



An efficient cheap source of activated carbon as solid phases for extraction and removal of Congo Red from aqueous solutions

Tahrer N. Majid ^a and Ali A. Abdulwahid ^{a,*}

^aUniversity of Basra, College of Science, Chemistry Department, PO Box 49, Basra, Iraq,

ARTICLE INFO:

Received 17 May 2022

Revised form 28 Jul 2022

Accepted 19 Aug 2022

Available online 29 Sep 2022

Keywords:

Solid phase extraction,
Active carbon,
Congo Red,
Enrichment factor,
UV-Vis technology

ABSTRACT

The present study reported the preparation of solid phases from various available and cheap natural sources represented by activated carbon to remove the polluting dye Congo Red (CR). Activated carbon derived from the leaves of the Consocarpus plant (C/AC) and Ziziphus Spina-Christi plant (Z/AC) and Myrtus plant (M/AC) by chemical activation. The prepared solid phases were diagnosed and examined using FTIR, FESE, and XRD. The results of the study indicated that the best amount for the solid phase was 0.25 g for the three solid phases used against dye, the optimal concentration of the CR was 100 mg L⁻¹, and the optimum acidity function was equal to 5 with a volume of 25 mL, as the optimization experiments indicated that the best flow rate of the eluting solution was equal to 0.5 ml min⁻¹. The elution processes were carried out using several solvents different in polarity and it was found that 8 mL of DMSO achieved the best percentage of recovery (%R). Also, this study included calculating adsorption capacity based on the optimal conditions that were obtained by applying Langmuir and Freundlich isotherm models, and q_{max} , according to the Langmuir model, was (21.74, 23.53, 22.17) mg g⁻¹ for (Z/AC), (C/AC), and (M/AC) adsorbents, respectively.

1. Introduction

In recent years, human pollution of natural waters has led to a significant reduction in operational freshwater resources on Earth [1]. These pollutants from multiple sources have caused significant environmental and health problems that threaten society and living organisms [2, 3]. Many contaminants such as toxic heavy metals, and organic contaminants, such as dyes, pesticides, drugs, degraded organic matter, and so on, are present in polluted waters [4]. Among these pollutants are dyed [5]. A dye is a coloring substance that can be natural, semi-synthetic, or fully synthetic and blend with the substrate to

which it is applied. Natural dyes can be non-toxic compared to synthetic dyes due to their natural origin. The primary sources of pollution of synthetic dyes are the textile, rubber, paper, plastic, printing, paint, and leather industries [6]. It is estimated that about 10,000 types of artificial and natural dyes are produced annually worldwide, with a significant number of dyes being wasted during manufacturing and application processes [7]. The main reason is the incomplete adhesion of the paints to the layers when painting. The amount of unstable dyes in textile effluents is higher than that of effluents discharged by other industries [8]. Many chemicals and dyes remain unused during the dyeing process of textiles, releasing excess liquid dye into the environment. It is estimated that textiles subject

*Corresponding Author: Ali A. Abdulwahid

Email: ali.abdulwahid@uobasrah.edu.iq

<https://doi.org/10.24200/amecj.v5.i03.205>

to dyeing can absorb about 80% of dye liquor due to their limited adsorption capacity [9]. Of all the colors, "azo" colors are most often used to dye different substrates. They are complex in nature and are potentially carcinogenic. Due to the larger molecular structures, their decomposition products are also toxic [10]. If azo dyes are absorbed into the soil from the water, they can alter the chemical and physical properties of the soil. This can lead to the destruction of the vegetation in the environment; if the toxic chemical dyes remain in the soil for a long time, they also kill beneficial microorganisms in the soil, significantly affecting agricultural fertility [11]. Therefore, these toxic dyes should be disposed of from wastewater as much as possible before they are released into terrestrial or aquatic resources in an environmentally sound manner [12]. The search for efficient and safe technologies for removing organic paints from aquatic systems is of great interest for environmental protection. The best water treatment methods chosen depend on several factors, including the nature, quantity and quality of the paint materials in the systems analyzed [13]. Great attention has been paid to technologies for removing paint from wastewater, and many chemical, biological and physical methods have been developed for this purpose [14,15], including adsorption, chemical oxidation, photocatalysis, electrochemical oxidation, biodegradation, ion-exchange filtration, coagulation/flocculation, membrane filtration, catalytic degradation and so on. Most conventional methods have major drawbacks of low selectivity, high power consumption, and low color degradation [16]. Many attempts have been made today to develop

new selective and sensitive techniques for the purification of samples and separation of selected materials, and solid phase extraction (SPE) is the most widely used method [17]. As SPE for sample pretreatment offers several advantages, including fast separation, low cost, low solvent consumption, high enrichment efficiency and recovery rates, short processing times, no emulsion formation, and the ability to combine with many advanced detection methods [18], simple composition, high recovery and high enrichment factor. The basic principle of the elements/species of particular interest is to transfer the target elements/species from the sample matrix to the active site of the SPE adsorbent. The sorbent is the main factor that determines the selectivity, sensitivity, and extraction/absorption dynamics of the relevant method [19]. In this study, three natural materials were selected to convert them into activated carbon and use the products as a solid phase in the study of the solid phase extraction technology (SPE), where *Ziziphus Spina-Christi* leaves, *Consocarpus* leaves and *Myrtus Communis* leaves were used. Materials in the preparation of solid phases (Z/AC), (C/AC) and (M/AC) respectively to remove Congo red (CR) in aqueous solutions using SPE under optimal conditions.

This paper aims to investigate the applicability of activated carbon prepared from cheap and available natural sources as a solid phase in SPE for the purify water contaminated with organic Congo red (CR) dye, [1-naphthalene sulfonic acid, 3, 30-(4, 40-biphenylenebis (azo)) bis (4-amino-) disodium salt] (Fig. 1).

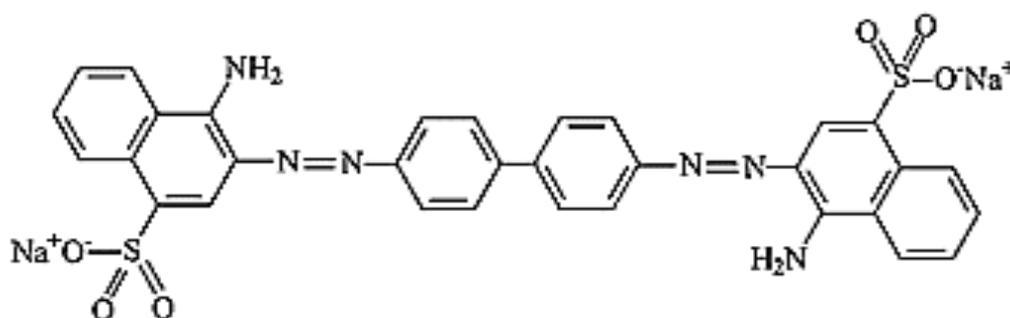


Fig. 1. Chemical structure of Congo red

2. Experimental

2.1. Chemicals and Materials

Chemical reagents including Congo Red (CR), 85% dye content ($C_{32}H_{22}N_6Na_2O_6S_2$, Mw: 696.665 g mol⁻¹) purchased from (Pub Chem). A stock solution (100 mg.L⁻¹) of (CR) was prepared by dissolving the required amount of dye in distilled water. The pH was adjusted with 0.1 mol L⁻¹ of NaOH (Univar) and 0.1 mol.L⁻¹ HCl (AnalaR) and measured with a pH meter (model SD 300, Germany). The potassium hydroxide (KOH), (Sigma-Aldrich) was used to activate the carbon that was prepared from multiple natural sources (Ziziphus Spina-Christi leaves, Consocarpus leaves, and Myrtus communis leave). The ethanol, methanol, dimethyl sulfoxide (DMSO), n-Hexane, and toluene (Sigma-Aldrich) were used in the solid phase elution to recover the dye. Distilled water was used throughout this study. AC was distinguished by FT-IR, XRD, TEM and SEM technologies. The absorbance of the CR dye solution was measured at the wavelength of 494 nm, using a UV-visible spectrophotometer (PG Instrument T80 + UV/VIS model). The percentage of dye removal efficiency, R and the amount of CR dye adsorbed per unit weight of adsorbent at time t, qt (mg g⁻¹) was calculated as Equation 1 and 2:

$$\%Recovery = \frac{\text{concentration of dye recoverd on extraction}}{\text{original concentration of dye}} \times 100\%$$

(Eq.1)

$$q = \frac{(C_o - C_e)V}{M}$$

(Eq.2)

Where C_e is the concentration of CR at time t, C_o is the initial dye concentration (mg L⁻¹), M is the mass of adsorbent (g) and V is the volume of solution (L).

2.2. Activated carbon preparation

Three categories of activated carbon were produced from Ziziphus Spina Christi leaves, Consocarpus leaves and Myrtus communis leaves, and were denoted by (Z/AC), (C/AC) and (M/AC) respectively. The

leaves of the plants were collected and washed well with distilled water; then each substance was boiled in two liters of water for two hours, to remove other water-soluble organic and phenolic compounds, then dried at 70°C in Oven for 8 hours. Subsequently, they were crushed and sieved (40–60 mesh). Afterward, 125 g of each type of dried plant leaf powder was used as the initial amount to produce every kind of activated carbon and impregnation of the plant leaves in a potassium hydroxide KOH (25%) by using a solution (KOH) to solid (plant leaves powder) ratio of 3:1 for 24 h, and then rinsed with distilled water several to reach the pH of the washing liquid. Then, the washed solid samples were dried at 100 °C; then pyrolyzed in a muffle furnace at 500 °C carbonization temperature for 1 hour. After that, the samples were washed with deionized water many times until the pH of the solution was equal to the pH of the distilled water. The resulting activated carbon was dried up at 100 °C and kept dry till usage in the experiment [20,21].

2.3. Solid phase extraction

The solid phase extraction method includes three basic stages, column preparation, loading, and elution [22,23]. The column of the polypropylene cartridge was prepared (Fig. 2). The column was filled with a permeable polypropylene film (disc) with a thickness of 1 mm. Four layers of glass paper were placed glass filter paper; then the column was filled with a fixed weight (0.5 gm) of the solid phase, which is the activated carbon prepared in this study from different natural sources (Z/AC), (C/AC), (M/AC). The steel was homogeneous, so, that it was free of voids and of equal height from the top, then a layer of glass paper was placed over the solid phase. The CR dye solution was passed at the pH_{pzc}, where the dye is bound at this stage to the solid phase pre-packed in the column and the unbound part of the dye passes from the column as well as the rest of the original components and at a running rate depends on gravity. As for the rinsing stage, it included passing the elution solution through the separation column, which breaks the link between the dye and the solid phase, and then transfers the solution to measurement using UV-

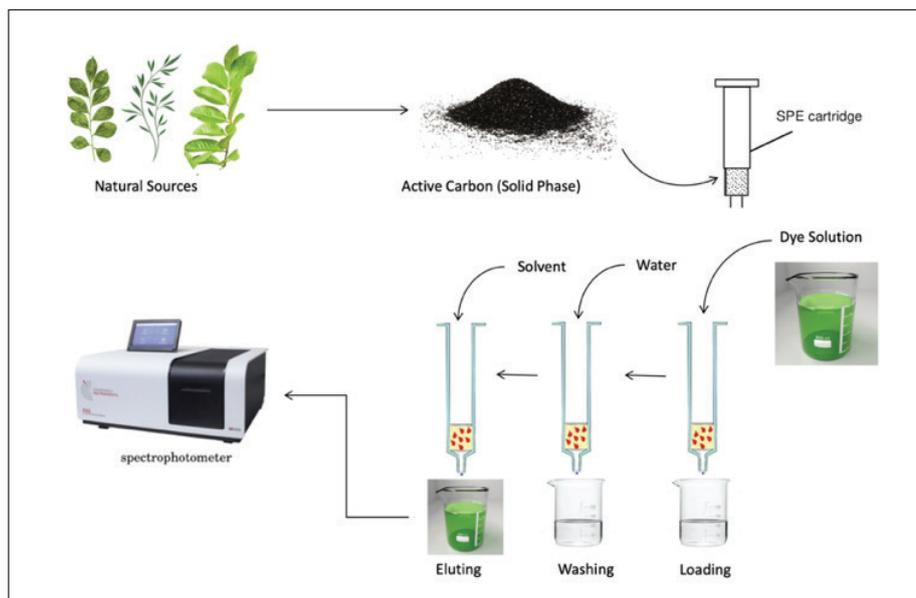


Fig. 2. Summary of preparation of activated carbon and extraction procedure

visible technology to know the concentration extracted from the dye. The ratio can be calculated as the percentage of recovery % through Equation 3, and this study included finding the ideal conditions for the optimization of the extraction process as shown below.

$$\% \text{Recovery} = \frac{\text{concentration of dye recovered on extraction}}{\text{original concentration of dye}} \times 100\% \quad (\text{Eq.3})$$

2.4. Characterization Methods

To investigate the surface characteristic of (Z/AC), (C/AC), and (M/AC), FT IR, XRD, and SEM spectra were studied. FT-IR spectroscopy was carried out to determine the type and nature of the functional groups present in the activated carbon. The presence of these functional groups increases heterogeneity and, thereby the extraction. The

spectra of (Z/AC), (C/AC), and (M/AC) samples are shown in Table 1. To explore the crystal lattice structure of activated carbon, an X-ray diffraction pattern was carried out; Figure 3 shows the XRD configuration of the three AC types (Z/AC), (C/AC) and (M/AC). In this pattern, several peaks were found corresponding to their semi-crystalline nature. XRD spectra of the fitted conditioners revealed a sharp diffraction peak of 29.5° for all solutions that (Z/AC), (C/AC), and (M/AC) and this is evidence for the possible presence of potassium compounds with high crystallinity after activation with KOH. The SEM is a tool for characterizing the surface morphology and physical properties of the adsorbent surface. It helps determine the particle shape, appropriate size distribution of the adsorbent and porosity. The surface morphology of the (Z/AC), (C/AC) and (M/AC) adsorbents are shown in Figure 4a-c.

Table 1. FT-IR analysis (Z/AC), (C/AC) and (M/AC)

	M\AC	C\AC	Z\AC
O-H	3422.06	3754.73	3438.46
\equiv CH	3302.5	-	3374.82
CH=	3267.79	-	3225.36
\equiv CH	2360.44	-	2369.12
CH-	2900.41	-	2948.63
C-O	1435.74	1432.85	1445.39
C=C	-	1609.13	-

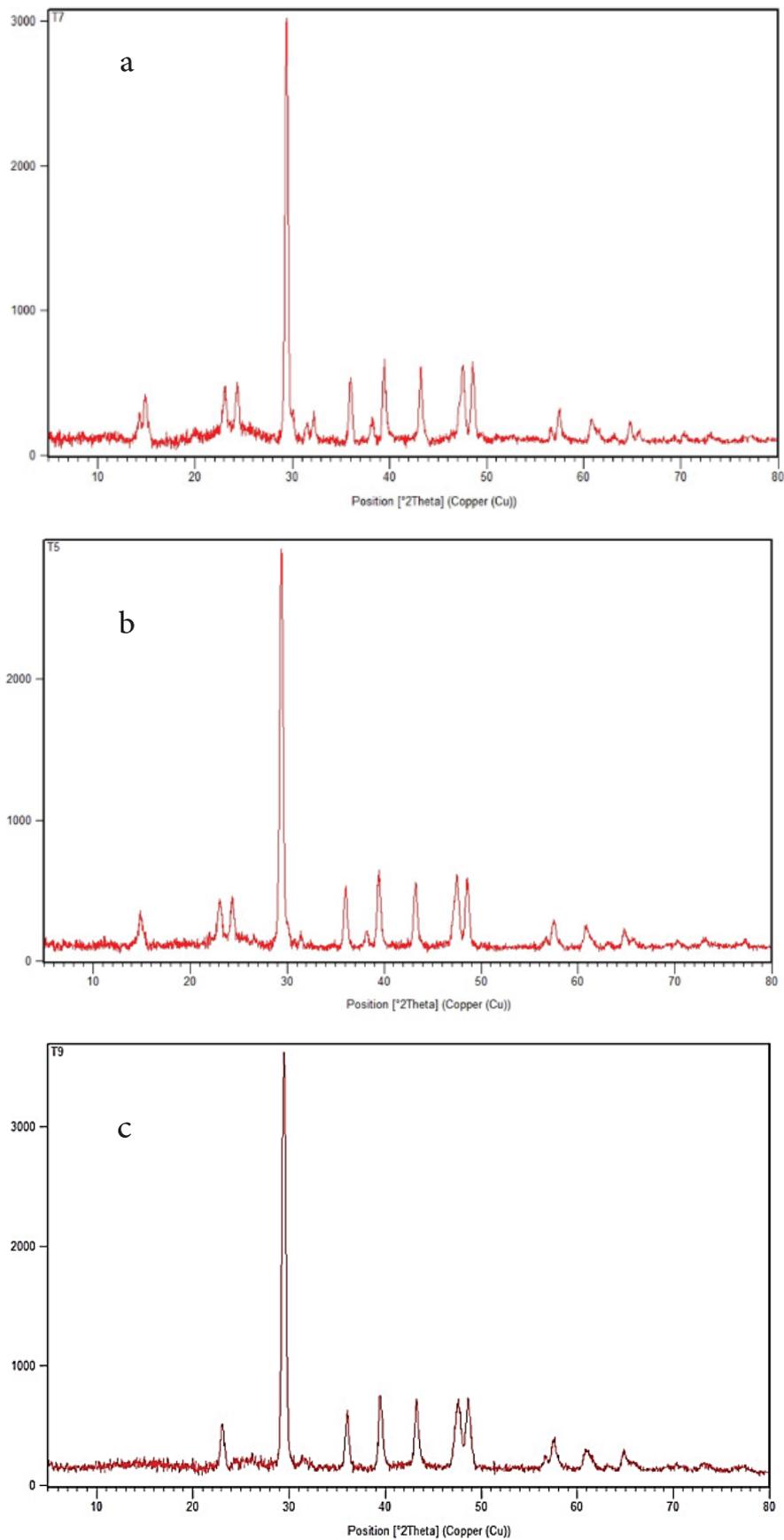


Fig. 3. XRD pattern of a: (Z/AC), b: (C/AC) and c: (M/AC)

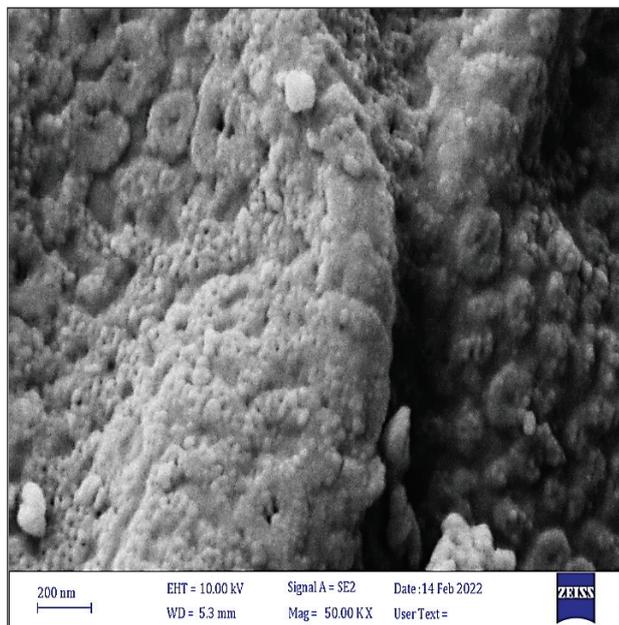


Fig. 4a. SEM of Ziziphus spina-christi (Z/AC)

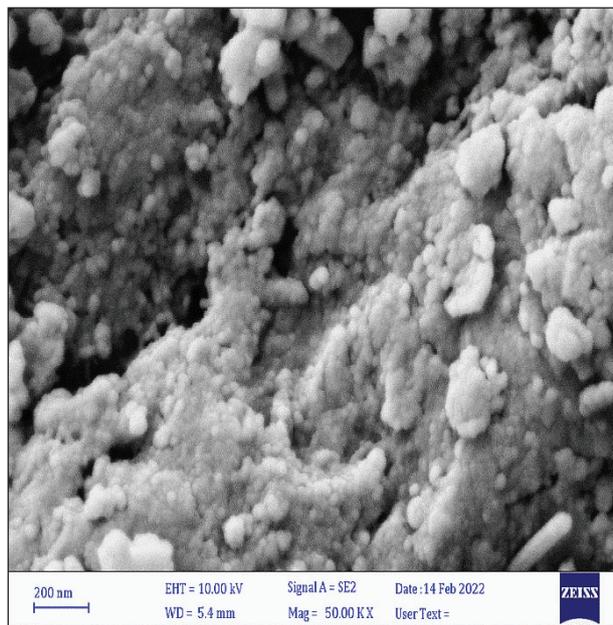


Fig. 4b. SEM of Consocarpus plant (C/AC)

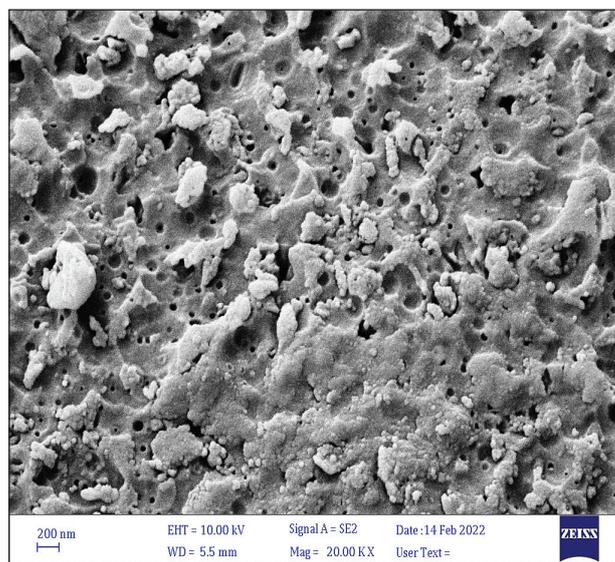


Fig. 4c. SEM image of Myrtus plant (M/AC)

3. Results and Discussion

3.1. Optimization of the extraction procedure

The study of finding the optimal conditions for any analytical method includes the process of changing one of the conditions of the experiment and fixing the rest of the other conditions that control the efficiency of the experiment. Adjusting the method to all the optimal values for all factors, and to find the ideal conditions and obtain the maximum efficiency of the process of extraction and removal of the dye, several experiments were conducted as follows:

3.2. Amount of solid phase

The effect of the weight of the packed solid phase in the separating column was studied, and the results proved that the percentage of retrieval varies according to the amount of the solid phase. Figure 5 shows an apparent behavior in increasing the retrieval percentage with increasing phase weight for the weights range (0.05-5.0) g, where the recovery percentage reaches the maximum value when using the weight of 0.25 g. Then the recovery percentages stabilize in the largest weights down to 0.5 g. This behavior was for all solid phases when studying the CR dye, which leads to the weight of 0.25 g of the solid phase being selected as a constant weight for all phases in all subsequent experiments.

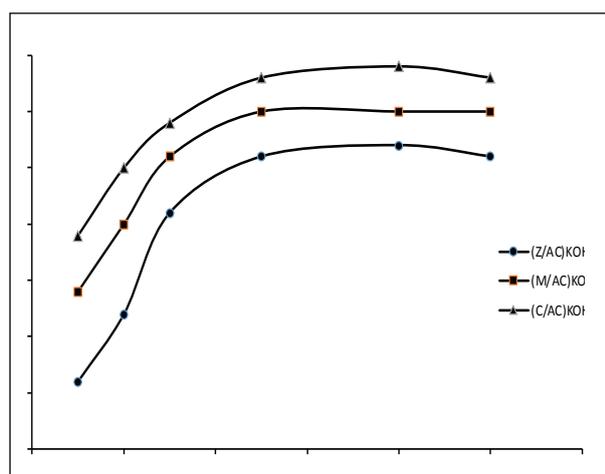


Fig. 5. Effect of the solid phase amount on the recovery of Congo Red

3.3. Effect of Dye concentration

The effect of the concentration of the CR solution was studied after packing the extraction column with 0.25 g of activated carbon and loading CR with a range of concentrations which is (50-400) mg L⁻¹ with the stabilization of the acidity function, the volume of the dye solution, the flow rate, the type and volume of the rinse solution, where a concentration of 100 mg L⁻¹ was chosen for the CR dye towards the corresponding solid phases, where this concentration achieves a recovery percentage ranging from 60-65% for the dyes. This ratio is necessary because the recovery efficiency was not at this stage at its maximum, and it is expected to increase it when conducting experiments on other factors affecting extraction. Due to Figure 6, the effect of the concentration of the CR solutions was shown.

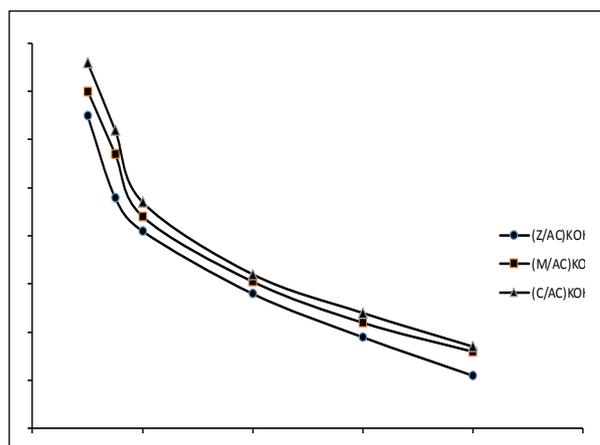


Fig. 6. Effect of Congo Red concentration on the recovery percentage

3.4. Effect of pH

The pH function is one of the critical factors in the study of extraction, which affects the surface charge of the solid phase and the composition of the dye [38]. The effect of acid functions on the solid phase extraction process with a range of (2-12) was studied. Figure 7 represents the effect of the acidity function on the percentage of recovery of CR (anionic) dye when extracted by (Z/AC) and (C/AC) and (M/AC) phases, as we notice that the %R values increase directly for the range of the acidity function (2-5) and then reach the optimal

acidity function $\text{pH} = 5$ and this increase in the %R values is attributed to the hydrostatic interactions between the solid phases and dyes, as for the acid functions that follow the optimum value and within the range (6-12), we notice a decrease in the values of %R, and this can be attributed to the fact that the hydroxyl radical OH^- whose concentration increases with the increase of the acidic function competes with the dye molecules towards the solid phases. The value of the optimal pH function in extracting or removing the CR dye is equal to 5 and was identical to the results of previous studies [24,25].

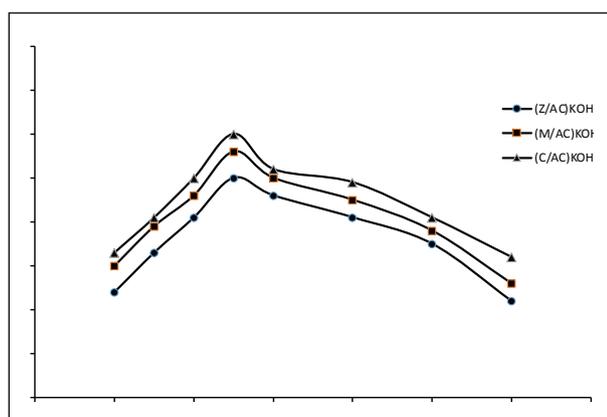


Fig. 7. Effect of pH on the recovery of Congo Red

3.5. Effect of dyes volume

Studying the effect of the target material solution's volume is essential in determining the optimal conditions for the solid phase extraction method [26,27]. Figure 8 showed that the percentages of recovery of CR dye were close to 100% for volumes less than 100 mL within the range of volumes (100-400) mL, the percentages of recovery gradually decreased. This behavior was very logical because the efficiency of the extraction decreases with the increase in the volume of the solution, as the concentration of the dye decreases with the increase in the volume of the solution, and therefore the remaining dye during the extraction process is more diluted the more the volume of the solution was more significant the extraction efficiency decreased. So, the volume of 25 mL is considered to be the optimum volume of the CR dye.

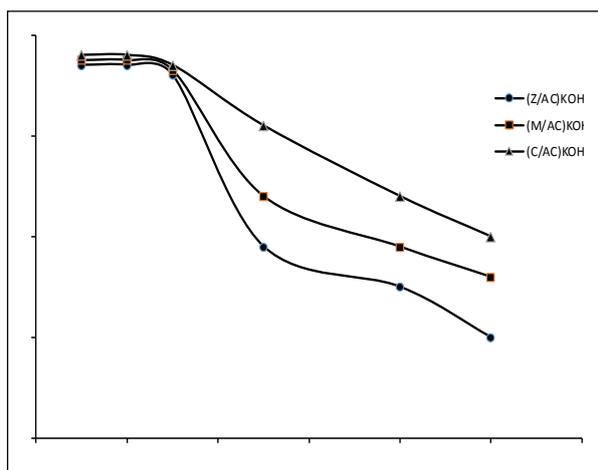


Fig. 8. Effect of Congo Red solution volume on the recovery percentage

3.6. Effect of flow rate

The effect of the flow rate of the dye solution is one of the critical factors affecting the efficiency of extraction in the solid phase. A balance in the flow rate is necessary in the sense that low flow rates do not achieve high rates of recovery of the target material due to the possibility of disengagement between the solid phase and the target material during the passage of the solution. Thus, the extraction efficiency decreases, and high flow rates are considered undesirable because they do not provide sufficient time for the connection between the solid phase and the material to be extracted. Figure 9 shows a graphic relationship between the percentages of dye recovery versus the rate of the flow rate of the CR solution. We found that the maximum flow rate was equal to 0.5 mL min.

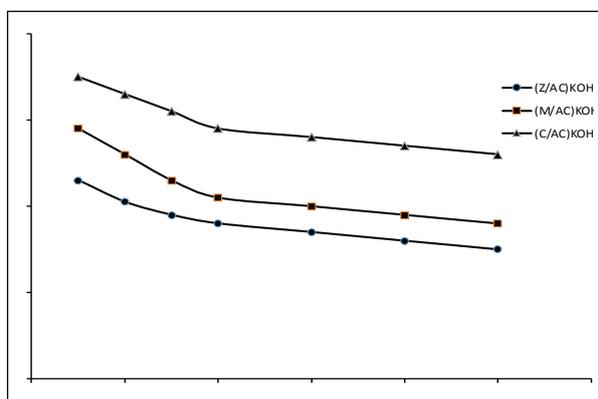


Fig.9. Effect of flow rate on the recovery of Congo Red

3.7. Effect of type and volume of eluting solution

Table 2 shows the solvents used as eluent solutions and their polarity index values, where the polarity coefficient represents the ability of the solvent to interfere with the solute[28], and Figure 10 shows the effect of the type of the solvent on the percentages of recovery of the two dyes. We note that the highest rate of recovery was achieved when the elution solution was DMSO with a polarity coefficient of 7.2 and the highest polarity among the solvents. It may be attributed to the great affinity of CR dyes towards the DMSO solvent because it is a polar dye. It makes the dye leave as a solid phase and moves with the more polar rinsing solution (Figure 10). we note that the percentages of recovery decrease with the decreasing polarity of the eluting solution. The study also included finding the optimum volume of the rinse solution; when observing in Figure 11, which represents the graphic relationship between the percentage of recovery of the CR dye and the volume of the rinse solution, we find that the volume that achieves the highest rate of recovery was equal to 8 mL. Finding the optimal volume of the rinsing solution leads us to calculate the enrichment factor, which evaluates

the extraction process, which can be calculated from Equation 4 [29].

$$\text{Enrichment Factor (EF)} = \frac{\text{Original Dye Volume}}{\text{Elution Solution Volume}} \quad (\text{Eq.4})$$

The enrichment coefficient can be calculated depending on the initial dye volume and the volume of the rinsing solution (Equation 4). Table 3 shows the values of the calculated enrichment coefficients for the extraction systems under study.

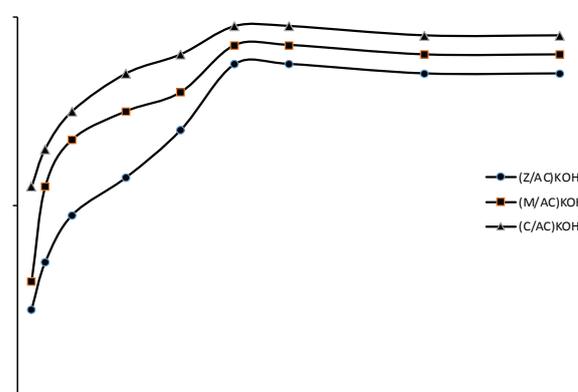


Fig. 11. Effect of DMSO volume on the recovery of Congo Red

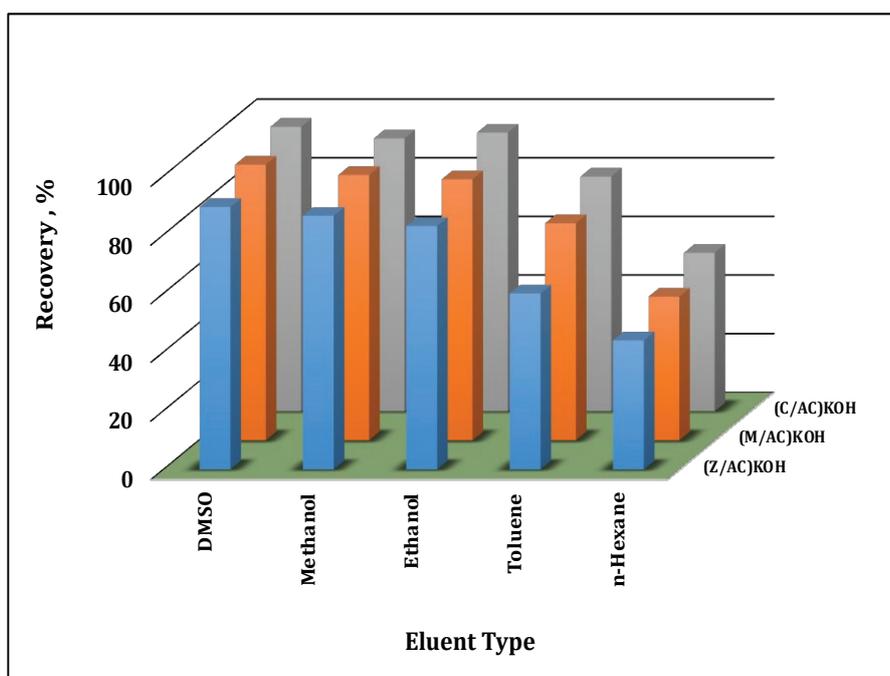


Fig. 10. Effect of elution type on the recovery of Congo Red

Table 2. Solvents used as elution solution and their polarity index

Solvent	Polarity index
DMSO	7.2
Methanol	5.1
Ethanol	4.3
Toluene	2.4
n-hexane	0.1

Table 3. Enrichment factors for extraction of CR

Solid Phase	Enrichment factor
(Z/AC)	3.125
(M/AC)	3.125
(C/AC)	3.125

3.8. Isotherm study

One of the most important benefits of the SPE extraction process is the removal of the target substance from its origin in which it is located [30]. Therefore, the results obtained in the extraction experiments can be employed in favor of the removal operations of CR from its aqueous solution. The residual concentration of the solutions of the CR dye was calculated and thus the weight adsorption capacity q (mg g^{-1}) was calculated based on Equation 5 [31, 32].

$$q = \frac{(C_o - C_e)V}{M} \quad (\text{Eq.5})$$

Through the study of the isotherm, it is possible to clarify the relationship between the solid phases and dye, and to suggest the mechanisms of interaction [33]. The study of the isotherm includes the application of many models, and the Langmuir and Freundlich models were chosen in this study.

3.9. Langmuir isotherm model

The Langmuir equation [34] which was developed in 1916 applies to monolayer or single-molecular adsorption of the target material on the surface of the adsorbent material or the solid phase (Equation 6), where this equation assumes the existence of homogeneous adsorption sites [35].

$$\frac{C_e}{q_e} = \frac{1}{(q_{\max} \times K_L)} + \frac{C_e}{q_{\max}} \quad (\text{Eq.6})$$

Figure 12 represents the Langmuir model for CR. Table 4 also shows the results obtained from this model. The values of the maximum adsorption capacity q_{\max} , Langmuir constant K_L and correlation coefficient R^2 were calculated by plotting the graphical relationship of the Langmuir equation between C_e/q_e on the Y-axis and C_e on the X-axis as in Figure 12, where the slope of the straight line represents $(1/q_{\max})$ and the cutoff represents $(1/q_{\max} \cdot K_L)$ and by noting the Table 4, we find that the maximum adsorption capacity of CR dye by the solid phase (C/AC) is the highest in comparison with the other two phases. This may be due to the nature of the interaction between this dye and the prepared solid phases, which certainly had the advantage compared to the nature of the association with CR dye, and also through Table 4 we find that the values of Langmuir constant rise in the same pattern, which indicates the extent of the strong interaction between the active sites in the dye and between the solid phase. It is also noted the values of the correlation coefficient very close to the right one, which indicates the relative applicability of the studied adsorption systems on the Langmuir model.

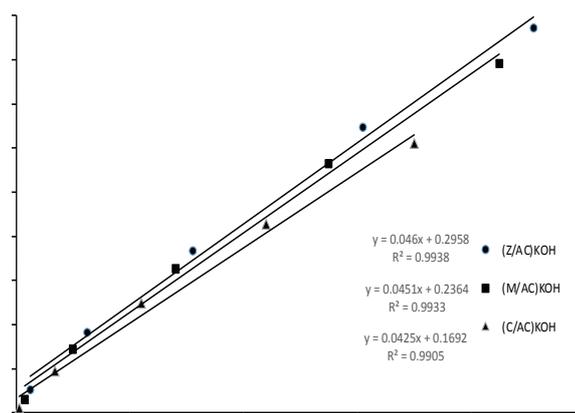


Fig. 12. Langmuir isotherm of adsorption of Congo Red

Table 4. Langmuir isotherm parameters for the adsorption of CR dye at 25 °C

Solid Phase	q_{\max} (mg. g ⁻¹)	K_L	R^2
(Z/AC)	21.7391	0.9938	1.5551
(M/AC)	22.1729	0.9933	1.90778
(C/AC)	23.5294	0.9905	2.51182

3.10. Freundlich isotherm model

As Equation 7, the Freundlich equation developed in 1926 [36] It explains the processes of interference and adsorption that occur on heterogeneous surfaces and assumes that adsorption occurs at sites of varying adsorption energy [37].

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

(Eq.7)

The Figure 13 represent Freundlich model for CR. Table 5 also shows the results obtained from this model. The values of Freundlich constant K_F and correlation coefficient R^2 were calculated by plotting the graph of Freundlich equation between $\ln q_e$ on the Y-axis and $\ln C_e$ on the X-axis as in Figure 13, where the slope of the straight line represents $(1/n)$ and the cut off represents $(\ln K_F)$. By noting the Table 5, we find that the highest value of K_F , which represents the adsorption energy between the solid phase and the dye [38] is for the adsorption system of the solid phase (C/AC) and this result is

in agreement with the q_{\max} values calculated from the Langmuir model. The values of $1/n$ give an indication that the adsorption process is preferred or unfavorable, as if the values of $1/n = 0$, this means that the adsorption is irreversible, but when it is $0 < 1/n < 1$, this indicates that the adsorption between the solid phase and target material is a preferred process, and adsorption may not be favorable when $1/n > 1$ [39]. When observing the values of $1/n$ from Table 5, we find that they are greater than zero and less than one for all solid phases. Thus, could be concluded that the adsorption systems in this study are preferred. After reviewing Tables 4 and 5, we find that the R^2 values of the Freundlich model for all systems are higher than the corresponding values in the Langmuir model leading to suggest a physisorption mechanism.

4. Conclusion

In conclusion, the efficient removal of the dyes CR from aqueous solutions was observed when using the active carbon (Z/AC), (C/AC) and (M/AC) as solid phases. The optimization approach

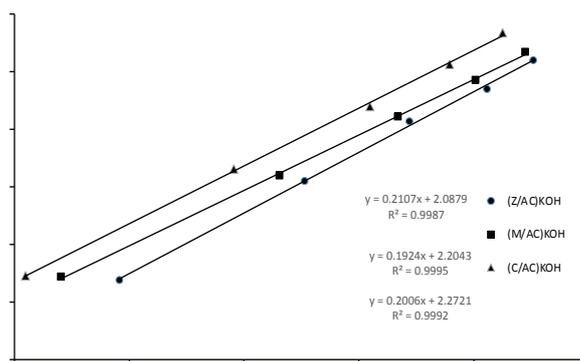


Fig. 13. Freundlich isotherm of adsorption of Congo Red

Table 5. Freundlich isotherm parameters for the adsorption of CR dye at 25 °C

Solid Phase	K_F	$1/n$	R^2
(Z/AC)	8.06795	0.2107	0.9987
(M/AC)	9.0639	0.1924	0.9995
(C/AC)	9.69975	0.2006	0.9992

for the extraction of CR observed that the optimum amount of solid phases was 0.25 g, the initial concentration of dye solution was 100 mg L⁻¹, the optimum pH was 5, the volume of dye solution was 25.0 mL with a flow rate equal to 0.5 mL min⁻¹, and the optimum elution solution was DMSO with a volume equal to 2.0 mL, from the linearized form (from the calculation of the Langmuir equation, q_{max}), values for the CR dye were (21.74, 23.53, 22.17) mg g⁻¹ for (Z/AC), (C/AC), and (M/AC), respectively.

5. References

- [1] X. Li, W. Bo, C. Yuhua, Z. Shuang, W. Hang, F. Xiao, Z. Junwen, M. Xiaojie, Water contaminant elimination based on metal-organic frameworks and perspective on their industrial applications, *ACS Sustain. Chem. Eng.*, 7 (2019). 4548–4563. <https://doi.org/10.1021/acssuschemeng.8b05751>.
- [2] N. Masoudian, M. Rajabi, M. Ghaedi, Titanium oxide nanoparticles loaded onto activated carbon prepared from bio-waste watermelon rind for the efficient ultrasonic-assisted adsorption of congo red and phenol red dyes from wastewaters, *Polyhedron*, 173 (2019) 114105. <https://doi.org/10.1016/j.poly.2019.114105>.
- [3] K. Hossienzadeh, A. Maleki, H. Daraei, M. Safari, R. Pawar, S. M. Lee, Sonocatalytic and photocatalytic efficiency of transition metal-doped ZnO nanoparticles in the removal of organic dyes from aquatic environments, *Korean J. Chem. Eng.*, 36 (2019) 1360–1370. <https://doi.org/10.1007/s11814-019-0299-6>.
- [4] J. C. G. Sousa, A. R. Ribeiro, M. O. Barbosa, M. F. R. Pereira, A. M. T. Silva, A review on environmental monitoring of water organic pollutants identified by EU guidelines, *J. Hazard. Mater.*, 344 (2018) 146–162. <https://doi.org/10.1016/j.jhazmat.2017.09.058>.
- [5] M. A. Hassaan, A. El Nemr, Health and environmental impacts of dyes: Mini review, *Am. J. Environ. Sci. Eng.*, 1

- (2017) 64-67. [https://doi: 10.11648/j.ajese.20170103.11](https://doi.org/10.11648/j.ajese.20170103.11).
- [6] K. Singh, S. Arora, Removal of synthetic textile dyes from wastewaters: A critical review on present treatment technologies, *Crit. Rev. Environ. Sci. Technol.*, 41 (2011) 807–878. [https://doi: 10.1080/10643380903218376](https://doi.org/10.1080/10643380903218376).
- [7] E. Errais, Efficient anionic dye adsorption on natural untreated clay: Kinetic study and thermodynamic parameters, *Desalination*, 275 (2011) 74–81. <https://doi.org/10.1016/j.desal.2011.02.031>.
- [8] E. Zabłocka-Godlewska, W. Przystaś, E. Grabińska-Sota, Possibilities of obtaining from highly polluted environments: new bacterial strains with a significant decolorization potential of different synthetic dyes, *Water Air Soil Pollut.*, 229 (2018)176. [https://doi: 10.1007/s11270-018-3829-7](https://doi.org/10.1007/s11270-018-3829-7).
- [9] M. S. El-Geundi, H. M. Ismail, K. M. E. Attyia, Activated clay as an adsorbent for cationic dyestuffs, *Adsorpt. Sci. Technol.*, 12 (1995) 109–117. [https://doi: 10.1177/026361749501200203](https://doi.org/10.1177/026361749501200203).
- [10] S. A. Jadhav, Recent advancements in silica nanoparticles based technologies for removal of dyes from water, *Colloid Interface Sci. Commun.*, 30 (2019) 100181. <https://doi.org/10.1016/j.colcom.2019.100181>.
- [11] X. Meng, Synthesis, characterization, and utilization of a lignin-based adsorbent for effective removal of azo dye from aqueous solution, *ACS omega*, 5 (2020) 2865–2877. [https://doi: 10.1021/acsomega.9b03717](https://doi.org/10.1021/acsomega.9b03717).
- [12] T. M. Budnyak, Methylene Blue dye sorption by hybrid materials from technical lignins, *J. Environ. Chem. Eng.*, 6 (2018) 4997–5007. [https://doi: 10.1016/j.jece.2018.07.041](https://doi.org/10.1016/j.jece.2018.07.041).
- [13] S. Banerjee, M. C. Chattopadhyaya, Adsorption characteristics for the removal of a toxic dye, tartrazine from aqueous solutions by a low cost agricultural by-product, *Arab. J. Chem.*, 10 (2017) S1629–S1638. [https://doi: https://doi.org/10.1016/j.arabj.2013.06.005](https://doi.org/10.1016/j.arabj.2013.06.005).
- [14] M. B. Ahmed, J. L. Zhou, H. H. Ngo, W. Guo, N. S. Thomaidis, J. Xu, Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: A critical review, *J. Hazard. Mater.*, 323 (2017) 274–298. <https://doi.org/10.1016/j.jhazmat.2016.04.045>.
- [15] Y. Zhou, J. Lu, Y. Zhou, Y. Liu, Recent advances for dyes removal using novel adsorbents: A review, *Environ. Pollut.*, 252 (2019) 352–365. [https://doi: 10.1016/j.envpol.2019.05.072](https://doi.org/10.1016/j.envpol.2019.05.072).
- [16] J. Wang, Two new uncommon 3D cobalt-based metal organic frameworks: Temperature induced syntheses and enhanced photocatalytic properties against aromatic dyes, *Dye. Pigment.*, 187 (2021), 109068. <https://doi.org/10.1016/j.dyepig.2020.109068>.
- [17] E. Dziurkowska, M. Wesolowski, Solid phase extraction purification of saliva samples for antipsychotic drug quantitation, *Molecules*, 23 (2018) 2946. [https://doi: 10.3390/molecules23112946](https://doi.org/10.3390/molecules23112946).
- [18] W. Jing, J. Wang, B. Kuipers, W. Bi, D. D. Y. Chen, Recent applications of graphene and graphene-based materials as sorbents in trace analysis, *TrAC Trends Anal. Chem.*, 137 (2021) 116212. [https://doi: https://doi.org/10.1016/j.trac.2021.116212](https://doi.org/10.1016/j.trac.2021.116212).
- [19] M. He, L. Huang, B. Zhao, B. Chen, B. Hu, Advanced functional materials in solid phase extraction for ICP-MS determination of trace elements and their species - A review, *Anal. Chim. Acta*, 973 (2017) 1–24. [https://doi: 10.1016/j.aca.2017.03.047](https://doi.org/10.1016/j.aca.2017.03.047).
- [20] M. H. Abdel-Aziz, DFT and experimental study on adsorption of dyes on activated carbon prepared from apple leaves,

- Carbon Lett., 31 (2021) 863–878. [https://doi: 10.1007/s42823-020-00187-1](https://doi.org/10.1007/s42823-020-00187-1).
- [21] H. Javadian, Using fuzzy inference system to predict Pb (II) removal from aqueous solutions by magnetic Fe₃O₄/H₂SO₄-activated Myrtus Communis leaves carbon nanocomposite, J. Taiwan Inst. Chem. Eng., 91 (2018) 186–199. [https://doi: 10.1016/j.jtice.2018.06.021](https://doi.org/10.1016/j.jtice.2018.06.021).
- [22] S. Farrokhzadeh, H. Razmi, B. Jannat, Application of marble powder as a potential green adsorbent for miniaturized solid phase extraction of polycyclic aromatic hydrocarbons from water samples, Sep. Sci. Technol., 55 (2020) 2737–2745. [https://doi: 10.1080/01496395.2019.1655054](https://doi.org/10.1080/01496395.2019.1655054).
- [23] J. Dai, Fabrication of novel ZIF-67 composite microspheres for effective adsorption and solid-phase extraction of dyes from water, Chem. Select, 3 (2018) 5833–5842. [https://doi: https://doi.org/10.1002/slct.201800778](https://doi.org/10.1002/slct.201800778).
- [24] H. S. Al-Niaeem, A. A. Abdulwahid, W. S. Hanoosh, Removal of carcinogenic dyes congo red (CR) and Bismarck brown Y (BBY) by adsorption onto reusable hydrogels derived from acrylamide, J. Phys. Conf. Ser., 2063 (2021) 012011. [https://doi: 10.1088/1742-6596/2063/1/012011](https://doi.org/10.1088/1742-6596/2063/1/012011).
- [25] A. A. Mizhir, A. A. Abdulwahid, H. S. Al-Lami, Adsorption of carcinogenic dye congo red onto prepared graphene oxide-based composites, Desalin. Water Treat., 202 (2020) 381–395. [https://doi: 10.5004/dwt.2020.26141](https://doi.org/10.5004/dwt.2020.26141).
- [26] A. A. Gouda, W. A. Zordok, Solid-phase extraction method for preconcentration of cadmium and lead in environmental samples using multiwalled carbon nanotubes, Turkish J. Chem., 42 (2018) 1018–1031. [https://doi:10.3906/kim-1711-90](https://doi.org/10.3906/kim-1711-90).
- [27] K. Hossein, Mahdi and Dalali, Nasser, Karimi, Ali and Dastanra, Solid phase extraction of copper, nickel, and cobalt in water samples after extraction using surfactant coated alumina modified with indane-1,2,3-trione 1,2-dioxime and determination by flame atomic absorption spectrometry, Turk. J. Chem., (2010), 805–814. <https://doi.org/10.3906/sag-1203-108>.
- [28] L. R. Snyder, Classification off the solvent properties of common liquids, J. Chromatogr. Sci., 16 (1978) 223–234. [https://doi: 10.1093/chromsci/16.6.223](https://doi.org/10.1093/chromsci/16.6.223).
- [29] Y. Li, W. Zhang, R.-G. Wang, P.-L. Wang, X.-O. Su, Development of a efficient and sensitive dispersive liquid–liquid microextraction technique for extraction and preconcentration of 10 β₂-agonists in animal urine, PLOS One, 10 (2015) 1–16. [https://doi: 10.1371/journal.pone.0137194](https://doi.org/10.1371/journal.pone.0137194).
- [30] R. Amer, H. Hadi, Application of CTAB-coated magnetic nanoparticles for solid-phase extraction of thiamine hydrochloride from pharmaceutical formulations and urine samples, Arab. J. Sci. Eng., 47 (2022) 429–440. [https://doi: 10.1007/s13369-021-05671-y](https://doi.org/10.1007/s13369-021-05671-y).
- [31] E. Yilmaz, G. Guzel Kaya, H. Deveci, Removal of methylene blue dye from aqueous solution by semi-interpenetrating polymer network hybrid hydrogel: Optimization through Taguchi method, J. Polym. Sci. Part A Polym. Chem., 57 (2019) 1070–1078. [https://doi: https://doi.org/10.1002/pola.29361](https://doi.org/10.1002/pola.29361).
- [32] M. T. Nakhjiri, G. Bagheri Marandi, M. Kurdtabar, Adsorption of methylene blue, brilliant green and rhodamine B from aqueous solution using collagen-g-p(AA-co-NVP)/Fe₃O₄@SiO₂ nanocomposite hydrogel, J. Polym. Environ., 27 (2019) 581–599. [https://doi: DOI:101007/s10924-019-01372-8](https://doi.org/10.1007/s10924-019-01372-8).
- [33] Y. Kuang, X. Zhang, S. Zhou, Adsorption of methylene blue in water onto activated carbon by surfactant modification, Water, 12 (2020) 587. [https://doi: 10.3390/w12020587](https://doi.org/10.3390/w12020587).
- [34] I. Langmuir, The constitution and fundamental properties of solids and

- liquids part 1 solids, *J. Am. Chem. Soc.*, 38 (1916) 2221–2295. [https://doi: 10.1021/ja02268a002](https://doi.org/10.1021/ja02268a002).
- [35] A. A. Mizhir, A. A. Abdulwahid, H. S. Al-Lami, Chemical functionalization graphene oxide for the adsorption behavior of bismarck brown dye from aqueous solutions, *Egypt. J. Chem.*, 63 (2020) 1679–1696. [https://doi: 10.21608/ejchem.2020.21260.2271](https://doi.org/10.21608/ejchem.2020.21260.2271).
- [36] Wi. B. Meldrum, Experiments in physical chemistry, *J. Chem. Educ.*, 28 (1951) 174. [https://doi: 10.1021/ed028p174.3](https://doi.org/10.1021/ed028p174.3).
- [37] I. Crisan, R. Vidican, Phytoremediation Potential of *Iris spp*, *Bull. Univ. Agric. Sci. Vet. Med. Cluj-Napoca. Agric.*, 78 (2021) 1–10. [https://doi: 10.15835/buasvmcn-agr:2020.0046](https://doi.org/10.15835/buasvmcn-agr:2020.0046).
- [38] P. Luo, B. Zhang, Y. Zhao, J. Wang, H. Zhang, J. Liu, Removal of methylene blue from aqueous solutions by adsorption onto chemically activated halloysite nanotubes, *Korean J. Chem. Eng.*, 28 (2011) 800–807. [https://doi: 10.1007/s11814-010-0426-x](https://doi.org/10.1007/s11814-010-0426-x).
- [39] A. S. Muhammad, M. A. Abdurrahman, Adsorption of methylene blue onto modified agricultural waste, *Moroccan J. Chem.*, 8 (2020) 412–427. <https://doi.org/10.48317/IMIST.PRSM/morjchem-v8i2.16692>.