RESEARCH ARTICLE Am. J. PharmTech Res. 2015; 5(2) ISSN: 2249-3387

AMERICAN JOURNAL OF PHARMTECH RESEARCH

Journal home page: http://www.ajptr.com/

Adsorption of Aqueous Methyl Orange by Lebanese *Eryngium Creticum*

Ali Mroweh[1,2], Akram Hijazi[1*], Hassan Rammal[1], Mohamad Alameh[1],Joumana Toufaily[2,3], Tayssir Hamieh[2]

1. Doctoral School of Science and Technology, Research Platform for Environmental Science (PRASE), Lebanese University, Lebanon.

2. Laboratory of Materials, Catalysis, Environment and Analytical Methods (MCEMA), Lebanese University, Lebanon.

3. School of Mechanical and Materials Engineering, Washington State University, Washington State, United State of America.

ABSTRACT

Using natural adsorbants for the removal of dyes from solutions may represent a new and effective method of dye control and treatment. In this study, the adsorption of methyl orange by Lebanese *Eryngiumcreticum* was evaluated. Removal rates of methyl orange were determined by UV-Vis spectrophotometry and the adsorption process was found to be affected by initial dye concentration, adsorbant concentration, and pH. Adsorption isotherms were also plotted and showed a type III isotherm at pH 2, and a type V isotherm at pH 10. The adsorption of *Eryngiumcreticum* was then compared to other synthetic adsorbants and was found to offer similar adsorption capacity to some.

Keywords: Methyl orange, *Eryngiumcreticum*, adsorption, isotherm.

*Corresponding Author Email: hijazi_akram@hotmail.com
Received 16 February 2015, Accepted 27 February 2015

Please cite this article as: Hijazi A *et al*., Adsorption of Aqueous Methyl Orange by Lebanese *Eryngium Creticum*. American Journal of PharmTech Research 2015.

INTRODUCTION

There is a global increase in the production of dyes. Industries such as textile, cosmetics, pharmaceuticals, and food use dyes extensively despite the fact that they pose great environmental hazards[1]. Azo-dyes, such as methyl orange, account for at least 50% of all dyes[2, 3], and are frequently attributed with being extremely toxic and possibly carcinogenic[2-4]. There is an abundance of published work regarding the removal of these dyes from wastewater. An approach that has been widely studied is adsorption which uses different adsorbents such as zeolites, clays, and polymeric materials[1]. However, most of the adsorbents are synthetic and few researchers have studied the possible uses of natural ones. *Eryngiumcreticum*, belongs to the family *Umbellifereae*, is a perennial plant found mainly in Middle Eastern countries[5, 6]. *E. creticum* was shown to contain considerable amounts of polyphenols[6]. Despite the lack of a universal definition, it is known that polyphenols contain large numbers of phenol structural units[7, 8]. Polyphenols also contain numerous radicals. Such structures may allow different forces between polyphenols and dyes to occur, and optimize dye adsorption efficiency. This paper discusses the possible use of *E. creticum* as an adsorbant of methyl orange, and describes the variation of the adsorption efficiency as a function of pH, amount of adsorbant, and concentration of methyl orange.

MATERIALS AND METHOD

Collection and Extraction of *E. creticum*

Fresh plant was gathered from south Lebanon on spring season between March and May in 2013. Then, plants were well cleaned and washed with water and then dried in the shade and at room temperature and dried inside the limit in humid, well-opened to prevent damage happen to samples. After this period, leaves and stems of the collected plants have been grinded and transformed to powder by a grinder. The powders were preserved in clean plastic containers, kept away from light and heat and moisture until use. 100g of plant powder were macerated in 300mL of distilled water for 12 hours at room temperature, followed by another maceration for 12 hours at 37°C. The macerate obtained was then filtered, the filtrate was lyophilised to produce 5g of dry extract[9].

Methyl Orange Powder

Methyl orange or 4-[4-(Dimethylamino)phenylazo]benzenesulfonic acid sodium salt was obtained from Aldrich.

Preparation of solutions

A 250mg/L stock solution of methyl orange was prepared by mixing 250mg of methyl orange powder with 1 L of distilled water in an erlenmeyer flask, and stirred for 24 hours using a magnetic stirrer. The solution was kept in the dark to prevent some photochemical reactions from taking place, which might interfere with our results.From the stock solution, 100mL of the following solutions were prepared after dilution with distilled water: 0,5,10,20,50,75,100,and 150mg/L. 25 mL of each solution was then added to 50mg of *E. creticum* powder and placed on a rotary shaker for 1 hour to allow the interaction between the plant and methyl orange particles to take place. In order to study this interaction at different pHs, we added few droplets of hydrochloric acid (HCl) or sodium hydroxide (NaOH) to obtain acidic and basic media, respectively, prior to the addition of the plant, while using a pH meter to measure the pH variation. Studies on pHs of 2,3,4,6,8,10, and12 were conducted.After removal from the shaker, the mixture was filtered using a Büchner funnel, and the filtrate was collected[10-12].

Determination of adsorption efficiency

Total adsorption of methyl orange was evaluated using spectrophotometric analysis by measuring the absorbance of methyl orange solutions before addition of *E. creticum* and after its addition (i.e. filtrate). Absorbance was read at 463nm using a UV-Visible spectrophotometer. The different absorbance levels were then compared to determine adsorption values[10-12].

RESULTS AND DISCUSSION

Three main parameters were studied in this experiment: initial dye concentration, concentration of adsorbant (*E. creticum*), and pH.

Effect of initial dye concentration

The increase in dye concentration caused a significant increase in removal efficiency by the plant, which almost doubled from 38% at 5mg/L to 72% at 200mg/L, indicating the presence of a strong linear correlation between the two factors (R^2=0.8681). These results are shown in figure 1. This response can be attributed to one or both the following reasons: (1) the increase in dye concentration triggered an increase in adsorption rate due to the utilization of more binding sites[1], (2) the adsorption of the dye on the adsorbant surface created more sites for other dye particles to bind to.

Effect of adsorbant concentration

Increasing the adsorbant concentration, while maintaining the initial concentration of the dye at 200mg/L, increases the efficiency of adsorption as well. Our data shows that there is a strong linear correlation between the concentration of the adsorbant and the adsorption efficiency (R^2=0.8847), and that the maximum adsorption was at the highest concentration of *E.*

*creticum*used(200mg/L). This is depicted in figure 2, which shows the variation of the optical density of the filtrate as a function of *E. creticum* concentration.

This response may be due to: (1) the increase in the number of binding sites as more adsorbant molecules are added, (2) the formation of complex structures at high *E. creticum* levels which may be able to adsorb methyl orange more strongly or for a longer time.

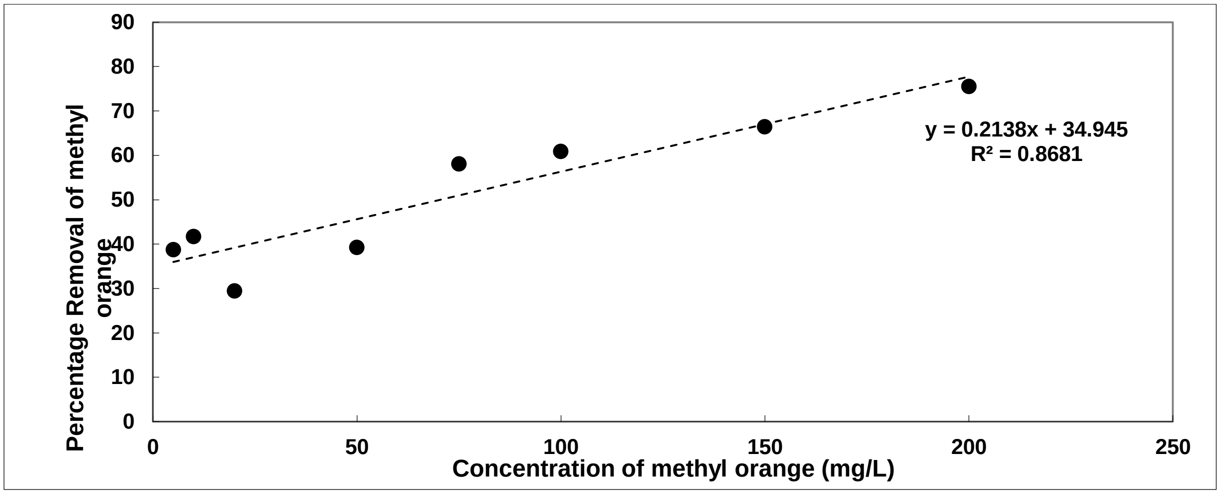

Figure 1: Percentage removal of methyl orange as function of concentration

Effect of pH

Optimum adsorption efficiency was observed at pH 3, where adsorption reached about 80% of initial dye concentration. However, there is no linear correlation between pH and adsorption efficiency, as the values retrieved from this experiment show a highly disorganized scatter plot, in which adsorption efficiency increases and decreases randomly with change in pH. It is important to note, however, that there is a slightly higher adsorbance rate at lower pH (R^2=0.1982) (figure 3).

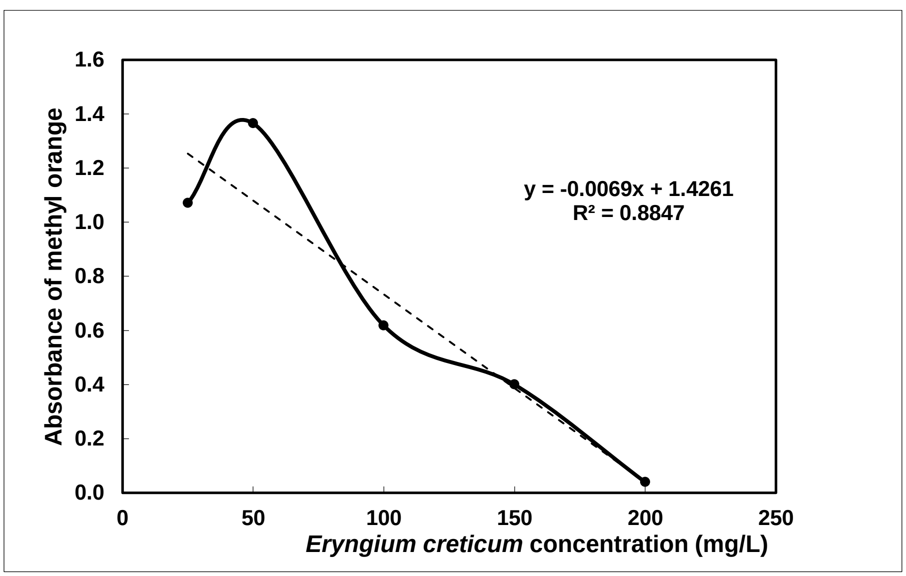

Figure 2 Percentage absorbance of methyl orange as function of concentration

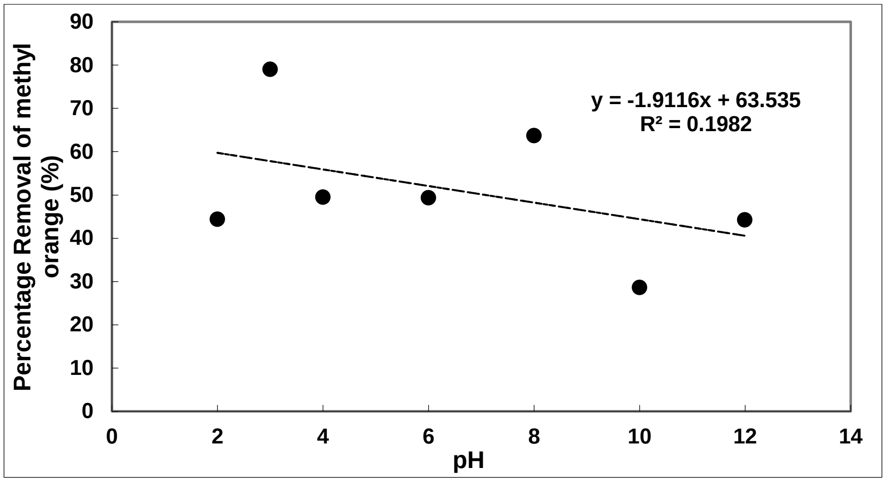

Figure 3 Percentage removal of methyl orange as function of PH

Adsorption isotherm studies

The adsorption of methyl orange by *E. creticum* could be explained by adsorption isotherms. These isotherms were studied at pH 2 and 10 (figures4 and 5) in order to show their behavior at a wide range of pHs, especially considering that methyl orange has a pKa in the range of 4.3-4.5[13, 14], or sometimes reported even less[15]. At pH 2, the adsorption isotherm follows the type III adsorption; an upward sloping convex function which increases exponentially at higher concentrations. Such adsorption type is characterized by weak adsorbate-adsorbant interactions[16], the driving force for the primary adsorption, which lead to the formation of the mono-layer. After the monolayer is formed, adsorbate-adsorbate interactions dominate the adsorption process, resulting in an accelerated increase in adsorption rate[17, 18]. At pH 10, the graph shows a similar shape at the beginning, but forms a "Plateau" at higher concentrations. This characterizes type V isotherms, and can be explained in the same manner as type III isotherms at low concentrations. At higher concentrations, however, there is a stagnation in the adsorption process which could be attributed to the formation of highly adsorbed structures that are not able to undergo any further interaction with methyl orange molecules. At pH 2, methyl orange forms a zwitterion after a hydrogen atom attaches to the azo-group[19]. *E. creticum*, on the other hand, may form protonated particles at such a low pH (pKa of phenol = 10.1)[20]. The presence of these chemical structures could mediate interactions between the adsorbant and the adsorbate through attractions between different charges and dipoles. However, after the monolayer forms, adsorbate-adsorbate interactions increase heavily, possibly through the formation of electrostatic bonds between different methyl orange molecules. At ph 10, methyl orange becomes negatively charged[15, 19, 21, 22] and *E. creticum* may form negatively charged particles as well (pH=pKa). Electrostatic repulsion between methyl orange and *E. creticum* might arise. This would probably explain the slow formation of the monolayer. Zhang and Fang[21] studied the adsorption of methyl orange on charged colloidal silver particles, and concluded that the benzene rings of methyl orange molecules probably allignnext to negatively charged silver particles. This could also happen between methyl orange and *E. creticum* particles, explaining the formation of the monolayer, and between methyl orange molecules themselves, explaining the increase in adsorption rate after the formation of the monolayer. The negative charge of methyl orange, on the other hand, could have mediated the weak overall adsorption capacity (with $Q_{pH2} >> Q_{pH10}$), and the formation of a "Plateau" at higher concentrations, since repulsion forces may interfere in adsorbate-adsorbate interactions. Compared to synthetic adsorbants, *E. creticum* offers similar and satisfactory results, reporting close adsorption capacities, especially at lower pHs[1]. However, some adsorbents report significantly higher capacities[15, 23]. Availability and cost of production must be taken into account before determining the feasability of using *E. creticum* as a methyl orange adsorbant, which are outside the scope of this article.

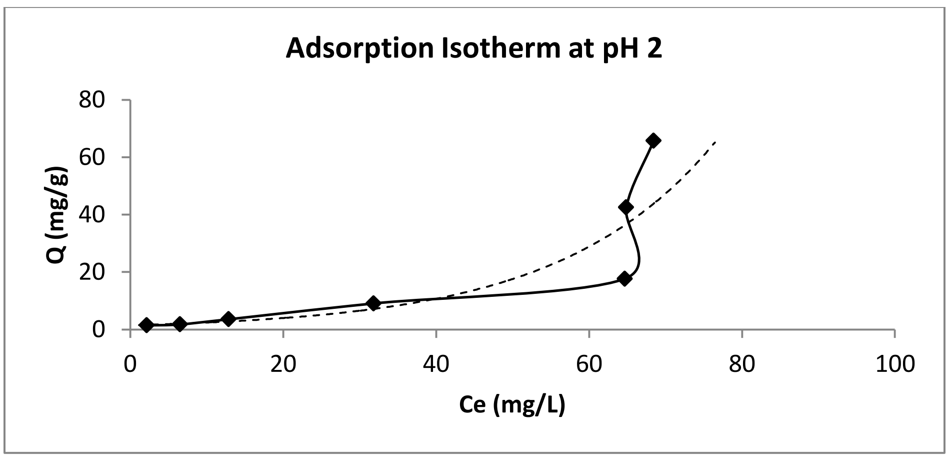

Figure 4: Adsorption capacity as function of methyl orange concentration at PH 2

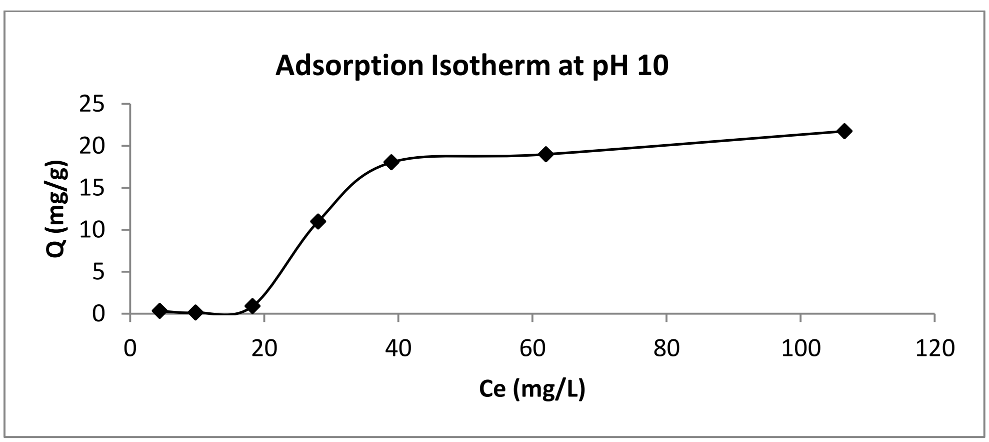

Figure 5: Adsorption capacity as function of methyl orange concentration at PH 10

CONCLUSION

The present study shows that *Eryngium creticum* can be used as a natural adsorbant for the removal of methyl orange from aqueous solutions. The effect of dye concentration, adsorbant concentration, and pH on the removal of methyl orange were studied. Adsorption isotherms were also plotted and studied at pH 2 and pH 10. Adsorption of methyl orange on *E. creticum* was shown to follow a type III isotherm at pH 2 and a type V isotherm at pH 10. In addition, adsorption rates of *E. creticum* were found to be satisfactory compared to other synthetic adsorbants.

REFERENCES

1. Derakhshan MS, Moradi O. The study of thermodynamics and kinetics methyl orange and malachite green by SWCNTs, SWCNT-COOH and SWCNT-NH_2 as adsorbents from aqueous solution. J Ind Eng Chem 2014; 20(5):3186-3194.
2. Kou T, Wang Y, Zhang C, Sun J, Zhang Z. Adsorption behavior of methyl orange onto nanoporous core-shell Cu@Cu_2O nanocomposite. Chem Eng J 2013; 223:76-83.
3. Li H, Guo J, Yang L, Lan Y. Degradation of methyl orange by sodium persulfate activated with zero-valent zinc. Sep Purif Technol 2014;132:168–173.
4. Liu W, Hu Q, Mo F, Hu J, Feng Y, Tang H et al. Photo-catalytic degradation of methyl orange under visible light by MoS2 nanosheets produced by H_2SiO_3 exfoliation. J Mol Catal A- Chem 2014;395:322–328..
5. Küpeli E, Kartal M, Aslan S, Yesilada E. Comparative evaluation of the anti-inflammatory and antinociceptive activity of Turkish Eryngium species. J Ethnopharmacol 2006;107:32-37.
6. Farhan H, Malli F, Rammal H, Hijazi A, Bassal A, Ajouz N et al. Phytochemical screening and antioxidant activity of Lebanese *Eryngium creticum* L. Asian Pacific Journal of Tropical Biomedicine 2012; 2(3):S1217-S1220.
7. Celep G.S., Rastmanesh R., Marotta F. Chapter 43—Microbial metabolism of polyphenols and health. In: Watson RR, Preedy VR, Zibadi S, editors. Polyphenols in Human Health and Disease. Academic Press; San Diego, CA, USA: 2014. pp. 577–589.
8. Vauzour D, Kerr J, Czank C. Plant Polyphenols as Dietary Modulators of Brain Functions. 2014;1:357-370
9. Rammal H, Bouayed J, Desor F, Younos C, Soulimani R. Validation et contribution a l'étude de l'effet antihyperglycémique d'une plante medicinale, le *Momordica charantia* L. Phytothérapie 2009; 7:191-196.
10. Moussawi MA, Rammal W, Hijazi A, Naoufal D, Rammal H, Annan H. Removal of Lead (II) ions from waste water using Lebanese *Scabiosaprolifera* (Carmel Daisy) as adsorbent. Am J PharmTech Res 2014; 4(5): 389-398.
11. Sobh M, Moussawi MA, Rammal W, Hijazi A, Rammal H, Reda M et al.Removal of Lead (II)

Ions from Waste Water by Using Lebanese *Cymbopogon citrates* (Lemon Grass) Stem as Adsorbent. Am J PhytomedClinTherap 2014;2(9):1070-1080.

12. Moussawi MA, Hijazi A, Hamad H, Rammal H, Rammal W, Alameh M,Naoufal D. Biosorption of methylene blue from waste water using *Scabiosaprolifera* (carmel daisy). World J Pharm Res, 2014; 3(8):45-56.
13. de Araujo R, Gomez A, Araujo C. Measurements of pKa of organic molecules using third-order nonlinear optics. ChemPhys Lett 2000; 330:347-353.
14. de Oliveira H. Determination of pKa of dyes by electrical impedance spectroscopy. Microchem J 2008; 88:32-37.
15. Mohammadi N, Khani H, Gupta VK, Amereh A, Agarwal S. Adsorption process of methyl orange dye onto mesoporous carbon material-kinetic and thermodynamic studies. J Colloid Interface Sci 2011; 362(2):457-462.
16. Kiselev AV. Adsorption properties of hydrophobic surfaces. J Colloid Interface Sci 1968; 28:430-442.
17. Somasundaran P. (2004). Encyclopedia of Surface And Colloid Science. New York: Marcele Dekker.
18. Lichtfouse JE, Didier R. Environmental Chemistry: Green Chemistry and Pollutants in Ecosystems. Berlin: Springer, 2005.
19. Akama Y, Tong A, Ito M, Tanaka S. The study of the partitioning mechanism of methyl orange in an aqueous two-phase system. Talanta 1999; 48:1133-1137.
20. Shen YH. Phenol sorption by organoclays having different charge characteristics. Colloids and Surfaces A: PhysicochemEng Aspects 2004; 232:143-149.
21. Zhang A, Fang Y. Adsorption orientations and interactions of methyl orange on negatively and positively charged colloidal silver particles. J Colloid Interface Sci 2007; 305(2):270-274.
22. Huang R, Liu Q, Huo J, Yang B. Adsorption of methyl orange onto protonated cross-linked chitosan. Arabian Journal of Chemistry 2013;doi:10.1016/j.arabjc.2013.05.017
23. Tanhaei B, Ayati A, Lahtinen M, Sillanpaa M. Preparation and characterization of a novel chitosan/Al_2O_3/magnetite nanoparticles composite adsorbent for kinetic, thermodynamic and isotherm studies of Methyl Orange adsorption. ChemEng J 2015; 259(1):1-10.