using chemically modified mesoporous silica in the presence of anionic surfactant - The temperature dependence and a thermodynamic multivariate analysis. *Journal of Hazardous Materials*. 161(1), 307-316.
- Chen, Z., Zhou, L., Zhang, F., Yu, C. and Wei, Z. (2012). Multicarboxylic hyperbranched polyglycerol modified SBA-15 for the adsorption of cationic dyes and copper ions from aqueous media. *Appl Surf Sci* 258: 5291–5298.

- Crini, G. (2005). Recent developments in polysaccharides-based materials used as adsorbents in wastewater treatment. *Prog. Polym. Sci.* 30, 38 – 70.
- Donia, A. M., Atia, A. A., Al-amrani, W. A. and El-Nahas, A. M. (2009). Effect of structural properties of acid dyes on their adsorption behaviour from aqueous solutions by amine modified silica. *Journal of Hazardous Materials*. 161(2–3), 1544-1550
- Drolet H. S., Ghittino, P., and Gomez, S. (2004). The principal aspect of bacterial fish diseases in Italy. Symposium of the Zoological Society London 30, 25-28.
- Duncan N. B., (1955). Multiple ranges and multiple F test. *Biometrical*, 11, 1-42.
- El-Sherbiny, M. F.; Hanna, M. A.; Al-Sarawy, A. A. and Farid, M. A. (2009). Removal of Some New Direct Sulpho Aryl Azo Dyes from Aqueous Solutions by Adsorption onto Different Types of Carbon. *Mansoura engineering journal*, (32) pp.: 1-20.
- Gaikwad, R. W. and Misal, S. A. (2010). Sorption Studies of Methylene Blue on Silica Gel. *International Journal of Chemical Engineering and Applications*, 1, 4 pp 342 – 345.
- Garg, V. K., Gupta, R., Yadav, A. B. and Kumar, R. (2003). Dye removal from aqueous solution by adsorption on treated qawdust, *Bioresource Technology*, Vol. 89, 121-124.
- Gupta, G. S., Prasad, G. and Singh, V. N. (1987). “Mordant Blue –13 removal from aqueous solution by fly ash –I (Equilibrium and rate process studies),” *Asian Env.*, PN. 29-30.
- Gupta, G. S., Prasad, G. and Singh, V. N. (1988a). “Removal of colour from wastewater by sorption for water reuse,” *Env. Sci. Health A23*, PN.205-217.
- Gupta, G. S., Prasad, G. and Singh, V. N. (1988b). “Removal of chrome dye from aqueous solutions on Flyash,” *Water Air Soil Poll.*, 37, PN.13-24.
- Hasan, B. (2008). “Adsorption of reactive azo dyes on chitosan/oil palm ash composites adsorbent :batch and continuous studies “ Masitah Binti Hasan University Sains Malaysia (2008).
- Kapdan, I. K., Kargi, F., McMullan, G. and Marchant, R. (2000). *Environmental Technology*, Vol. 21, 231-236.

- Karanjkar, D. M., Muley, D. V. and Manjare, S. A. (2000). Acute toxicity of industrial effluents to *Labeo rohita*. *Proc. Acad. Environ. Biol.*, 9 (Suppl.), 30.
- Katheresan, V., Kansedo, J. and Lau, S. Y. (2018). Efficiency of various recent wastewater dye removal methods: a review. *J Environ Chem Eng* 6:4676–4697.
- Khalaf, M. N. (ed) (2016). Green polymers and environmental pollution control. CRC Press; Apple Academic Press Inc, Oakville, p 436.
- Khan, A. R., Tahir, H., Uddin, F. and Uzma, H. (2005). “Adsorption of methylene blue from aqueous solution on the surface of wool fiber and cotton fiber.” *J. of Applied Science and env. Manag.*, 9(2): 29-35.
- Kumar, M. N. V. R. (2000). “A Review of Chitin and Chitosan Applications,” *Reactive and Functional Polymers*, Vol. 46, No. 1, pp. 1-27.
- Kurita, K. (2001). Controlled functionalization of the polysaccharide chitin. *Progress in Polymer Science* 26: 1921–1971.
- Liu, D. H. F., Liptak, B. G. (eds) (2000). Wastewater treatment. CRC Press, Boca Raton.
- Lopes, A., Martins, S. and Marao, A. (2004). Degradation of textile dye C.I. Direct Red 80 by Electro chemical process”, *Portugaliaea Electrochemical Acta*, pp.279 - 294.
- Ngadi, N. A, Ee, C. C. and Yusoff, N. A. (2013). Removal of Methylene Blue Dye by Using Eggshell Powder. *Jurnal Teknologi (Sciences & Engineering)* 65(1) 63–71.
- O’Mahony, T., Guibal, E. and Tobin, J. M. (2002). *Enzyme and Microbiology Technology*, Vol. 31, 456.
- Özer, A. and Dursun, G. (2007). Removal of Methylene Blue from Aqueous Solution by Dehydrated Wheat Bran Carbon”, *J. of Hazardous Materials* 146, pp. 262-269.
- Piaskowski, K., Swiderska-Dabrowska, R. and Zarzycki, P. K. (2018). Dye removal from water and wastewater using various physical, chemical, and biological processes. *J AOAC Int* 101:1371–1384.
- Porter, J. F., McKay, G. and Choy, K. H. (1999). The prediction of sorption from a binary mixture of acidic dyes using single-and mixed isotherm variants of the ideal adsorbed solute theory. *Chemical Engineering Science* 54:5863-5885.

- Rana, K. S. and Raizada, S. (1999). Acute toxicity of tannery and textile dye effluents on a common teleost, *Labeo rohita*: Histological alterations in liver. *J. Environ. Biol.*, 20(1), 33-36.
- SAS (2009). Statistical Analysis System, SAS User's Guide: Statistics. SAS Institute Inc. Editors, Cary, NC, USA.
- Selvam, K., Swaminathan, K. and Chae, K. S. (2003). Bioresource Technology., Vol. 88, 115-119.
- Sharma, K. P., Sharma, S., Sharma, S., Singh, P. K., Kumar, S., Grover, R. and Sharma, P. K. (2007). A comparative study on characterization of textile wastewaters (untreated & treated) toxicity by chemical and biological tests. *Chemosphere* 69:48–54.
- Shashikala, M., Nagapadma, M., Pinto, L. and Nambiar, S. N. (2013). Studies on the Removal of Methylene Blue Dye from Water Using Chitosan. *International Journal of Development Research*. 3:8, pp 40-44.
- Steel, R. G. D. and J. A. Torrie (1980). Principles and procedures of statistics. 2nd ed., USA McGraw Hill pp. 183 – 193.
- Tacon, A. G. J. and Forster, I. P. (2003). Aquafeeds and the environment: Policy implications. *Aquaculture*, 226(1-4), 181-189.
- Uddin, M. T., Islam, M. S. and Abedin, M. Z. (2007). Adsorption of phenol from aqueous solution by water hyacinth ash.” *ARPN J of Engineering and Applied sciences*, 2(2): 121-128.
- Verma, V. K. and Mishra, A. K. (2010). Kinetic and isotherm modeling of adsorption of dyes onto rice husk carbon. *Global Nest J.*, (12) 2, pp 190-196.
- Yan, Z., Li, G., Mu, L. and Tao, S. (2006a) Pyridine-functionalized mesoporous silica as an efficient adsorbent for the removal of acid dyestuffs. *J Mater Chem* 16: 1717–1725.
- Zollinger, H. (1991). Color chemistry: synthesis, properties and applications of organic dyes and pigments, 2 nd Ed. VCH Publisher, New York.
- Zubair, B. and AbdelKhader, B. (2007). Correlation with different models of adsorption isotherms of m-xylene and toluene on zeolites.” *J. of Applied Sciences in Environ. sanitation*, 2(2): 43-46.

مقارنه بين المواد التقليديه والمنخفضة التكلفة لإزالة بقايا صبغة الميثيلين الأزرق من المحاليل المائية

حسام أحمد محمد مؤنس، ريهام عبد الوهاب عبد الحي

قسم الليمولوجي، المعمل المركزي لبحوث الثروة السمكية، العباسه، مركز البحوث الزراعيه، مصر.

الملخص العربي

تعتبر الأصباغ من الملوثات الضاره التي تشكل تهديداً خطيراً للبيئة المائية، والتي تتطلب مواد باهظة الثمن للتخلص منها، وبالتبعيه ينتج عنه وضع حرج يتطلب توافر جميع الجهود لحلها، خاصة في ظروف ندرة المياه المتوقعه في المستقبل القريب. ومن هنا كانت الحاجة الماسه لاستخدام مواد إدمصاص رخيصة الثمن وصديقة للبيئة بدلاً من المواد التقليديه لتنقية المياه وإعادة استخدامها عدة مرات، وهو من أهم الدوافع لإجراء هذا البحث. أجريت هذه التجربه لمقارنة تأثير استخدام مادة ممتزه منخفضة التكلفة مقابل ماده تقليديه بجرعات مختلفه مع فترات معالجه مختلفه في ظل ظروف محيطه من الأس الهيدروجيني ودرجة الحراره المناسبه لتربية الأحياء المائية لإزالة بقايا صبغة الميثيلين الأزرق من المياه. أقصى كفاءة للإزالة بجرعه ٠,١ جم من الشيتوزان وهلام السيليكا تجاه ١٠٠ مجم / لتر من صبغة الميثيل الأزرق كانت ٩٣,١ % و ٨٦,٩ % على التوالي بعد فترة معالجه ٦٠ دقيقه. تم تطبيق بيانات سلوك الإدمصاص جيداً علي النموذجان الرياضيان لانجموير وفرندليتش. وبناءا علي النتائج المحققه، نوصي باستخدام مادة الشيتوزان في تنقية البيئة المائية من بعض الملوثات العضويه كالصبغات والمستخدمه بكثره في العديد من الصناعات، لما يتميز به الشيتوزان من مزايا متمثله في التكلفة المنخفضه والتوافر الواسع والأمن تماماً على البيئة.

الكلمات المفتاحيه: الميثيل الأزرق، الصبغه، الشيتوزان و سيليكا جيل.