Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1017744

57 (2016) 8330–8335
April

Taylor & Francis
Taylor & Francis Group

Removal of methyl orange from synthetic wastewater using nano-MgO and nano-MgO/UV combination

Mohamad Reza Rezaii Mofrad[a], GholamReza Mostafaii[a], Reza Nemati[b], Hossein Akbari[c], Narges Hakimi[a,*]

[a]*Department of Environmental Health, School of Public Health, Kashan University of Medical Sciences, Kashan PO Box: 87159 73449, Iran, Tel. +98 3155540021; Fax: +98 3155540111; emails: rezaeimofrad_mr@kaums.ac.ir (M.R. Rezaii Mofrad), mostafai_gr@kaums.ac.ir (G. Mostafaii), Narges.hakimi63@gmail.com (N. Hakimi)*
[b]*Department of Environmental Health, School of Public Health, Shahid Beheshti University of Medical Sciences, Tehran PO Box: 19835 35511, Iran, Tel. +98 2122432040; Fax: +98 2122432036; email: Reza.nemati84@gmail.com*
[c]*Department of Biostatistics and Public Health, School of Health, Kashan University of Medical Sciences, Kashan PO Box: 87159 73449, Iran, Tel. +98 3155545155; Fax: +98 3155540111; email: Akbari1350_h@yahoo.com*

Received 26 September 2014; Accepted 4 February 2015

ABSTRACT

In this study, the potential of MgO nanoparticles in the adsorption of methyl orange (MO) as an azo dye and also the effectiveness of UV radiation in the performance improvement of MgO nanoparticles in terms of MO dye adsorption were assessed. The dye removal experiments were carried out in the batch reactors. MgO dosage in the range of 0.1–3.5 g/L, mixing time of 0–120 min, dye concentration of 100–800 mg/L, and pH of 8–10 were applied. The results of this investigation showed that the optimum dose of azo dye, optimum dose of MgO nanoparticles, and optimum contact time for obtaining the best performance in dye adsorption were about 300 mg/L, 1.5 g/L, and 10 min, respectively. UV light improved MgO efficiency in MO adsorption. In the presence compared to the absence of UV light, to obtain 90% adsorption efficiency of 100 mg/L MO, only half the dose of MgO was needed. The isotherm studies showed that the Langmuir isotherm was the best adoption to express the adsorption behavior.

Keywords: Adsorption; Langmuir adsorption model; Dye removal; Methyl orange

1. Introduction

In recent decades, the growth of industrial activities and production of large amounts of wastes has led to large amounts of pollutant release into the environment. One of the main pollutants that cause serious health, environmental, and aesthetical problems is the dyes found in some industrial wastes, such as textile, wood, paper, leather, cosmetics, food, etc. These industries produce various types and quantities of colored wastes. Dye, at low concentrations (10–50 mg/L) in river water and sewage, can be recognized by eyes [1]. Among various industries, textile industries are the largest consumers of dyes [2], which consume water as large as 200–500 m^3 per ton of product (depending on the production process), and produce large volumes of wastewater with high dye concentrations in the range of 10–200 ppm [3–5].

*Corresponding author.

Textile wastewaters contain a variety of different colors, which are usually synthetic and have high molecular weight, complex chemical structure, and low biodegradability [6]. Therefore, these dyes must be removed using appropriate methods prior to discharge to the environment. Among the various applied methods, adsorption is a favorable method for the treatment of these wastes because of the simplicity of design, cost-effective feasibility, recycling of adsorbent, and the absence of unsafe residues [7]. Recently, researchers have shown that MgO nanoparticles due to high adsorption surface area, high surface to volume ratio, large numbers of highly reactive edges, and destructive sorbents, have considerable adsorption capacity for the discoloration of wastewaters [4,8,9]. When adsorbates react in adsorption surface and are degraded to a less-toxicity compound, it is known as a destructive adsorption [10].

Azo dyes, an important group of synthetic organic dyes, are used in textile industries. These compounds have one or more azo bond (N=N) [11] and constitute about 70% of total applied dyes [4]. UV radiation has been used in many studies in combination with other agents to remove pollutants such as dyes [12–15]. UV radiation has the potential to upgrade many processes in the removal of pollutants.

In this study, the potential of MgO nanoparticles in the adsorption of methyl orange (MO) as an azo dye and also the effectiveness of UV radiation in the performance improvement of MgO nanoparticles in the adsorption of MO dye were assessed.

2. Materials and methods

2.1. Materials

Magnesium oxide nanoparticles with the size of 20 nm, purity of 98%, and surface area of >60 m^2/g were purchased from US Research Nanomaterials (Houston, TX, USA). MO dye and sodium hydroxide were procured from Merck (Darmstadt, Germany). In the studies with UV light present, samples were irradiated with 125 W UV-light source (Narva, Berlin, Germany).

2.2. Methods

2.2.1. Dye removal experiments

The stock solutions at the desired concentration were prepared by dissolving the dye in distilled water. By these solutions, the synthetic samples (with the concentrations of 100–800 mg/L) were prepared. The required pH of the sample solutions were adjusted using 0.1 N HCl or NaOH solutions.

The batch dye removal experiments were carried out by 250 mL flasks in batch reactors. The solutions were stirred continuously using magnetic stirring bars during the adsorption process. Each test consisted of preparing a 100 mL of dye solution with the selected initial concentration and pH by diluting the stock dye solution and distilled water. Different dosages of nano-MgO were then added to the flask, and immediately stirred for a predefined time. After the mixing time, the suspension was allowed to settle for 30 min and the supernatant was analyzed for the residual dye. The dye removal efficiency was determined using the following expression (Eq. 1):

$$\text{Dye removal efficiency } (\%) = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where C_i and C_e represent the initial and final (following adsorption) dye concentrations, respectively. The experiments were repeated at least three times using the equivalent results. Mean of the three measurements was also reported. All the experiments were performed at room temperature. The ranges of the experimental variables were as follows: dye concentrations were prepared in the range of 100–800 mg/L, pH of 8–10, MgO dosage of 0.5–3.5 g/L, and mixing time of 0–120 min. These dosages and conditions were selected according to the results of the pretests and also, from the reports of the similar previous studies.

2.2.2. Method of analysis

The amounts of primary color and residual color (after adsorption in different predefined conditions) were measured using a spectrophotometer 2010DR. The spectrophotometer was calibrated at the wavelength of maximum absorption of the dye MO ($\lambda_{max} = 464$ nm). Correlation coefficient of the best fit line equation (R^2) was 0.995.

2.2.3. Adsorption isotherms

The adsorption equilibrium isotherm data are necessary for the evaluation, design, and operation of adsorption systems. In this paper, Langmuir, BET, and Freundlich adsorption isotherms were used to model the equilibrium adsorption data. To determine the parameters of the isotherms of the MO adsorption onto MgO nanoparticles, various doses of MgO nano particles (0.5–2 g/L) were added separately to a series of 250 mL volumetric flask containing 100 mL synthetic solution with 300 mg/L initial MO concentration. The pH of these synthetic solutions was adjusted

to 8. Then the flasks were stirred at room temperature for 48 h to reach the equilibrium. Afterward, the stirrer was turned off and the settled solutions (after 30 min) were analyzed to determine the remaining dye concentrations.

The quantity of removed dye (adsorbed dye) was calculated by following mass balance equation (Eq. 2):

$$q_e \cdot m = V\ (C_i - C_e) \tag{2}$$

where q_e (mg/g) is the mg adsorbed dye onto the unit of adsorbate (g), m is mass of dry adsorbate added (g), V is volume of the dye solution, C_i and C_e are the initial and equilibrium dye concentrations, respectively.

In this study, to determine the relationship between q_e and equilibrium concentration dye (C_e), Freundlich, BET (Brunauer–Emmett–Teller), and Langmuir isotherms were used.

The linearized formulation of the Freundlich equation is expressed as Eq. 3 [16]:

$$\log q_e = \frac{1}{n}\log C_e + \log K_f \tag{3}$$

In this equation, n, which is constant, is reciprocal reaction order, and K_f (also constant) shows capacity of the adsorbent for the adsorbate. K_f is a function of adsorption strength. Drawing log q_e vs. log C_e provides n and K_f values.

The Langmuir equation, in its linearized form is expressed as follows [17]:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \tag{4}$$

where, b is a constant related to the adsorption energy and q_{max} term is the surface concentration at monolayer coverage (maximum value of q_e that can be achieved as C_e is increased).

BET isotherm is given by the following equation [18]:

$$\frac{C}{(C_s - C)(X/m)} = \left(\frac{A-1}{A \cdot q}\right) \cdot \left(\frac{C}{C_s}\right) + \left(\frac{1}{A \cdot q}\right) \tag{5}$$

In this equation, C is solute residual concentration in the solution at equilibrium (mg/L), C_s is solute saturation concentration (mg/L), X/m is the sorbated quantity per sorbent unit weight (mg/g), A is constant equivalent to the energy of interaction with the surface, and q is amount of solute sorbated per unit sorbent weight in forming a complete monolayer on the surface (mg/L).

3. Results and discussion

3.1. Effect of MgO dosage

Fig. 1 shows the effect of MgO nanoparticle dosage (adsorbent) on MO dye (adsorbate) removal efficiency at three different dye concentrations and constant time (40 min).

As seen in Fig. 1, the dye removal efficiency increased when adsorbent dosage increased; also it decreased when adsorbate dosage increased.

These can be attributed to the increase and decrease of the available adsorption sites with the

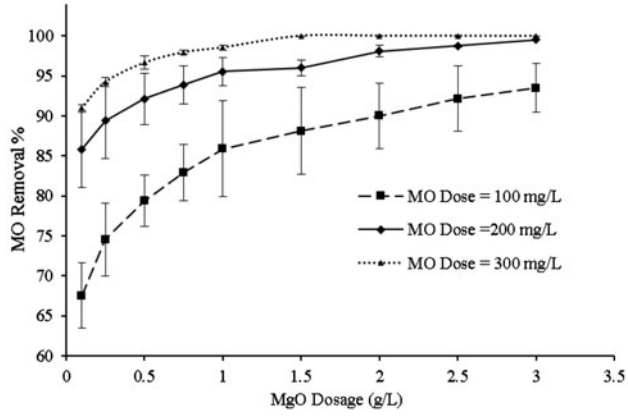

Fig. 1. Effect of MgO dose on the MO removal percentage (Mean ± SD) at three different MO concentrations (temp. = 20 ± 2.8°C, initial adjusted pH 8 ± 0.02).

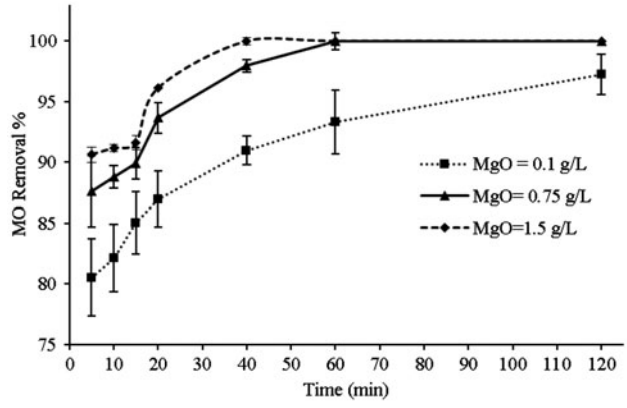

Fig. 2. Effect of contact time and initial MgO concentration on the dye removal efficiency (mean ± SD) (initial MO concentration = 300 mg/L, temp. = 20 ± 2.4°C, and initial adjusted pH 8 ± 0.02).

increase of adsorbent dose and also increase of adsorbate dose, respectively. Hence, the percent dye removal depends upon adsorbent dose and initial adsorbate concentration [19]. Addition of the MgO nanoparticles increases the pH of the dye solution. By increasing pH of the solution close to magnesium pH_{zpc} (12.4) [20], surface of MgO nanoparticles tends to have more positively charged surfaces. Therefore, the negatively charged surface of dye and positive adsorbent surfaces make favorable conditions for dye adsorption. Removal efficiency in each of the three dye concentrations with the adsorbent dosage of less than about 1.5 g/L of MgO dosage was increasing relatively faster than higher adsorbent dosage. According to this figure, it can be concluded that until sufficient adsorption sites are available, dye removal efficiency is independent from the adsorbent concentration. In briefly, the remarkable MO removal efficiency by MgO nanoparticles has been attributed to the large surface area, coral-like hierarchical structure, and the porous nanoflakes network [8].

3.2. Effect of contact time

Contact time, which is one of the most important design parameters in adsorption processes, was studied in this investigation and the results are shown in Fig. 2. According to Fig. 2, by increasing contact time, dye removal efficiency was increased. In the first 10 min of contact time, this increase was sharp and then was gradually flattened out. Therefore, it seems that best effective adsorption time can be considered as about 10 min.

The exposure time achieved for equilibrium adsorption onto MgO is shorter than most of the reported values for dye adsorption onto other adsorbent. For example, it is reported that to reach equilibrium in adsorption of reactive red dye onto wheat bran, required time is almost 4 h [21]. Table 1 displays the optimum adsorption time of some of the other adsorbents toward dyes in comparison with MgO nanoparticles.

3.3. Effect of dye dosage

In Fig. 3, the plot of MO removal (%) vs. dye concentration at the constant concentration of MgO nanoparticle (1.5 g/L as optimum dosage) and different times of adsorption are shown.

As observed, the dye removal efficiency increased steadily as initial dye concentration increased from 100 to 300 mg/L, and then it decreased sharply with increasing dye concentration, which may be caused by decreasing the number of remaining adsorption sites. Also, at lower contact time (15 min) and at higher dye concentrations (greater than about 400 mg/L), with increasing initial dye concentration, removal efficiency was more steadily decreased, which may be related to

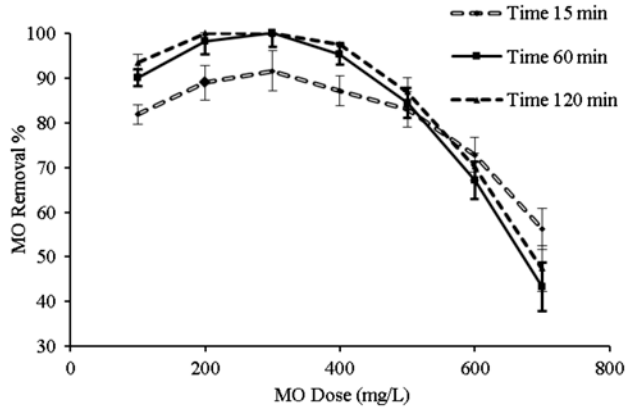

Fig. 3. Effect of MO (dye) concentration and contact time on MO removal efficiency (mean ± SD) (MgO concentration = 1.5 g/L, temp. = 20 ± 1.9 ℃, and initial adjusted pH 8 ± 0.03).

Table 1
Comparison of optimum adsorption contact time of different adsorbents with MgO nanoparticles

Dye(s)	Treatment method adsorbent	Optimum adsorption time (min)	References
Alizarin yellow, fast green, and methyl violet	Bottom ash	240	[22]
Basic red 29	Activated carbon	120	[23]
Methylene blue	UV/TiO_2	180	[24]
Reactive black 5(RB5)	Penicillium restrictum biomass	75	[25]
Safranin O	Fe_3O_4 magnetic nanoparticles	10	[26]
Remazol brilliant blue R (RB19) & remazol red 133 (RR 198)	MgO nanoparticles	5	[4]
Methyl orange	MgO nanoparticles	10	This work

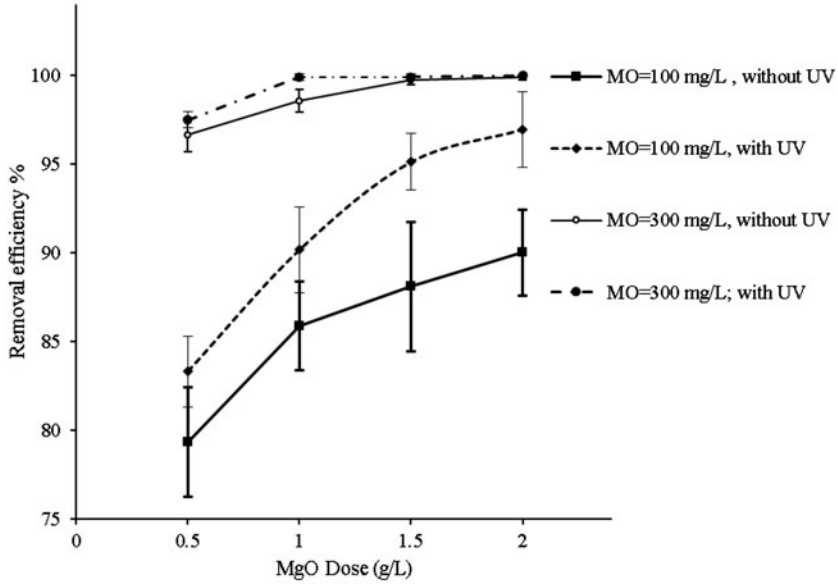

Fig. 4. Effect of UV irradiation presences on MO removal efficiency (mean ± SD) by MgO nanoparticles (temp. = 20 ± 1.5°C, initial adjusted pH 8 ± 0.02).

desorption phenomena occurring at the more contact times. Similar findings have been also reported by other researchers [4,9].

3.4. Effect of simultaneous use of MgO and UV

Decolorization of MO in the coupled MgO/UV system was investigated at different MgO nanoparticle doses when the initial dye concentrations were 100 and 300 mg/L. Contact time in this section was constant and 10 min. All other experimental conditions were the same as the previous ones.

Dye removal efficiency comparison of MgO nanoparticles with and without UV radiation present is shown in Fig. 4. Accordingly, dye removal efficiency had an increasing tendency in the presence of UV radiation, and this increase was more significant at lower (100 mg/L) dye concentration.

Also in Fig. 4, it can be seen in the presence compared to the absence of UV light, to obtain 90% adsorption efficiency of 100 mg/L MO, only half the dose of MgO was required.

3.5. Adsorption isotherm modeling

The equilibrium adsorption data of MO onto MgO nanoparticles adsorbent were evaluated with Langmuir, Freundlich, and BET models. To compare the fitness of the models, correlation coefficient (R^2) of the linear regression plot was used. Table 2 summarizes

Table 2
Adsorption isotherms parameters of MO onto MgO at room temperature (initial MO dose = 300 mg/L, initial adjusted pH 8 ± 0.04, and equilibrium time 48 h)

Langmuir equation		Freundlich equation		BET equation	
q_{max}	301.85	K_f	7.685	A	−51.34
B	0.13	n	4.99	X/m	139.84
R^2	0.999	R^2	0.957	R^2	0.988

Langmuir, Freundlich, and BET isotherm constant parameters for the adsorption of MO onto MgO. As shown in Table 2, the best correlation between these three models was Langmuir equation, which indicates that the adsorption of MO onto MgO nanoparticles was well described by the Langmuir model than the BET and Freundlich models. This indicates that the adsorption happens as the monolayer dyes adsorb onto the homogenous adsorbent surface. Other studies have also reported a Langmuir model for the adsorption of other dyes as well [4,10].

4. Conclusion

This study investigated the efficiency of MgO and MgO/UV in the removal of an azo dye from synthetic wastewater sample. MgO dose, MO dose (as an azo dye), contact time, and UV light (the absence and presence of UV) were the variable parameters in this work.

Results of this investigation showed that the optimum dose of MO, optimum dose of MgO nanoparticles, and optimum contact time for obtaining the best performance in MO adsorption were about 300 mg/L, 1.5 g/L, and 10 min, respectively. UV light improved MgO efficiency in MO adsorption. UV light had a more observable effect on lower dye concentrations. The results obtained from the isotherm studies showed that the best fitting isotherm was found to be the Langmuir.

Acknowledgment

This research was supported by Kashan University of Medical Sciences, Kashan, I.R. Iran grant.

References

[1] O. Demirci, D.A. Hamamcı, Antioxidant responses in *Phanerochaete chrysosporium* exposed to Astrazone Red FBL textile dye, Cell Biochem. Funct. 31(1) (2013) 86–90.
[2] R. Khan, U.C. Banerjee, Decolorization of azo dyes by immobilized bacteria, In: H. Atacag Erkurt (Ed.), Biodegradation of Azo Dyes, Springer, Berlin, 2010, pp. 73–84.
[3] M. Villanueva-Rodríguez, A. Hernández-Ramírez, J. Peralta-Hernández, E.R. Bandala, M.A. Quiroz-Alfaro, Enhancing the electrochemical oxidation of acid-yellow 36 azo dye using boron-doped diamond electrodes by addition of ferrous ion, J. Hazard. Mater. 167(1–3) (2009) 1226–1230.
[4] G. Moussavi, M. Mahmoudi, Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles, J. Hazard. Mater. 168(2–3) (2009) 806–812.
[5] M. Marcucci, G. Ciardelli, A. Matteucci, L. Ranieri, M. Russo, Experimental campaigns on textile wastewater for reuse by means of different membrane processes, Desalination. 149(1–3) (2002) 137–143.
[6] A.L. Ahmad, W.A. Harris, B.S. Ooi, Removal of dye from wastewater of textile industry using membrane technology, Jurnal Teknologi. 36(1) (2012) 31–44.
[7] M.F. Attallah, I.M. Ahmed, M.M. Hamed, Treatment of industrial wastewater containing congo red and naphthol green B using low-cost adsorbent, Environ. Sci. Pollut. Res. 20(2) (2013) 1106–1116.
[8] K. Mageshwari, R. Sathyamoorthy, Studies on photocatalytic performance of MgO nanoparticles prepared by wet chemical method, Trans. Indian Inst. Met. 65(1) (2012) 49–55.
[9] R. Wanchanthuek, W. Nunrung, The adsorption study of methylene blue onto MgO from various preparation methods, J. Environ. Sci. Technol. 4(5) (2011) 534–542.
[10] T.G. Venkatesha, R. Viswanatha, Y. Arthoba Nayaka, B.K. Chethana, Kinetics and thermodynamics of reactive and vat dyes adsorption on MgO nanoparticles, Chem. Eng. J. 198–199 (2012) 1–10.
[11] U. Zissi, G. Lyberatos, Axo-dye biodegradation under anoxic conditions, Water Sci. Technol. 34(5–6) (1996) 495–500.
[12] I. Arslan, I.A. Balcioglu, T. Tuhkanen, D. Bahnemann, H_2O_2/UV-C and Fe_2+/H_2O_2/UV-C versus TiO_2/UV-A treatment for reactive dye wastewater, J. Environ. Eng. 126(10) (2000) 903–911.
[13] P.C. Fung, K.M. Sin, S.M. Tsui, Decolorisation and degradation kinetics of reactive dye wastewater by a UV/ultrasonic/peroxide system, Color. Technol. 116 (5–6) (2000) 170–173.
[14] F.I. Hai, K. Yamamoto, K. Fukushi, Hybrid treatment systems for dye wastewater, Crit. Rev. Environ. Sci. Technol. 37(4) (2007) 315–377.
[15] C.C. Liu, Y.H. Hsieh, P.F. Lai, C.H. Li, C.L. Kao, Photodegradation treatment of azo dye wastewater by UV/TiO_2 process, Dyes Pigm. 68(2) (2006) 191–195.
[16] H.M.F. Freundlich, Over the adsorption in solution, J. Phys. Chem. 57 (1906) 385–471.
[17] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40(9) (1918) 1361–1403.
[18] S. Brunauer, P.H. Emmett, E. Teller, Adsorption of gases in multimolecular layers, J. Am. Chem. Soc. 60 (2) (1938) 309–319.
[19] G. Sreelatha, P. Padmaja, Study of removal of cationic dyes using palm shell powder as adsorbent, J. Environ. Prot. Sci. 2 (2008) 63–71.
[20] K. Mahendar, A. Sarma, P. Raghavaiah, M.L. Kantam, K.J. Klabunde, Synthesis of β-hydroxy α-sulfanyl esters by using nanocrystalline magnesium oxide, Helv. Chim. Acta. 94(8) (2011) 1533–1542.
[21] M.T. Sulak, H.C. Yatmaz, Removal of textile dyes from aqueous solutions with eco-friendly biosorbent, Desalin. Water Treat. 37(1–3) (2012) 169–177.
[22] V. Gupta, I. Ali, V. Saini, T. Van Gerven, B. Van der Bruggen, C. Vandecasteele, Removal of dyes from wastewater using bottom ash, Ind. Eng. Chem. Res. 44 (10) (2005) 3655–3664.
[23] P. Sivakumar, P. Palanisamy, Adsorption studies of basic Red 29 by a non-conventional activated carbon prepared from *Euphorbia antiquorum* L, Int. J. Chem-Tech. Res. 1(3) (2009) 502–510.
[24] K. Joshi, V. Shrivastava, Removal of methylene blue dye aqueous solution using photocatalysis, Int. J. Nano Dimens. 2(4) (2012) 241–252.
[25] C.F. Iscen, I. Kiran, S. Ilhan, Biosorption of reactive black 5 dye by Penicillium restrictum: The kinetic study, J. Hazard. Mater. 143(1–2) (2007) 335–340.
[26] S. Shariati, M. Faraji, Y. Yamini, A.A. Rajabi, Fe_3O_4 magnetic nanoparticles modified with sodium dodecyl sulfate for removal of safranin O dye from aqueous solutions, Desalination. 270(1–3) (2011) 160–165.