

## Ultrasound-assisted adsorption of Methyl Parathion using commercial Granular Activated Carbon from aqueous solution

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### Abstract

The removal of Methyl parathion (MP) by ultrasound-assisted adsorption using commercial Granular Activated Carbon (GAC) was studied. The effect of sonication time on the adsorption were studied using the batch technique. The adsorption kinetic data were analyzed using the Pseudo First Order (PFO) and Pseudo Second Order (PSO) models. For kinetic study, the adsorption process fitted the PSO model. Three adsorption isotherms namely the Langmuir, Freundlich and Redlich–Peterson isotherms in their non-linear forms were applied to the adsorption equilibrium data. Both the Langmuir and Redlich–Peterson models were found to fit the adsorption isotherm data well, but the Redlich–Peterson model was better. The monolayer adsorption capacity,  $q_m$ , was found to be 20.20 mg g<sup>-1</sup>. It can be concluded that the commercial GAC is an efficient adsorbent for the removal of MP from aqueous solution via ultrasound-assisted adsorption. Attempt to explain the reactivity of MP on GAC by theoretical calculations was made.

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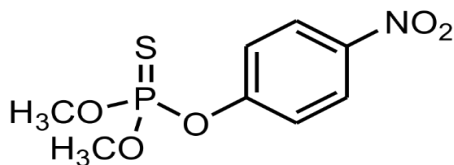
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## 1. Introduction

Pesticides have become essential for agriculture for protecting crops and livestock, which are vital to our food supply. However, the widespread use of pesticides has also resulted in serious public health [1-5]. Organophosphate pesticides represent 70 % of these substances and they have been used for several decades in the control of domestic pests and in agriculture [6, 7]. However, these organophosphates can be harmful to humans and animals as they can contaminate water sources. The Organophosphate pesticides, such as Methyl Parathion (MP) (Fig. 1), affect proteins like the acetylcholinesterase, which plays an important role in both the peripheral and the central nervous system [8].



**Fig. 1.** MP chemical structure

Pesticides cause a number of severe health effects and illnesses. Khalili Tanha *et al.* 2020 [9] summarized various risks that pesticides provoke to human health. Cabello *et al.* 2001 [10], observed through their investigation on the effects of malathion and parathion on the mammary glands of mice, that these compounds enhanced the growth of the mammary gland epithelial cells and caused tumour in the animals [11]. The removal of pesticides from water is one of the major environmental concerns nowadays. There are several procedures that were used for MP removal from water such as degradation [12], photocatalytic degradation [13], electrochemical [14], coagulation /flocculation [15] and adsorption [16]. Among all the methods, adsorption by activated carbon is one of the most popular methods and is currently considered as an effective, efficient, and economic method for water purification [17, 18]. However, one of the innovative technologies used in combination with adsorption is sonication. It has been reported that the removal efficiency can be improved by the combination of ultrasonication and adsorption due to the disadvantages of the application of adsorption alone such as high cost, ineffectiveness for the removal of some pollutants, operation problems and production of toxic secondary pollutants [19]. This technique has been used to study the removal of a variety of hazardous compounds [20-27]. A variety of activated carbon materials have been used, such as, granular activated carbon (GAC), powdered activated carbon (PAC), carbon cloth, fibers, felts or carbon cloth electrodes, black carbon from wheat residues (WC), carbon black and commercial activated carbon (AC). The forms GAC and PAC are the most used since they are considered very capable and effective materials for the adsorption of a variety of pesticides. GAC has been used in many processes for the treatment of drinking water supplies and industrial wastewaters [28]. The objective of this work was to study the removal of MP from aqueous solutions using the ultrasound assisted batch operation for the adsorption of MP onto commercial GAC from aqueous solution. For this purpose, kinetic and isotherm studies have been carried out with the non-linear methods. Theoretical calculations were used to explain the reactivity of MP on GAC.

## 2. Materials and methods

### 2.1. MP preparation and analysis

A stock solution containing 1,000 mgL<sup>-1</sup> of MP was prepared by dissolving 100 mg of MP in 100 mL of methanol. MP solutions were prepared by diluting stock solution of MP to the desired concentrations in ultrapure water. All samples were filtered using a micro filter syringer and analyzed by High Performance

Liquid Chromatography (HPLC). Ultra-pure water and methanol (20:80 V/V) were used as a mobile phase at a flow rate of 0.5 mL min<sup>-1</sup> at a selected wave length of 265 nm.

## 2.2. Adsorbent

GAC was supplied by PROLABO (physical characteristics described in table 1). The quantification of the GAC by Boehm titration reveals that the GAC has also the greatest content of acidic surface than the basic surface groups. The specific surface for GAC was found to be 1045 m<sup>2</sup> g<sup>-1</sup>.

**Table 1.** Physical and chemical characteristics of the commercial GAC

Parameters	Value
Total acidity (meq g <sup>-1</sup> )	0,580
Total basicity (meq g <sup>-1</sup> )	0,204
Specific surface (m <sup>2</sup> g <sup>-1</sup> )	1045
Particle size (μm)	2000-3000

## 2.3. Batch experiments

In order to investigate the effect of sonicate time on MP removal by adsorption, 0.1 g of GAC was added to 25 mL of MP at 5 mg L<sup>-1</sup>, which sonicate with using ultrasonic bath (Fisherbrand FB15050). Adsorption isotherms were obtained by varying the initial MP concentration from 2.5 to 100 mg L<sup>-1</sup>. The concentrations of MP in the solutions before and after adsorption were determined using a HPLC. At the end of each experiment, the sonicated solution mixture was micofiltered and the residual concentration of MP was determined. The adsorption uptake at equilibrium time,  $q_e$ , was expressed by equation (1):

$$q_e = \frac{(C_i - C_e)V}{m} \quad (1)$$

Where  $q_e$  is the amount of MP adsorbed by GAC (mg g<sup>-1</sup>),  $C_i$  is the initial MP concentration (mg L<sup>-1</sup>),  $C_e$  is the MP concentration at equilibrium (mg L<sup>-1</sup>),  $V$  is the solution volume (L) and  $m$  is the mass of GAC used (g). All batch experiments were conducted in triplicate and the mean values are reported.

## 2.4. Kinetics and equilibrium adsorption modeling

A number of kinetic models have been described in an attempt to find a suitable mechanism explanation for solid-liquid adsorption systems, in which Lagergren's pseudo-first-order models (PFO) [29] and Ho's pseudo-second order (PSO) model [29] are the two most widely applied. The kinetic study was done for the GAC in order to estimate the equilibrium time of adsorption and the best fitted PFO and PSO kinetic models. The nonlinear kinetics PFO and PSO models may be expressed by (2) and (3), respectively:

$$q_t = q_e(1 - \exp^{-k_1 t}) \quad (2)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (3)$$

Where  $q_t$  is the amount of MP adsorbed per unit mass of GAC (mg g<sup>-1</sup>) at time  $t$ ,  $k_1$  (L min<sup>-1</sup>) is the PFO rate constant,  $k_2$  (gm g<sup>-1</sup>min<sup>-1</sup>) is the PSO rate constant for adsorption,  $q_e$  (mg g<sup>-1</sup>) the amount of MP adsorbed at equilibrium and  $t$  is the sonicate time (min).

In this work, the three parameter isotherm equations, namely Langmuir, Freundlich and Redlich-Peterson were tested for describing the experimental results.

The Langmuir adsorption isotherm assumes that the adsorption takes place at specific homogeneous surface sites within the adsorbent [30]. The nonlinear Langmuir model can be expressed by equation (4):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

Where  $q_e$  is the amount of MP adsorbed per unit mass of GAC ( $\text{mg.g}^{-1}$ ),  $K_L$  is the Langmuir constant related to the adsorption capacity ( $\text{L.g}^{-1}$ ),  $C_e$  is the concentration of MP in the solution at equilibrium ( $\text{mg.L}^{-1}$ ),  $q_m$  is the maximum uptake per unit mass of GAC ( $\text{mg.g}^{-1}$ ). The Freundlich isotherm is employed to describe heterogeneous systems [31]. The nonlinear representation of the Freundlich model is as in equation (5):

$$q_e = K_F C_e^{1/n} \quad (5)$$

Where  $K_F$  ( $\text{mg.g}^{-1}$ ) ( $\text{L.mg}^{-1}$ )<sup>n</sup> and  $1/n$  are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Redlich–Peterson isotherm model combines elements from both the Langmuir and Freundlich equation [32]. The nonlinear representation of the Redlich–Peterson model is as in equation (6):

$$q_e = \frac{K_{RP} C_e}{1 + \alpha_{RP} C_e^n} \quad (6)$$

Where  $K_{RP}$  ( $\text{L.g}^{-1}$ ) and  $\alpha_{RP}$  ( $\text{L.mol}^{-1}$ ) are the Redlich-Peterson isotherm constants, while  $n$  is the exponent, which lies between 0 and 1. The Sum of the Squares of the Errors (SSE) and the correlation coefficient ( $R^2$ ) values are determined respectively by following equations (7) and (8) [33, 34]:

$$\text{SSE} = (q_{\text{exp}} - q_{\text{mod}})^2 \quad (7)$$

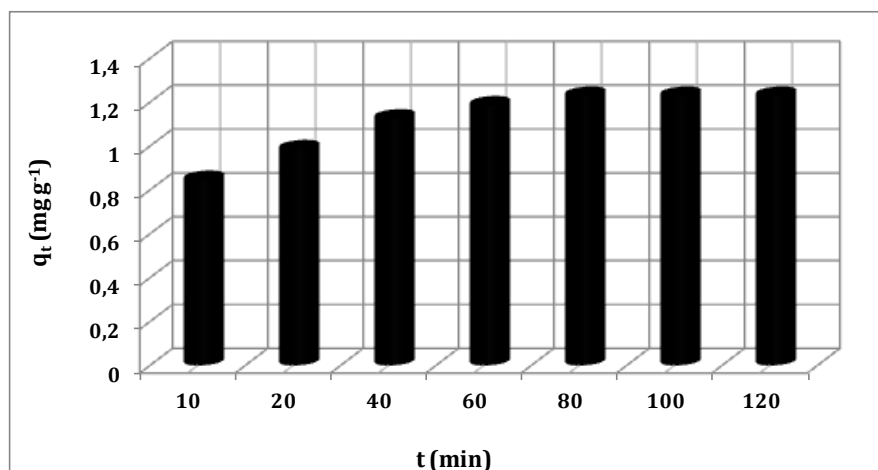
$$R^2 = 100 \left( 1 - \frac{\|q_{\text{exp}} - q_{\text{mod}}\|^2}{\|q_{\text{exp}} - q_{\text{avr}}\|^2} \right) \quad (8)$$

Where  $q_{\text{exp}}$  ( $\text{mg.g}^{-1}$ ) is equilibrium capacity from the experimental data,  $q_{\text{avr}}$  ( $\text{mg.g}^{-1}$ ) is equilibrium average capacity from the experimental data and  $q_{\text{mod}}$  ( $\text{mg.g}^{-1}$ ) is equilibrium from model. So that  $R^2 \leq 100$  – the closer the value is to 100, the more perfect is the fit.

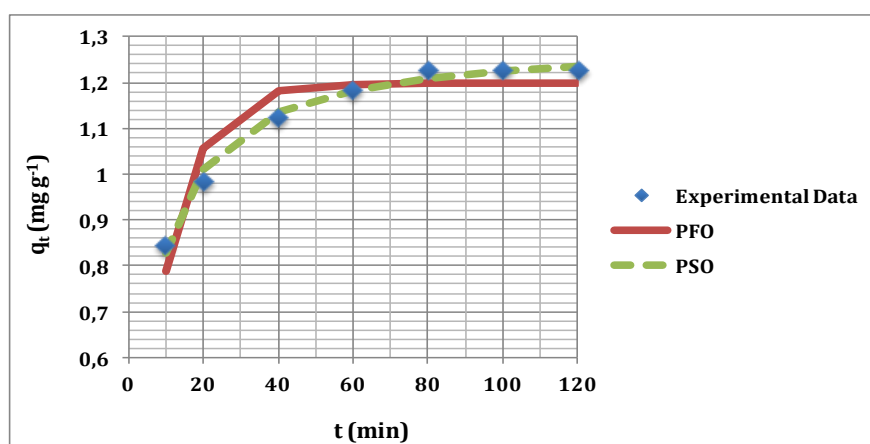
### 3. Results and discussion

#### 3.1. Kinetic study

Fig. 2 show the adsorption capacity of MP versus sonicates time of MP with GAC for  $5 \text{ mg.L}^{-1}$ . It is clearly evident from the Fig. 2 that the adsorption capacity of MP by GAC was increased with sonicate time and then reached to equilibrium at about 80 min. We can notice that the adsorption capacity of the GAC is  $1.228 \text{ mg.g}^{-1}$ . Fig. 3 shows the experimental data and the predicted theoretical kinetics for the adsorption of MP onto GAC for  $5 \text{ mg.L}^{-1}$ . The values of model parameters  $k_1$ ,  $k_2$ , SSE and  $R^2$  are presented in Table 2. However, the  $R^2$  value showed that the PSO model fits better with the experimental data than the PFO model. In addition, the SSE test was also done to support the best fit adsorption model (Table 2). SSE values were lower for PSO model than the PFO model. Based on  $R^2$  and SSE values it was confirmed that PSO model best fits the adsorption data, an indication of chemisorptions mechanism. Similar phenomena have been described for pesticides adsorption on various adsorbents [35, 36].



**Fig. 2.** Variation of MP uptake onto commercial GAC against time



**Fig. 3.** PFO and PSO nonlinear for MP adsorption by commercial GAC

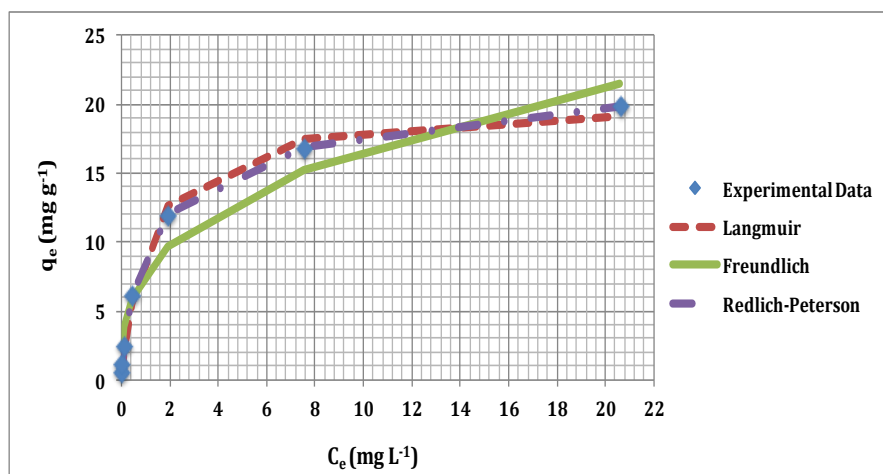
**Table 2.** PFO and PSO models constants, SSE and  $R^2$  for the adsorption of MP by commercial GAC

Model	Parameters	Values
PFO	$q_{exp}$	1.228
	$q_e$	1.198
	$K_1$	0.107
	SSE	0.0146
	$^2R$ (%)	98.44
PSO	$q_e$	1.294
	$K_2$	0.137
	SSE	0.0014
	$^2R$ (%)	98.93

### 3.2. Adsorption isotherms

Fig. 4 show the experimental data fitted to non-linear forms of the three isotherms for MP adsorption by GAC. The isotherms constants related to Langmuir, Freundlich and Redlich–Peterson models determined from the plots shown in Fig. 4 are listed in Table 3. As can be clearly seen from Table 3, the Redlich–Peterson and Langmuir models gave the highest  $R^2$  and low SSE values showing that the adsorption isotherms of MP by GAC were best described by these two models. The suitability of the Langmuir isotherm to fit the data was confirmed by the exponent value of the Redlich–Peterson model,  $n$ , which was

near to 1. It was observed that both the Langmuir and Redlich-Peterson isotherms could well represent the experimental adsorption data, but the Redlich-Peterson isotherm model was better. Based on the Langmuir isotherm model, the adsorption of MP on GAC adsorbent is likely to occur via chemisorption due to the monolayer formation [37]. GAC adsorbent is assumed to have homogeneous surface-active sites which are all identical and energetically equivalent. The monolayer adsorption capacity,  $q_m$ , was found to be 20.20 mg g<sup>-1</sup>. To compare the efficiency of GAC in removing aqueous MP via ultrasound-assisted adsorption, some tests by the mechanical shaking has been used and showed a capacity removal of 6.57 mg g<sup>-1</sup>. The results revealed the efficiency of using GAC as an adsorbent for the removal of MP from aqueous solution via ultrasound-assisted adsorption.



**Fig. 4.** Comparison between the experimental and predicted isotherms for the adsorption of MP by commercial GAC

**Table 3:** Langmuir, Freundlich and Redlich-Peterson isotherm models constants, SSE and R<sup>2</sup> for the adsorption of MP by commercial GAC

Model	Parameters	Values
Langmuir	$q_m$	20.20
	$K_L$	0.86
	SSE	1.94
	$^2R$ (%)	99.47
Freundlich	$1/n$	0.34
	$K_F$	7.73
	SSE	19.06
	$^2R$ (%)	94.82
Redlich-Peterson	$K_{RP}$	24.60
	$\alpha_{RP}$	1.63
	$n$	0.90
	SSE	0.076
	$^2R$ (%)	99.98

## Computational Details

To explain the activity of adsorption process of MP on GAC, the power of the interaction between activated carbon and methyl parathion was investigated in terms of Hard and Soft Acid-Base Principle. Chemical

hardness represents the resistance of chemical species against the polarization. HSAB Principle of Pearson states that “hard acids prefer the binding to hard bases and soft acids prefer the binding to soft bases.” Conceptual Density Functional Theory (CDFT) presents the following equations to compute the hardness ( $\eta$ ) and electronegativity ( $\chi$ ) [38-40].

$$\chi = -\left[\frac{\partial E}{\partial N}\right]_{v(r)} = \frac{I + A}{2}$$

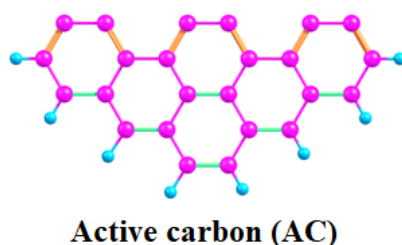
$$\eta = \left[\frac{\partial^2 E}{\partial N^2}\right]_{v(r)} = I - A$$

In the given equation obtained in the light of a finite differences approach, I and A represents the ground state ionization energy and electron affinity of the chemical system, respectively. Koopmans Theorem is widely preferred to predict the ionization energy and electron affinity of chemical systems. In the light of this theorem, we can write the following equations for hardness and electronegativity

$$\chi = \frac{-E_{HOMO} - E_{LUMO}}{2}$$

$$\eta = E_{LUMO} - E_{HOMO}$$

In the study, CDFT calculations for activated carbon and methyl parathion were made through B3LYP /6-311G\*\* calculation level. Atomistic model for active carbon is given below.



**Fig. 5.** Atomistic models of the active carbon

**Table 4:** some parameters determined

Parameter	Active carbon	Methyl parathion
<b>E<sub>HOMO</sub> (eV)</b>	-5.63	-9.40
<b>E<sub>LUMO</sub> (eV)</b>	-2.61	-1.14
<b>I</b>	5.63	9.40
<b>A</b>	2.61	1.14
<b>χ</b>	4.17	5.27
<b>η</b>	3.02	8.26

The deduced parameters issued are gathered in Table 4. Chemical hardness values of active carbon and methyl parathion are quite high. Hard-hard and soft-soft interaction are powerful interactions because hard-hard interaction is mainly electrostatic and soft-soft interactions is mainly covalent [41]. For that reason, the performance of activated carbon in the adsorption of methyl parathion from aqueous solution is compatible



with the predictions made within the framework of HSAB Principle. Another important electronic structure principle is Sanderson's Electronegativity Equalization Principle (EEP) [42]. According to this principle, "when two or more atoms initially different in electronegativity combine chemically, their electronegativities have become equalized". This principle is widely used to explain the electron transfer between chemical systems. It is apparent from the related table that There is a difference of 1.10 eV between the electronegativities of the activated carbon and methyl parathion. This difference supports the power of the interaction with activated carbon of methyl parathion

## Conclusion

The ultrasound-assisted adsorption of MP from aqueous solution using commercial GAC has been studied. The adsorption kinetic uptake for MP by GAC was analyzed by non-linear curve fitting analysis method to fit the PFO and PSO equations. The obtained results showed that the PSO model fit the experimental data well. The equilibrium data were analyzed using non-linear method by fitting them to the Langmuir, Freundlich and Redlich–Peterson model equations. Both the Langmuir and Redlich–Peterson isotherms represent well the experimental adsorption data, but the Redlich–Peterson model was better. The maximum adsorption capacity was found to be 20.20 mg g<sup>-1</sup>. It can be, therefore, concluded that the commercial GAC is an efficient adsorbent for the removal of MP from aqueous solution via ultrasound-assisted adsorption

## References

- [1] H. Zerouali, A. Zaafarani, R. Salghi, A. Hormatallah, B. Hammouti, L. Bazzi, Pesticides residues in tomatoes grown in greenhouses in Morocco and dissipation of endosulfan and deltamethrin, *Fresenius Environmental Bulletin*, 15 4 (2006) 267-271.
- [2] H. Garoiz, M. Berrabah, A. Elidrissi, B. Hammouti, Development GC-MS method determination of organochlorid pesticides in olive oil, *Phys. Chem. News*, 62 (2011) 134-137.
- [3] LH. Bazzi, R. Salghi, A. Zarrouk, H. Zarrok, B. Hammouti, Phytobac, a practical tool management of pesticides wastes (Le phytobac, un outil pratique de gestion des effluents phytosanitaires) Hormatallah, *Phys. Chem. News*, 64 (2012) 112-119
- [4] LH. Bazzi, M. Errami, R. Salghi, A. Hormatallah, A. Zarrouk, H. Zarrok., B. Hammouti, Analyse des Residus de Pesticides sur Peches et Nectarines de la Region de Souss (Analysis of Pesticide Residues in Peaches and Nectarines in Region de Souss), *J. Mater. Environ. Sci*, 4 (1) (2013) 159-164.
- [5] O. Benabbi, E. Elazzouzi, M. Fekhaoui, A. Bellaouchou, Pesticides for agricultural use in the province of Ben Slimane, Morocco: Inventory, toxicity and physicochemical quality of groundwater. *J. Chem. Pharm. Res.* 8 (2016) 266-275.
- [6] C.S. Pundir, A. Malik, Preety, Bio-sensing of organophosphorus pesticides: a review, *Biosens Bioelectron.* 140 (2019) 111348,
- [7] M. Bouterfas, F. Soufiane, C. Zouheir, H. Elhalouani, M. Melhaoui, A. Chafi, Evaluation of farmers' phytosanitary practices in the plain of Triffa (Eastern Morocco), Identification and evaluation of sanitary and environmental risks, *Mor. J Chem.*, 8 (2) (2020) 345-358, <https://doi.org/10.48317/IMIST.PRSM/morjchem-v8i2.19573>
- [8] N. Gao, C. He, M. Ma, Z. Cai, Y. Zhou, G. Chang, X. Wang, Y. He, Electrochemical co-deposition synthesis of Au-ZrO<sub>2</sub>-graphene nanocomposite for a nonenzymatic methyl parathion sensor, *Anal. Chim. Acta*, 1072 (2019) 25–34



- [9] G. Khalili Tanha, A. Ali Barzegar, M. Shokrzadeh, N. Nikbakhsh, Z. Ansari, Correlation between serum concentration of diazinon pesticide and breast cancer incidence in Mazandaran Province, northern Iran, *Caspian J. Environ. Sci.*, 18 (3) (2020) 197-204, <https://doi.org/10.22124/cjes.2020.4132>
- [10] G. Cabello, M. Valenzuela, A. Vilaxa, V. Durán, I. Rudolph, N. Hrepic, G. Calaf, A rat mammary tumor model induced by the organophosphorous pesticides parathion and malathion, possibly through acetylcholinesterase inhibition. *Environ Health Perspect*, 109 (2001) 471-479. <https://doi.org/10.1289/ehp.01109471>
- [11] J. G. Brody, R. A. Rudel, Environmental pollutants and breast cancer. *Environmental Health Perspectives*, 111 (2003) 1007-1019, <https://dx.doi.org/10.1289%2Fehp.6310>
- [12] S. Yuan, C. Li, Y. Zhang, H. Yu, Y. Xie, Y. Guo, W. Yao, Degradation of parathion methyl in bovine milk by high-intensity ultrasound: *Degradation kinetics*, 327 (2020) 127103, <https://doi.org/10.1016/j.foodchem.2020.127103>
- [13] L. Zheng, F. Pi, Y. Wang, H. Xu, Y. Zhang, X. Sun, Photocatalytic degradation of Acephate, Omethoate, and Methyl parathion by Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@mTiO<sub>2</sub> nanomicrospheres. *Journal of Hazardous Materials*, 315 (2015) 11-22, <https://doi.org/10.1016/j.jhazmat.2016.04.064>
- [14] G.H.S. Rodrigues, C.M. Miyazaki, R.J.G. Rubira, C.J.L. Constantino, M. Ferreira, Layer-by-layer films of graphene nanoplatelets and gold nanoparticles for methyl parathion sensing. *ACS Appl. Nano Mater.*, 2 (2019) 1082-1091,
- [15] R. Saini, P. Kumar, Simultaneous removal of methyl parathion and chlorpyrifos pesticides from model wastewater using coagulation/flocculation: Central composite design. *Journal of Environmental Chemical Engineering*, 4 (1) (2016) 673-680
- [16] J. Henych, P. Janoš, M. Kormunda, J. Tolasz, V. Štengl, Reactive adsorption of toxic organophosphates parathion methyl and DMMP on nanostructured Ti/Ce oxides and their composites. *Arabian Journal of Chemistry*, 12 (8) (2019) 4258-4269, <https://doi.org/10.1016/j.arabjc.2016.06.002>
- [17] Q. Jiuhui. Research progress of novel adsorption processes in water purification: A review, *Journal of Environmental Sciences* 20 (2008) 1-13
- [18] S. Jodeh, N. Basalat, A. Abu Obaid, D. Bouknana, B. Hammouti, T. B. Hadda, W. Jodeh, I. Warad, Adsorption of some organic phenolic compounds using activated carbon from cypress products, *J. Chem. Pharmac. Res.*, 6 2 (2014) 713-723
- [19] A. Hassani, R.D.C. Soltani, M. Kıranşan, S. Karaca, C. Karaca, A. Khataee, Ultrasound-assisted adsorption of textile dyes using modified nanoclay: Central composite design optimization. *Korean J. Chem. Eng.*, 33 (1) (2016) 178-188,
- [20] W. Zheng, M. Maurin, M.A. Tarr, Enhancement of sonochemical degradation of phenol using hydrogen atom scavengers. *Ultrason Sonochem.*, 12 (2005) 313-317.
- [21] H. Fu, R.P. Suri, R.F. Chimchirian, E. Helmig, R. Constable, Ultrasound-induced destruction of low levels of estrogen hormones in aqueous solutions. *Environ Sci Technol.*, 41 (2007) 5869-5874.
- [22] C. Djelloul, A. Hasseine, Ultrasound-assisted removal of methylene blue from aqueous solution by milk thistle seed. *Desalin Water Treat.*, 5 (2013) 5805-5812.
- [23] A. Asghari, M. Hemati, M. Ghaedi, M. Rajabi, B. Mirtamizdoust, Ultrasonic assisted adsorption of basic dyes from binary component systems onto ZnO nanoparticles loaded on activated carbon derived from almond shell: optimization by central composite design. *J Nanostruct.*, 4 (2014) 17-30.
- [24] A. Asfaram, M. Ghaedi, S. Hajati, A. Goudarzi, A.A. Bazrafshan, Simultaneous ultrasound-assisted ternary adsorption of dyes onto copper-doped zinc sulfide nanoparticles loaded on activated carbon: optimization by response surface methodology. *Spectrochim Acta A*, 145 (2015) 203-212.

- [25] M. Roosta, M. Ghaedi, A. Daneshfar, R. Sahraei, Ultrasound assisted microextraction- nano material solid phase dispersion for extraction and determination of thymol and carvacrol in pharmaceutical samples: experimental design methodology, *J. Chromatogr. B*, 975 (2015) 34–39.
- [26] R. Zare-Dorabei, S.M. Ferdowsi, A. Barzin, A. Tadjarodi, Highly efficient simultaneous ultrasonic-assisted adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) ions from aqueous solutions by graphene oxide modified with 2, 2'-dipyridylamine: central composite design optimization, *Ultrason. Sonochem.* 32 (2016) 265–276.
- [27] E. Moradi, R. Rahimi, and V. Safarifar, Sonochemically synthesized microporous metal– organic framework representing unique selectivity for detection of  $\text{Fe}^{3+}$  ions, *Polyhedron*, 159 (2019) 251– 258.
- [28] G. Kyriakopoulos, D. Doulia, Adsorption of pesticides on carbonaceous and polymeric materials from aqueous solutions: A review. *Sep Purif Rev.*, 35 (2006) 97–191.
- [29] L. Guo, G. Li, J. Liu, Y. Meng, G. Xing, Nonlinear Analysis of the Kinetics and Equilibrium for Adsorptive Removal of Cd(II) by Starch Phosphate, *Journal of Dispersion Science and Technology*, 33:3 (2012) 403-409.
- [30] I. Langmuir, the adsorption of gases on planes surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* 40 (1918) 1361-1403,
- [31] H.M.F. Freundlich, over the adsorption in solution, *J. Phys. Chem.* 63 (1959) 1024-1036
- [32] O. Redlich, D.L. Peterson, , A Useful Adsorption Isotherm; *J. Phys. Chem.* 63(6) (1959) 1024,
- [33] A.D. N'diaye, M.S.A. Kankou, Valorization of Balanites aegyptiaca seeds from Mauritania: Modeling of adsorption isotherms of caffeine from aqueous solution, *Journal of Environmental Treatment Techniques*, 7, 3 (2019) 450-455
- [34] A.D. N'diaye, M.A. Bollahi, M.S.A. Kankou, Sorption of Paracetamol onto Groundnut Shell from aqueous solution, *Journal Materials and Environmental Science*, 10 (2019) 553-562
- [35] J. M. Salman, V.O. Njoku, B.H. Hameed, Bentazon and Carbofuran adsorption onto date seed activated carbon: kinetics and equilibrium. *Chemical Engineering Journal* 173 (2011) 361–368.
- [36] S.G. Mohammad, S.M. Ahmed, Preparation of environmentally friendly activated carbon for removal of pesticide from aqueous media. *Int J Ind Chem* 8 (2017) 121–132.
- [37] G.H. Safari, M. Zarrabi, M.M. Hoseini, H. Kamani, J. Jaafari, A.H. Mahvi, Trends of natural and acid-engineered pumice onto phosphorus ions in aquatic environment: adsorbent preparation, characterization, and kinetic and equilibrium modeling, *Desalin. Water Treat.*, 54 (11) (2015) 3031–3043.
- [38] S. Kaya, & C. Kaya, A simple method for the calculation of lattice energies of inorganic ionic crystals based on the chemical hardness. *Inorganic chemistry*, 54(17) (2015) 8207-8213.
- [39] S. Kaya, & C. Kaya, A new equation for calculation of chemical hardness of groups and molecules. *Molecular Physics*, 113(11) (2015) 1311-1319.
- [40] N. Islam, & S. Kaya, (Eds.). Conceptual density functional theory and its application in the chemical domain. CRC Press (2018).
- [41] S. Kaya, & C. Kaya, A new method for calculation of molecular hardness: a theoretical study. **Computational and Theoretical Chemistry**, 1060 (2015) 66-70.
- [42] S. Kaya, & C. Kaya, A new equation based on ionization energies and electron affinities of atoms for calculating of group electronegativity. *Computational and Theoretical Chemistry*, 1052 (2015) 42-46.