OPEN ACCESS

Online ISSN:2353-0391

Algerian Journal of Natural Products
www.univ-bejaia.dz/ajnp

Type of the Paper (Article)

Removal of Xylenol Orange from Aqueous Solution by Adsorption on Polyurethane Foam

Samah Ali [1,2] , Bushra Alharbi [1,*]

[1] Chemistry Department, College of Science, Taibah University, Al-Madinah Al-Munawarah, Saudi Arabia.
[2] The National Organization for Drug Control and Research, Al-Agouzah, Giza, Egypt.
** Corresponding author: E-mail: boooshra@taibahu.edu.sa*
Tel.: +966565153313

Received: 08/10/2020 /Accepted: 05/12/2020

Abstract: A simple, low cost and fast method for the removal of xylenol orange from wastewater using poly urethane foam. The maximum removal was obtained by studying different parameter such as pH, contact time, adsorbent dose, and drug capacity. The optimum conditions for the removal of xylenol orange at pH=10 by using 0.1 g of PUF with contact time 60 min and 250 rpm The experimental isotherm data was studied using Langmuir and Freundlich isotherms. The results indicate that Langmuir isotherm can describe the adsorption process with adsorption capacity (qm) equal to 0.904 mg/g and with correlation coefficient (R^2) equal to 0.972.

Keywords: *adsorption;dyes; xylenol orange; polyurethane foam; UV-Vis spectrophotometry*

I. Introduction

Xylenol Orange (XO), 3,3'-bis[N,Nbis(carboxymethyl)-aminomethyl]-ocresolsulfonphthalein is anionic organic dye as shown in Figure 1(a) [1, 2]. It is most commonly used for determination of heavy metals. XO used in certain processes in the manufacturing and textile industries [3]. Groundwater and soils pollution has been widespread in the last few decades due to synthetic organic chemicals [4]. Dye wastes, consider as one of the organic pollutants , remain in the water in large amounts and cause environmental problems which reduces light penetration and photosynthesis efficiency of aquatic plants. In addition most dyes are toxic to humans, microorganisms, and fish species. The presence of dyes in water is highly visible and undesirable even in very low concentrations[6]. Dyes have many uses in industry such as textiles, rubber, paper, Plastic, leather and cosmetics. Among these different industries, the textile industry takes first place in the use of various types of dyes to paint its products [7]. Dyes can be classified according to charge into anionic, cationic and nonionic compounds. Among them, anionic dyes are widely used [4]. Removal of OX from water is very important to protect aquatic and terrestrial life because the XO causes a variety of health problems for humans and aquatic animals [8]. There are many techniques for determination of dyes such aselectrochemistry [9], voltammetry [10], high performance liquid chromatography [11], capillary electrophoresis [12] and UV–vis spectrophotometry [13]. UV-Vis spectrophotometry is most commonly used as a dye detection method, and it has many advantages which are high efficiency, simplicity, good reliability and low cost [14].

Several methods have been used to remove dye from water such as adsorption [15], Electrocoagulation [16], Photocatalytic [17]. From all the adsorption is the most attractive method for wastewater treatment due to its simplicity, low costs and the ability to provide efficient processes. Adsorption can remove both organic and inorganic pollutants [3]. Biosorbents are biological materials; they can be easily produced using inexpensive growth media or obtained as an industrial by-product [18]. Biosorbents have the ability to adsorb and remove pollutants from the aquatic environment.

Biosorbents have advantages over conventional adsorbents such as easy availability, low cost, attractive adsorption efficiency, easy operation, satisfactory reuse, and prevention of a second contamination [19]. Polyurethane foam (PUF) is a polymer that has polar and non-polar groups as shown in Figure 1(b) hence can adsorb a wide variety of chemicals [20]. It is one of the most versatile porous polymer materials [21]. It has been used recently to remove contaminants from water by adsorption [22]. PUF as an absorbent has many advantages such as low cost, high mechanical strength, reusability and flexibility on a scale, resistance to the growth of fungi and bacteria, and lack of toxicity to living organisms [23]. On our work removal of XO dye by PUF from the aqueous solution and several parameters were studied such as pH, contact time, adsorbent dose, and dye capacity. Figure 2 represent simplest diagram for proposal work.

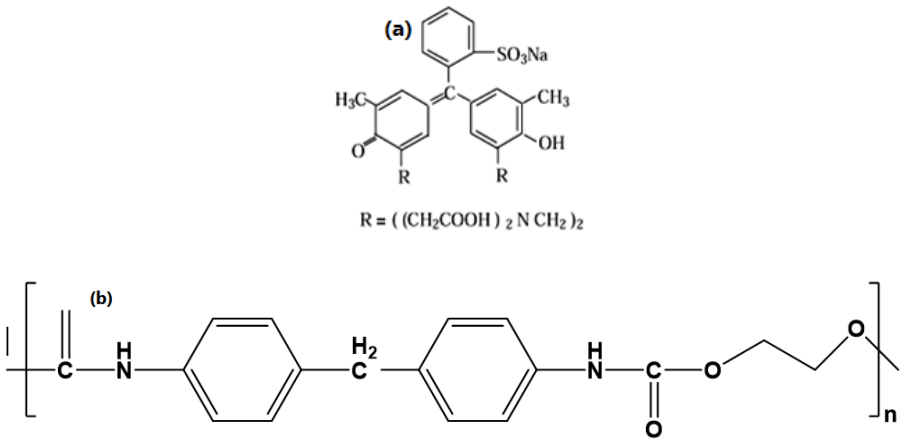

Figure 1. *Chemical structure of (**a**) Xylenol Orange and (**b**) Polyurethane foam (PUF).*

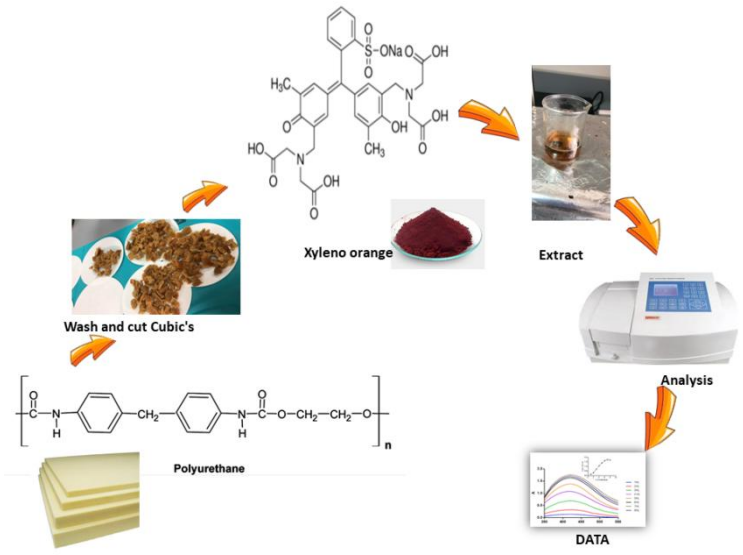

Figure 2. *Simplest diagram for proposal work.*

II. Experimental Section

II.1. Chemicals and Reagents

All reagents used had been bought from Panreac Applichem Company. All chemicals substances used within the experiments have been of analytical grade and bought from Aldrich Chemical Co Open cell polyether-type PUF (31.6 kg m^{-3}), was given by the Egyptian company for foam production, Cairo, Egypt. All laboratory glassware is soaked in the chromic acid solution overnight.

Buffer solutions were prepared with using 0.1M acetic acid – 0.1 M sodium acetate for pH from 3.6 to 5.6, 0.1 M sodium phosphate monobasic – 0.1 M sodium phosphate dibasic for pH from 6.4 to 8, ammonium chloride – ammonia solution for pH 10. The buffer solutions are prepared with pure deionized water.

II.2. Apparatus

UV–Vis spectrophotometer Model G10S (Thermo Fisher Scientific) was used to measure the absorbance and spectrophotometric of the dye using a plastic cell. Hanna digital pH-meter (HANNA Instruments) was used to measure the pH of the aqueous solutions.

II.3. Adsorption experiments

The PUF was cut into small portions and soaked in 500 mL of 2M HCl for 120 min to remove all inorganic impurities and washed with deionized water. Finally soaked in acetone for 30 min and allowed to dry at room temperature.

To record the adsorption conditions 12.5 ml of XO dye solution (80 ppm) mixed with 0.1 g PUF and adding 2.5 ml of different buffer solution (pH 5.6 -11), then shaking for 60 min. After completion of the adsorption, the removal rate of XO was measured.

To investigate the amount of sorbent, different amount of PUF (0.1 - 1.5 g) add to 12.5 ml XO dye solution (80 ppm); at pH=10. Shaking time also studied at a speed of 250 rpm for various times interval (10 to 120 min). The concentration of XO was measured spectrophotometry at λ_{max} 440 nm. The percentage of removal (R%) and the amount of dye uptake per unit of adsorbent (q) was calculated by using following equations.

$$\mathbf{R}\% = (\mathbf{Ci} - \mathbf{Ce}) \times \mathbf{100}/\mathbf{Ci} \quad (1)$$

$$\mathbf{q} = (\mathbf{Ci} - \mathbf{Ce}) \times \mathbf{V}/\mathbf{m} \quad (2)$$

Where C_e and Ci (mg/L) were the final and initial concentrations of XO in solution, respectively. V is the volume of dye solution (mL), and m is the weight of the adsorbents (g) [23].

III. Results and Discussion

III.1. Effect of initial dye concentration

Figure 3 shows the percentage removal adsorption as a function of different XO concentration. The results show that the percentage removal of XO by PUF was increased with decreasing dye concentration. This attribute to low ratio number of dye molecules to the active sites available on the adsorbent, which indicates the possibility of interaction between the XO molecules and the active sites available in the adsorbent. The active sites become saturated, with an increase in the number of dye molecules relative to the number of surface active sites on the adsorbent. At high concentration there would no longer be any active sites on the PUF available for the molecules of the dye [24]. The optimum XO concentration was found at 2 ppm in which the removal efficacy R% equal 99.58 %.

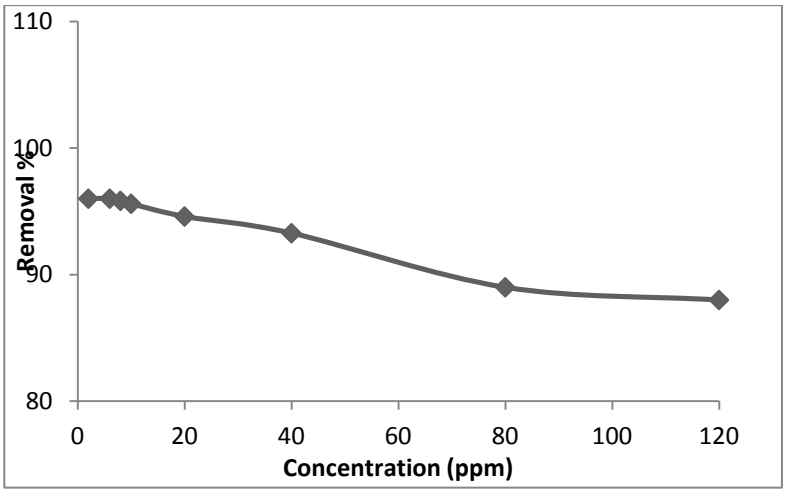

Figure 3. *Effect of initial XO concentration on removal XO by PUF.*

III.2. Effect of pH

The adsorption of XO was studied as a function of pH as presented in Figure 4. At high pH value indicates a favorable adsorption of XO on PUF because of the van der Waals and electrostatic attractive forces submit between negatively charged ions (OH^-) in the adsorbate and positively charged ions (H+) on the surface of the PUF. So the result shows the optimum pH value at pH= 10 [25].

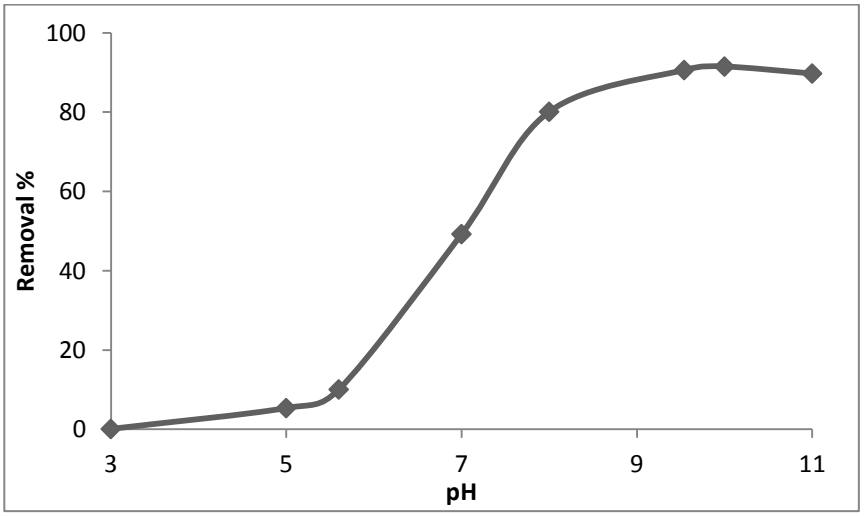

Figure 4. *Effect of pH on removal XO by PUF.*

III.3. Effect of contact time

The effect of contact time on adsorption of XO on PUF was investigated. As shown in Figure 5, the percentage removal gradually increased with the increasing of the contact time until 60 min, which the amount of adsorbed dye reached the equilibrium state. Followed by decreasing of percentage removal to 120 min which attributed to reduced surface area and saturated the active sites of PUF [26].

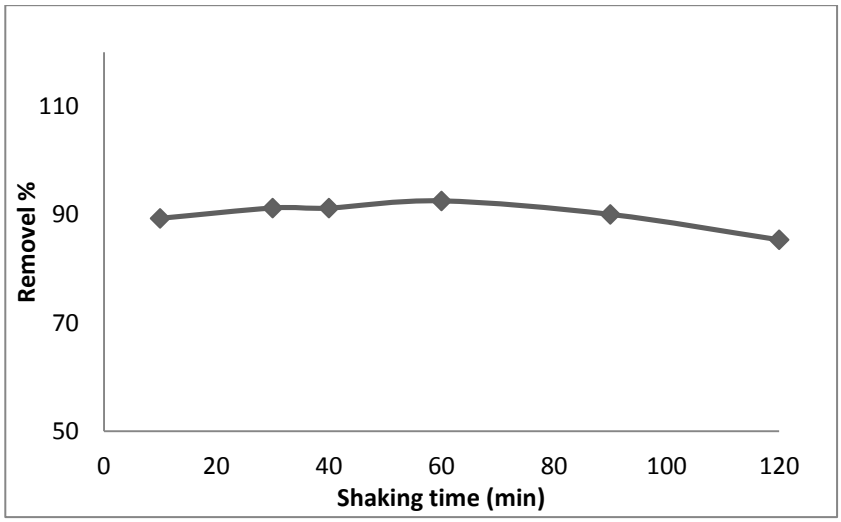

Figure 5. *Effect of contact time on removal XO by PUF.*

III.4. Effects of adsorbent amount

The adsorption of XO on PUF was studied according to different of adsorbent amount. The results show that the percentage of the removal of XO increases with increasing PUF dose. However, as shown in Figure 6 when the addition of PUF exceeded 0.1 g, the removal rate decreased with an apparent intracellular dissolution phenomenon. This result indicates that the overloading of the adsorbent reduces the efficiency of the PUF. Furthermore, a higher adsorbent dose could result in insufficient binding between XO and the chelation sites on the surface of the adsorbent, which could lead to a lower removal rate [22]. Thus, the optimum adsorbent amount was 0.1 g.

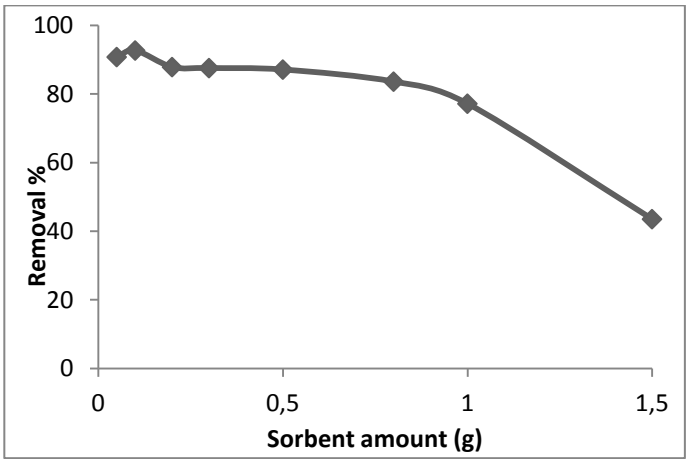

Figure 6. *Effect of adsorbent amount on removal XO by PUF.*

III.5. Recycle and regeneration

The PUF adsorbent was regenerated with HCl solution. Figure 7 shows that the percentage removal of XO on PUF decrease with adsorption cycles but the reused PUF still had the capacity to adsorb XO.

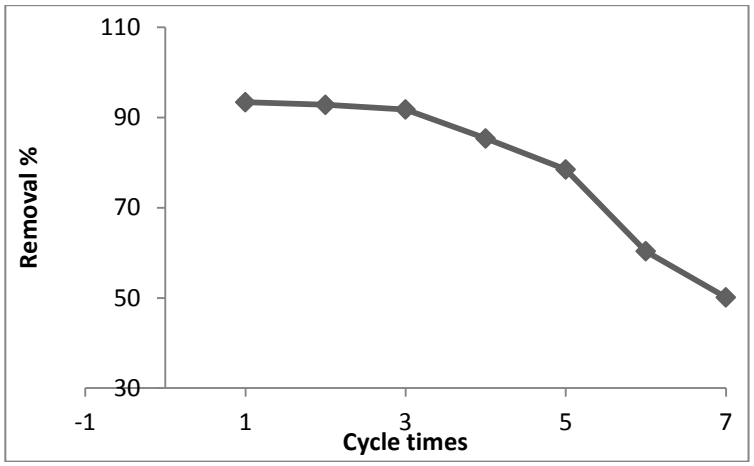

***Figure 7**. Effect of recycle PUF on removal XO*

III.5. Adsorption isotherms

Adsorption isotherms describe how adsorbents interact with adsorbent materials, so it can be used to optimize their application [4]. The most generally used adsorption isotherm equations are Langmuir and Freundlich isotherms, which was used in this study.

The Langmuir isotherm model based on the premise that the surface of the adsorbents is uniform and the energy of each adsorption center is the same, and under certain conditions, the adsorption rate of adsorption is equal to the rate of desorption, then the adsorption equilibrium is reached [27]. Linear form of the Langmuir model can be written by Equation 3.

$$\mathbf{Ce/qe = 1/(KL \times qm) + Ce/qm} \quad (3)$$

Where, the equilibrium concentration of XO ($mg.L^{-1}$) is defined by Ce, qe is the amount of XO adsorbed at equilibrium ($mg.g^{-1}$), K_L is the Langmuir constant (L/mg) and qm is the amount of adsorption corresponding to complete coverage (mg/g) [28]. A linear plot of (*Ce*/*q*e) versus *C*e is obtained from the model as shown in Figure 8.

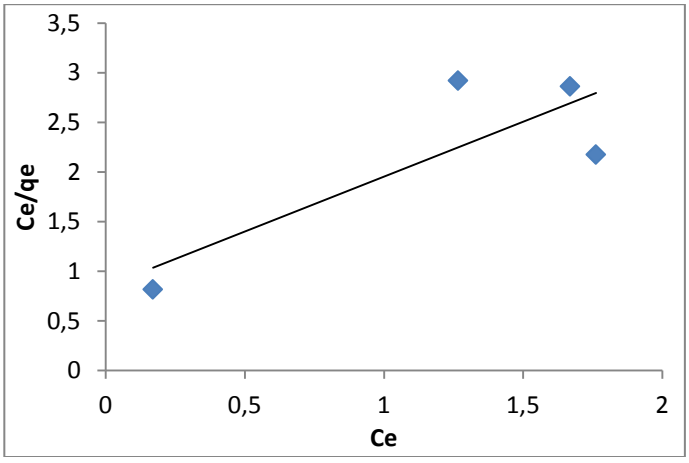

***Figure 8.** Langmuir isotherm model.*

The Freundlich isotherm model considered to be reversible and can be used to describe the multi-layer adsorption [27, 28]. The linear form of Freundlich isotherm model can be expressed by Equation 4.

$$\mathbf{Log\ qe = \log KF + \frac{1}{n} \log Ce} \quad (4)$$

Where,
qe: represent the amount of solute adsorbed per unit weight of adsorbent ($mg \cdot g^{-1}$),
Ce: the concentration of dye at equilibrium ($mg \cdot L^{-1}$),
and KF and n are the Freundlich constants [27].

A linear plot of log qe versus log Ce is obtained from the model as shown in Figure 9. Freundlich and Langmuir were able to explain the adsorption behavior of XO on PUF. Freundlich model can predict equilibrium adsorption behavior better, and the correlation coefficients (R^2) of the Freundlich model is higher than that of the Langmuir model. Table 1 indicates the adsorption parameters obtained from the simulated isotherm models. Many researchers have studied the removal of XO for various applications. Table 2 shows the comparison of the adsorption capacity for removing XO by different adsorbents.

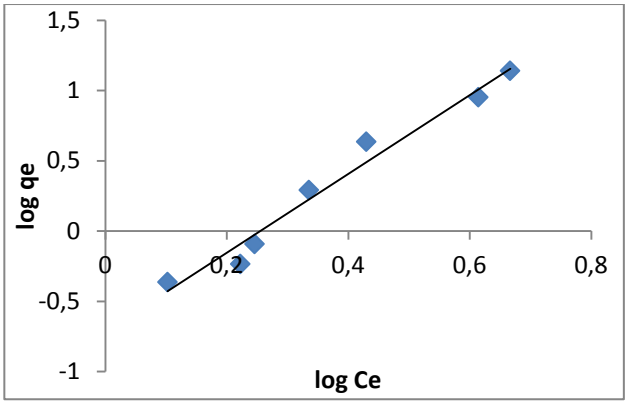

Figure 9. *Freundlich isotherm model.*

Table 1. *Adsorption parameters for isotherm models.*

sorbent	Langmiur Isotherm			Freundlich Isotherm		
	q_m (mg g^{-1})	b (L mg^{-1})	R^2	K_F	n	R^2
PUF	0.904	1.304	0.681	0.1923092	0.3561254	0.972

Table 2. *Comparison of the adsorption capacity for removing XO by different adsorbents.*

Adsorbent	Adsorption capacity (mg/g)	Removal efficiency	Reference
Bi-porous chitosan foams	122 mg/g	90%	[4]
Silica nanoparticles	9.08 mg/g	--	[5]
Sodium dodecyl sulfate (SDS) SMES	--	89.77%	[29]
Vitreous tuff mineral(VT)	45.17 mg/g	--	[16]
Molecularly Imprinting Polymers(MIP-R2)	--	80%	[7]
Coal ash	0.74mg/g	80%	[30]
This study	0.904 mg/g	99.58%	--

IV. Conclusion

This study introduced PUF as adsorbent to remove XO by adsorption which is characterized by high efficiency, low cost and stability in an aqueous solution. It was found that the best values for the experimental parameters 10 pH, 60 min, 0.1 g and 250 rpm, corresponding to a concentration of XO, pH, contact time, dose and stirring speed, respectively, to achieve maximum removal efficiency of at least 99.58%. The adsorption process follows the Freundlich isotherm, while Langmuir isotherm presented the maximum adsorption capacity for XO at 0.904 mg/g.

V. References

[1] Saleem, B.A. Spectrophotometric determination of sulphite and thiamin hydrochloride via Xylenol orange dye. *Journal of university of Anbar for Pure science*12 (2018)18-27.

[2] Longhinotti, E.; Pozza, F.; Furlan, L.; Sanchez, M.d.N.d.M.; Klug, M.; Laranjeira, M.; Fávere, V.T. Adsorption of anionic dyes on the biopolymer chitin. Journal of the Brazilian Chemical Society9 (1998)435-440.

[3] Aguiar, J.; Cecilia, J.; Tavares, P.; Azevedo, D.; Castellón, E.R.; Lucena, S.; Junior, I.S. Adsorption study of reactive dyes onto porous clay heterostructures. *Applied Clay Science*135 (2017)35-44.

[4] Wang, X.; Kong, W.; Xie, W.; Li, L.; Liu, Y.; Wu, X.; Gao, J. Bi-porous bioinspired chitosan foams with layered structure and their adsorption for xylenol orange. *Chemical engineering journal*197 (2012)509-516.

[5] Zhang, L.; Zhang, G.; Wang, S.; Peng, J.; Cui, W. Cation‐ functionalized silica nanoparticle as an adsorbent to selectively adsorb anionic dye from aqueous solutions. *Environmental Progress & Sustainable Energy*35 (2016)1070-1077.

[6] Gebrezgiher, M.; Kiflie, Z. Utilization of Cactus Peel as Biosorbent for the Removal of Reactive Dyes from Textile Dye Effluents. *Journal of Environmental and Public Health*2020 (2020).

[7] Bhawani, S.A.; Daud, N.A.B.; Bakhtiar, S.; Roland, R.M.; Ibrahim, M.N.M. Synthesis of Molecularly Imprinting Polymers for the Removal of Xylenol Orange from Water. *Nature Environment and Pollution Technology*19 (2020) 825-830.

[8] Horakova, E.; Barek, J; Vyskocil, V. Determination of Methyl Violet 2B using Polarographic and Voltammetric Methods at Mercury Electrodes. *Analytical Letters*49 (2016)56-65.

[9] Chen, L.; Hu, J.; Zhang, W.; Zhang, J.; Guo, P.; Sun, C. Simultaneous determination of nine banned azo dyes in foodstuffs and beverages by high-performance capillary electrophoresis, *Food analytical methods*8 (2015)1903-1910.

[10] Omidi, F.; Behbahani, M.; Samadi, S.; Sedighi, A.; Shahtaheri, S.; Coupling of molecular imprinted polymer nanoparticles by high performance liquid chromatography as an efficient technique for sensitive and selective trace determination of 4-chloro-2-methylphenoxy acetic acid in complex matrices. *Iranian journal of public health*43 (2014) 645–657.

[11] Sha, O.; Zhu, X.J. Simultaneous ionic liquid aqueous two-phase extraction and spectrophotometric determination of amaranth and brilliant blue in food samples. *Journal of Analytical Chemistry*70 (2015)558-565.

[12] Behbahani, E.S.; Dashtian, K.; Ghaedi, M.; Fe/Co-chalcogenide-stabilized Fe3O4 nanoparticles supported MgAl-layered double hydroxide as a new magnetically separable sorbent for the simultaneous spectrophotometric determination of anionic dyes. *Microchemical Journal*152 (2020).

[13] Almeida, C.; Debacher, N.; Downs, A.; Cottet, L.; Mello, C. Removal of methylene blue from colored effluents by adsorption on montmorillonite clay. *Journal of colloïd and interface science*332 (2009) 46-53.

[14] Vinothkumar, K.; Sugumaran, T.; Venkateshwari, S. Electrocoagulation coupled with adsorption for effective removal of eosin yellow and nigrosin dyes in aqueous solution. *Journal of Applied and Natural Science*11 (2019) 97-106.

[15] Mohammed, N.A.; Alwared, A.I.; Salman, M.S.; Photocatalytic Degradation of Reactive Yellow Dye in Wastewater using H2O2/TiO2/UV Technique. *Iraqi Journal of Chemical and Petroleum Engineering*21 (2020)15-21.

[16] Garrudo-Guirado, M.; Blanco-Flores, A.; Toledo-Jaldin, H.; Sánchez-Mendieta, V.; Vilchis-Néstor, A. Reuse of sustainable materials for xylenol orange dye and copper (II) ion ammoniacal removal. Journal of environmental management206 (2018) 920-928.

[17] Pathak, B.; Gupta, S.; Verma, R. Biosorption and Biodegradation of Polycyclic Aromatic Hydrocarbons (PAHs) by Microalgae. Green Adsorbents for Pollutant Removal; G. Crini, E. Lichtfouse; Springer International Publishing: Cham, 2018; pp. 215–247.

[18] Huang, D.; Li, B.; Ou, J.; Xue, W.; Li, J.; Li, Z.; Li, T. Chen, S.; Deng, R.; Guo, X. Megamerger of biosorbents and catalytic technologies for the removal of heavy metals from wastewater: Preparation, final disposal, mechanism and influencing factors. *Journal of Environmental Management*261 (2020).

[19] Marlina, M.; Iqhrammullah, M.; Darmadi, D.; Mustafa, I.; Rahmi, R. The application of chitosan modified polyurethane foam adsorbent. *Rasayan J. Chem*12 (2019)494-501.
[20] Moghaddam, S.T.; Naimi-Jamal, M.R.; Rohlwing, A.; Hussein, F.B.; Abu-Zahra, N. High Removal Capacity of Arsenic from Drinking Water Using Modified Magnetic Polyurethane Foam Nanocomposites. *Journal of Polymers and the Environment*27 (2019) 1497-1504.
[21] Lefebvre, L.; Agusti, G.; Bouzeggane, A.; Edouard, D. Adsorption of dye with carbon media supported on polyurethane open cell foam. *Catalysis Today*301 (2018)98-103.
[22] Zhao, W.; Zhou, T.; Zhu, J.; Sun, X.; Xu, Y. Adsorption of cadmium ions using the bioadsorbent of Pichia kudriavzevii YB5 immobilized by polyurethane foam and alginate gels. *Environmental Science and Pollution Research*25 (2018)3745-3755.
[23] Vimonses, V.; Lei, S.; Jin, B.; Chow, C.W.; Saint, C. Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials. *Chemical Engineering Journal*148 (2009) 354-364.
[24] Gebreslassie, Y.T. Equilibrium, Kinetics, and Thermodynamic Studies of Malachite Green Adsorption onto Fig (Ficus cartia) Leaves. *Journal of Analytical Methods in Chemistry*2020 (2020).
[25] Popoola, L.T.; Aderibigbe, T.A.; Yusuff, A.S.; Munir, M.M. Brilliant green dye adsorption onto composite snail shell–rice husk: Adsorption isotherm, kinetic, mechanistic, and thermodynamics analysis. *Environmental Quality Management*28 (2018)63-78.
[26] Sabah, I. Adsorption of Congo Red Dye from Aqueous Solutions by Wheat husk. Journal of Engineering, 25 (2019)72-84.
[27] Wang, Q.; Liang, L.; Tian, G.; Mao, Q.; Meng, X. Adsorption of Azo Dye Malachite Green onto Rice Wine Lees: Kinetic and Adsorption Isotherms. *Nature Environment and Pollution Technology*19 (2020)563-570.
[28] Wang, Q.; Liang, L.; Xi, F.; Tian, G.; Mao, Q.; Meng, X. Adsorption of Azo Dye Acid Red 73 onto Rice Wine Lees: Adsorption Kinetics and Isotherms. *Advances in Materials Science and Engineering*2020 (2020).
[29] Shakeel, F.; Haq, N.; Alanazi, F.K.; Alsarra, I.A. Removal of xylenol orange from its aqueous solution using SDS self-microemulsifying systems: optimization by Box–Behnken statistical design. *Environmental Science and Pollution Research*21 (2014)5187-5200.
[30] Ishaq, M.; Saeed, K.; Ahmad, I.; Sultan, S.; Akhtar, S. Coal ash as a low cost adsorbent for the removal of xylenol orange from aqueous solution. Ir*anian Journal of Chemistry and Chemical Engineering (IJCCE)*33 (2014)53-58.