

Isotherm Study of Methyl Orange Dye Adsorption

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Abstract— Water pollution is caused by a number of pollutants, such as natural resource extraction, oil pollution, agricultural practices, nuclear waste spillage, and industrial waste. One such industry is the textile industry that utilises a great deal of water and synthetic dyes that can cause harmful effect to living organism. In order to save human life and aquatic eco system, adsorption is the most efficient technique used for treatment of wastewater containing dyes. The aim of this research is to study the adsorption isotherm of MO dye on the adsorption process using the low rank coal (LRC) as adsorbents. Different amount of adsorbent (60 - 140 mg) was placed in contact with the dye's solution in the required contact time (5 - 60 min). After the adsorption process was ended, the shaker was turned off and the remained MO dyes concentration was measured using UV-Vis spectrophotometer. The adsorption isotherm of MO dye solution well fit to Freundlich adsorption isotherm.

Keywords— Adsorbent, adsorption, freundlich, isotherm, low rank coal.

I. INTRODUCTION

The release of synthetic dyes into water bodies has caused a major environmental pollution problem worldwide. As a result of industrial activities, significant amounts of various dyes enter the aquatic ecosystem. Many synthetic dyes are used in various industries such as textile, leather, paper, paint, pigments, printing etc [1].

Anionic dyes contain a negative charge, bind to components of positively charged and water-soluble materials [2]. Most dye molecules used in the textile industry have complex aromatic structures and functional groups. Synthetic dyes are resistant to aerobic/anaerobic conditions, resistant to heat and light, have a moderate oxidation effect, and are difficult to break down the dye molecules. Dyes can penetrate into different layers of the soil, pollute groundwater and have a harmful effect on living organisms. Methyl orange (MO) is one of the most common dyes used in the textile industry [3]. It is also used as a pH indicator in titrations [4].

The treatment of the industrial effluent is a great concern for the industry in a bid to make their process environmentally friendly [5–7]. Various treatment methods can be utilised for the MO dye removal from solutions, include; sedimentation, electro-chemical degradation, reverse osmosis, ozonation, anaerobic/aerobic treatment [8], advanced oxidation processes [9], photocatalytic degradation [10], ultra-filtration [11], electrochemical degradation [12], and coagulation-flocculation [13]. However, these methods have disadvantages such as high operational cost, complexity in design and operational, produce toxic sludge and time-consuming[14]. Due to the disadvantages of other treatment approaches, adsorption as a technique is preferred to these other methods in the mitigation of MO and dye removal from aqueous environments [15] because of its

simplicity in design and operation, indifferent sensitivity towards toxicants and low operational cost [16].

Several research have been studied the use of some materials as an adsorbent for adsorption process to remove dyes from aqueous environment such as baggase, lemongrass, chitosan, zeolite, clay, etc. [17,18]. The most popular and widely used adsorbent material was activated carbon, which has a large number of microporous structures, higher adsorption capacity and large surface area. However, the disadvantage of using activated carbon is that it is expensive and requires high-quality adsorbents. Therefore, the utilization of activated LRC, which is widely found in the natural environment, especially in East Kalimantan as a cheap and low-cost adsorbent can be an alternative adsorbent on the adsorption process for MO dye removal from aqueous environments.

In the adsorption process, the isotherms analysis is most significance to formulate an equation that can be effectively utilized for the goal of design [19]. Most of the research in several countries regarding the isotherm of the MO dye adsorption process uses different types of adsorbents [20]. The objective of this research is to study the adsorption isotherm of MO dye on the adsorption process using the low rank coal (LRC) as adsorbents.

II. METHODOLOGY

2.1 Material

The adsorbent used in this research derived from activated East Kalimantan LRC which supplied by Tribins Company, Samarinda. Meanwhile, MO dye supplied by Chemical Engineering Laboratory, Polytechnic State of Samarinda.

2.2 Adsorption of MO dye

Batch adsorption experiments were performed in Erlenmeyer flasks with stirring at 150 rpm, 30 °C. About 100 ml of dyes solution was used to prepare 50, 100, 150, 200, and 250 mg/L under an optimum pH of MO was 4; 60 - 140 mg adsorbent dosage was placed in contact with the MO dye's solution in 5, 10, 20, 30, 40, 50, and 60 minutes. After the adsorption process was done, the shaker was turned off and the remained MO dye concentration was measured using UV-Vis spectrophotometer at the 664nm maximum wave length.

III. RESULT AND DISCUSSION

There are four parameters of isotherm models; the Langmuir, Freundlich, Temkin and Dubinin-R isotherms models, were used to describe the MO dye equilibrium of the adsorption process. The Langmuir model is based on the assumptions that the monomolecular layer is formed during adsorption without any interaction between the adsorbed

molecules (samsiripan). The model assumes uniform energies of adsorption into the adsorbent surface and no transmigration of dye molecules in the plane of surface. In contrast, the Freundlich model is based on the assumptions that heterogeneous adsorption occurs on the surface level and adsorbent has active sites with different energies. Temkin's isothermal model assumes that the heat of adsorption of all molecules in a layer decreases linearly, not logarithmically, with coverage. The uniform distribution of the binding energies up to some maximum binding energy was carried out.

Meanwhile, the Dubinin-R model is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface.

The linear plots of the Langmuir, Freundlich, Temkin and Dubinin-R isotherms for the MO dye adsorption at different adsorbent dosage are as shown in Figure 1, Figure 2, Figure 3, and Figure 4 respectively, meanwhile the equilibrium constants derived from the four isotherms models are presented in Table 1.

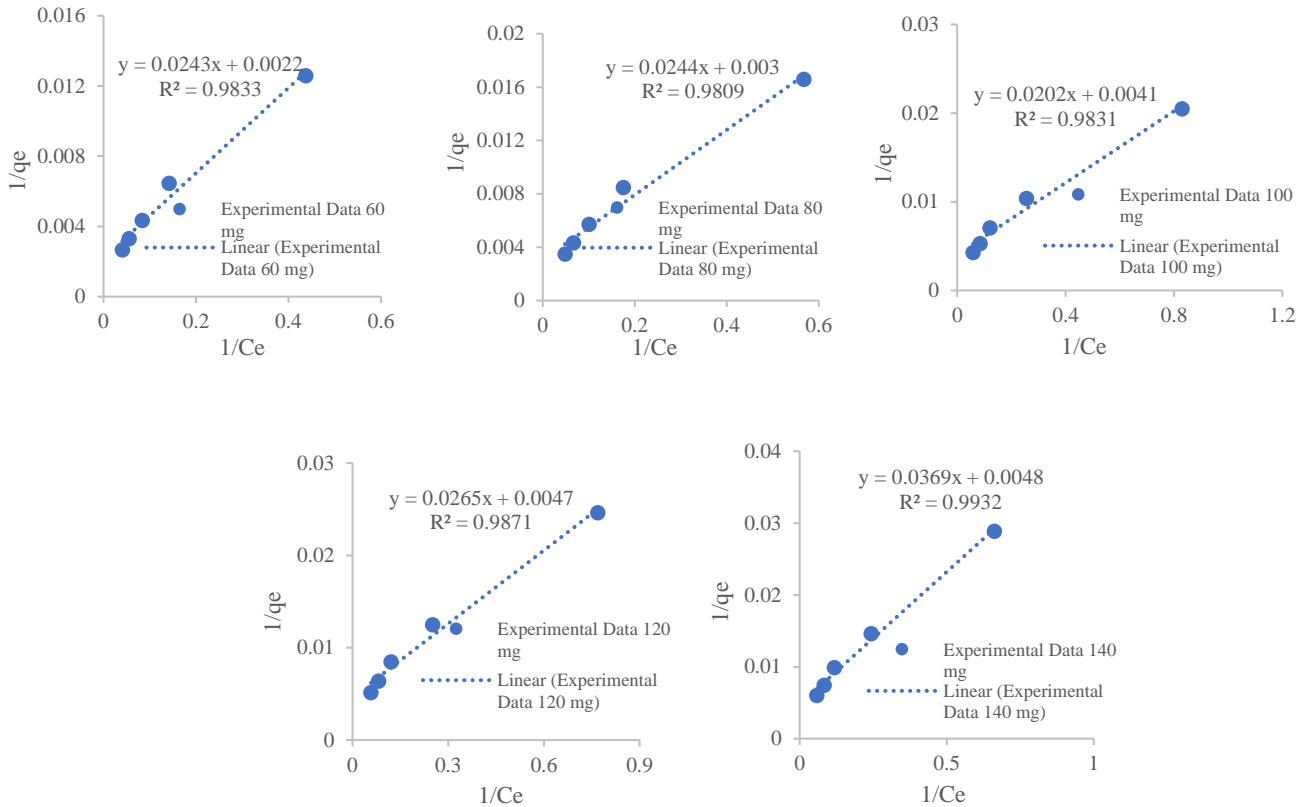
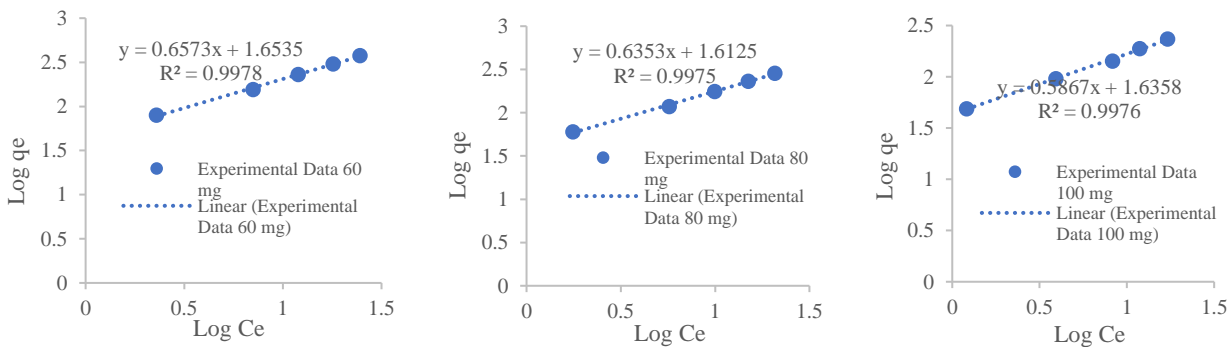


Fig. 1. Langmuir isotherm plot for MO dye adsorption.



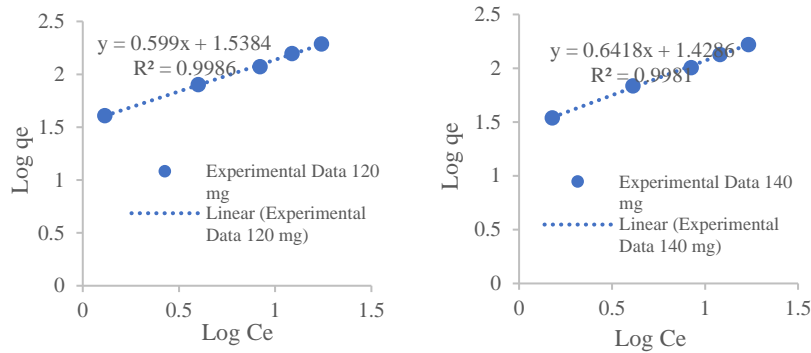


Fig. 2. Freundlich isotherm plot for for MO dye adsorption.

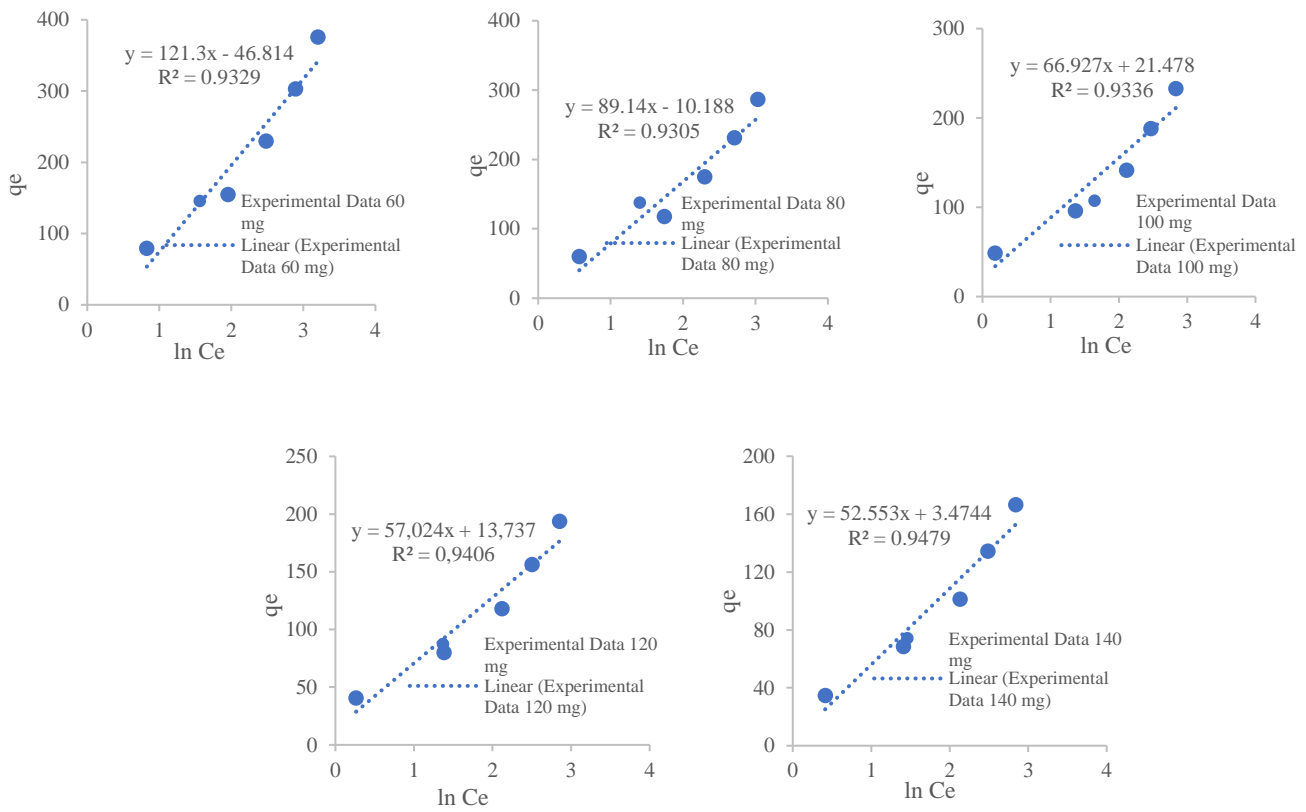
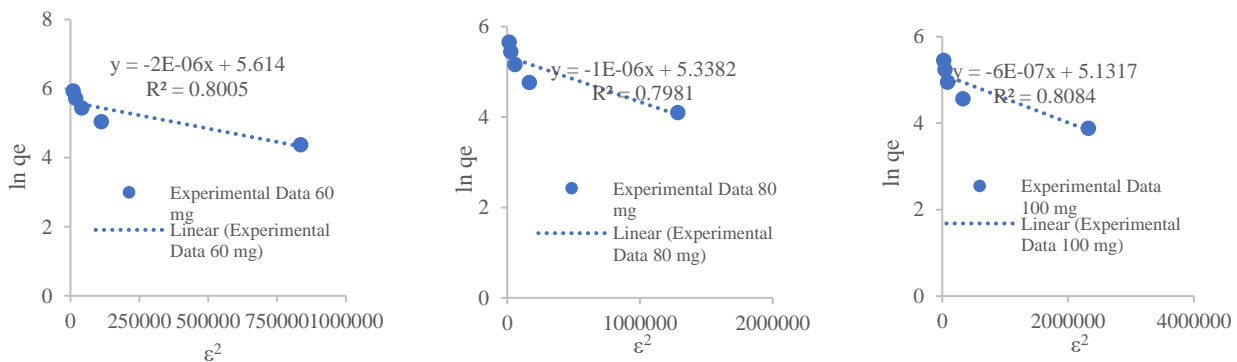


Fig. 3. Temkin isotherm plot for for MB dye adsorption.



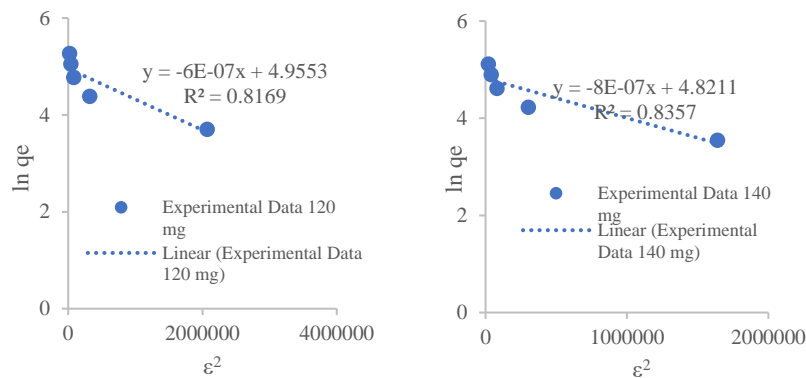


Fig. 4. Dubinin-Radushkevich isotherm plot for for MO dye adsorption.

TABLE I. Isotherm model parameters for MO dye adsorption.

Isotherm Model	Model Parameters	Adsorbent Dosages, mg				
		60	80	100	120	140
Langmuir	q_m (mg/g)	454.5455	333.3333	243.9024	212.766	208.3333
	K_L (L/mg)	0.0905	0.1229	0.203	0.1774	0.1301
	R^2	0.9833	0.9809	0.9831	0.9871	0.9932
	R_L	0.0995	0.0752	0.2030	0.0534	0.0714
Freundlich	K_f	45.0298	40.9732	43.2315	34.5462	26.8287
	n_f	1.5214	1.5740	1.7044	1.6694	1.5581
	R^2	0.9978	0.9975	0.9976	0.9986	0.9981
Temkin	B (J/mol)	121.300	89.1400	66.927	57.0240	52.5530
	A_T (L/g)	0.6798	0.8920	1.3784	1.2724	1.0683
	R^2	0.9329	0.9305	0.9336	0.9406	0.9479
Dubinin-R	q_m (mg/g)	274.239	208.1377	169.3047	141.9252	124.1015
	K_{ad} (mol ² /k ² .J ²)	2.00E-06	1E-06	6E-07	6E-07	8E-07
	E (KJ/mol)	500.000	707.1068	912.8709	912.0719	790.5694
	R^2	0.8005	0.7981	0.8084	0.8169	0.8357

The adsorption isotherm was observable and showed that dyes adsorptive behaviour satisfied to Langmuir, Freundlich, Temkin and Dubinin-R's assumptions. The dimensionless constant separation factor, also known as the equilibrium parameter (R_L), showed the types of Langmuir isotherm, either the irreversible ($R_L=0$), favourable ($0 < R_L < 1$), linear ($R_L=1$) or unfavourable ($R_L > 1$) types. In this study, the $R_L < 1$ showed that the adsorption of MO dye is favourable. A higher value of correlation coefficients (R^2) suggested that the experimental data fitted well with the Langmuir and Freundlich isotherm models. However, for the Freundlich isotherm model, the R^2 value converged closely to 1.000. Therefore, the removal of MO dye adsorption using activated LRC of East Kalimantan as adsorbent obeyed the Freundlich isotherm model.

IV. CONCLUSION

The isotherm of MO dye on the adsorption process using activated East Kalimantan LRC as adsorbent fits to Freundlich isotherm models adsorption.

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REFERENCES

- Belala Z, Jeguirim M, Belhachemi M, Addoun F, Trouvé G. Biosorption of basic dye from aqueous solutions by Date Stones and Palm-Trees Waste: Kinetic, equilibrium and thermodynamic studies. Desalination [Internet]. 2011;271(1–3):80–7. Available from: <http://dx.doi.org/10.1016/j.desal.2010.12.009>
- Bazrafshan E, Zarei AA, Nadi H, Zazouli MA. Adsorptive removal of methyl orange and reactive red 198 dyes by Moringa Peregrina ash. Indian J Chem Technol. 2014;21(2):105–13.
- Rajeev Kumar JR and MAB. Synthesis and characterization of a starch–AlOOH–FeS 2 nanocomposite for the adsorption of congo red dye from aqueous solution. RSC Adv. 2014;4(72):38334–40.
- Zaggout FR, El-Ashgar NM, Zourab SM, El-Nahhal IM, Motawah H. Encapsulation of methyl orange pH-indicator into a sol-gel matrix. Mater Lett. 2005;59(23):2928–31.
- Ighalo JO, Igwegbe CA, Aniagor CO, Oba SN. A review of methods for the removal of penicillins from water. J Water Process Eng [Internet]. 2021;39(December 2020):101886. Available from: <https://doi.org/10.1016/j.jwpe.2020.101886>
- Barakat MA. New trends in removing heavy metals from industrial wastewater. Arab J Chem [Internet]. 2011;4(4):361–77. Available from: <http://dx.doi.org/10.1016/j.arabjc.2010.07.019>
- Al-Musawi TJ, Rajiv P, Mengelizadeh N, Mohammed IA, Balarak D. Development of sonophotocatalytic process for degradation of acid orange 7 dye by using titanium dioxide nanoparticles/graphene oxide nanocomposite as a catalyst. J Environ Manage [Internet]. 2021;292(March):112777. Available from: <https://doi.org/10.1016/j.jenvman.2021.112777>

- [8]. Selvasembian R, Gwenzi W, Chaukura N, Mthembu S. Recent advances in the polyurethane-based adsorbents for the decontamination of hazardous wastewater pollutants. *J Hazard Mater* [Internet]. 2021;417(January):125960. Available from: <https://doi.org/10.1016/j.jhazmat.2021.125960>
- [9]. Paul Guin J, Bhardwaj YK, Varshney L. Mineralization and biodegradability enhancement of Methyl Orange dye by an effective advanced oxidation process. *Appl Radiat Isot* [Internet]. 2017;122(February 2016):153–7. Available from: <http://dx.doi.org/10.1016/j.apradiso.2017.01.018>
- [10]. Machrouhi A, Khiar H, Elhalil A, Sadiq M, Abdenmouri M, Barka N. Synthesis, characterization, and photocatalytic degradation of anionic dyes using a novel ZnO/activated carbon composite. *Watershed Ecol Environ* [Internet]. 2023;5:80–7. Available from: <https://doi.org/10.1016/j.wsee.2022.12.001>
- [11]. Fradj A Ben, Boubakri A, Hafiane A, Hamouda S Ben. Removal of azoic dyes from aqueous solutions by chitosan enhanced ultrafiltration. *Results Chem*. 2020;2.
- [12]. Igwegbe CA, Mohammadi L, Ahmadi S, Rahdar A, Khadkhodai D, Dehghani R, et al. Modeling of Adsorption of Methylene Blue Dye on Ho-CaWO₄ Nanoparticles Using Response Surface Methodology (RSM) and Artificial Neural Network (ANN) techniques. *MethodsX* [Internet]. 2019;6:1779–97. Available from: <https://doi.org/10.1016/j.mex.2019.07.016>
- [13]. Igwegbe CA, Onukwuli OD, Ighalo JO, Umembamalu CJ. Electrocoagulation-flocculation of aquaculture effluent using hybrid iron and aluminium electrodes: A comparative study. *Chem Eng J Adv* [Internet]. 2021;6(March):100107. Available from: <https://doi.org/10.1016/j.ceja.2021.100107>
- [14]. Ogemdi IK, Gold EE. Physico-Chemical Parameters of Industrial Effluents From a Brewery Industry in Imo State, Nigeria. *Adv J Chem A*. 2018;1(2):66–78.
- [15]. Ighalo JO, Iwuozor KO, Igwegbe CA, Adeniyi AG. Verification of pore size effect on aqueous-phase adsorption kinetics: A case study of methylene blue. *Colloids Surfaces A Physicochem Eng Asp* [Internet]. 2021;626(July):127119. Available from: <https://doi.org/10.1016/j.colsurfa.2021.127119>
- [16]. Li H, Zhu X, Zhao J, Ling G, Zhang P. Emerging adsorbents: Applications of sodium alginate/graphene oxide composite materials in wastewater treatment. *J Water Process Eng* [Internet]. 2024;59(March):105100. Available from: <https://doi.org/10.1016/j.jwpe.2024.105100>
- [17]. Aguayo-Villarreal IA, Hernández-Montoya V, Rangel-Vázquez NA, Montes-Morán MA. Determination of QSAR properties of textile dyes and their adsorption on novel carbonaceous adsorbents. *J Mol Liq* [Internet]. 2014;196:326–33. Available from: <http://dx.doi.org/10.1016/j.molliq.2014.04.008>
- [18]. Gad HMM, El-Sayed AA. Activated carbon from agricultural by-products for the removal of Rhodamine-B from aqueous solution. *J Hazard Mater*. 2009;168(2–3):1070–81.
- [19]. Afkhami A, Moosavi R. Adsorptive removal of Congo red, a carcinogenic textile dye, from aqueous solutions by maghemite nanoparticles. *J Hazard Mater*. 2010;174(1–3):398–403.
- [20]. El-Gamal SMA, Amin MS, Ahmed MA. Removal of methyl orange and bromophenol blue dyes from aqueous solution using Sorel's cement nanoparticles. *J Environ Chem Eng* [Internet]. 2015;3(3):1702–12. Available from: <http://dx.doi.org/10.1016/j.jece.2015.06.022>