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Kinetics and Thermodynamic Study of the Pesticide Absorption in Contaminated Waters using Biotite Silicate in Boroujerd, Lorestan, Iran

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Abstract

Contamination of water sources by pesticides is considered as one of the environmental problems which are on growth due to agricultural development and the variation of herbal pesticides. The present study aims at making a Biotite absorber to omit the organic pollutant of water. In the current study, Biotite, which is found naturally in Boroujerd, west of Iran, is used to absorb pesticides including Permethrin, Diazinon, and Malathion. The effect of concentration, pH, and contact time on pesticide absorption was studied. The findings revealed that the aforesaid absorber has had the appropriate return to absorb the mentioned pesticides. The highest percentage of permethrin absorption by Biotite took place in the concentration of 4 ppm, pH= 7, and contact time of 20 minutes, while the highest percentage of Malathion by Biotite occurred in the concentration of 4 ppm, pH= 7, and contact time of 40 min. The findings indicated that the process of diazinon absorption follows isotherms like Langmuir and Freundlich. However, the process of permethrin and Malathion absorption follows Langmuir isotherm and Freundlich isotherm respectively. Generally, the findings from the present study can be used to plan various ways to control contamination in the industrial scale, decreasing destructive environmental effects in the waters contaminated by pesticides.

***Key words**: Pesticide, Absorption, Biotite, Water Pollutan*

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1. Introduction

As the most important element of nature and the most vital factor of life in human societies, water has had a great role in the heath of society, as a result, water contamination is considered an environmental threat. Freshwater is the most vital condition used not only for drinking, agriculture, and water industries – a thermal powerhouse, refineries, and petrochemical industries- but also in chemical reactions in a water environment. Therefore, due to the great importance of water and the growing demand of the human community and industry, it is necessary to work on the chemistry and quality of water. As it is used for household, agriculture, industry, etc., it changes to wastewater which can pollute the environment. Therefore, preventing contamination, some strategies are needed to filter and reuse this wastewater (Goudie 2018). Human communities have always been curious to recognize and control the pollutant sources of their environment. The entrance of pollutants like pathogens, poisonous compounds to the human-environmental sources like water, air, and soil has always been regarded as a severe threat for community health (Abdel-Raouf et al., 2012). The pesticide is one of these pollutants which are used increasingly in agriculture mostly due to the rapid growth of human beings. In fact, the more human growth, the more demands for agricultural production and food (Arjmandi et al., 2010). Four main groups of pesticides are insecticides, fungicides, herbicides, and bactericides. The most popular poisons of pesticides are organochlorine, organophosphate, carbamate, and pepperidge. Organophosphate compounds are the largest and the most diverse of the pesticides making approximately 40% of recorded pesticides in the world (Pirsaheb et al., 2014). Unfortunately, developing countries have the highest transaction of pesticides nowadays. In fact, organophosphate, carbamate, pepperidge, and organochlorine are sold 40%, 20/4%, 18/4%, and 6/1% respectively. Organophosphate poisons have destructive effects on the immune system, nervous system, respiratory system, endocrine, and reproduction. The increase of Organochlorine resistance is a reason making it get replaced by organophosphate (Blair et al., 2015; Jayaraj et al., 2016). As an organic pollutant resisting decomposition (POPs), pesticides are recognized as one of the compounds in wastewater coming from the producers of agricultural pesticides and drainage (El Bakouri et al., 2008). As a result, water, as a life source, is in danger of contamination. As a matter of fact, pesticides can enter water sources through direct wash or irrigation. Since they are mostly applied during spring, they are washed by rain leading them to surface water in poisoned regions and before decomposition. Moreover, pesticides can find a way to groundwaters by water penetrating soil layers. Therefore, water sources should be preserved. Measuring left pesticides in water has—great importance not only in maintaining human health but also a controlled environment, so, as the first step, it is really necessary to determine the poison concentration carefully and compare them with the standard rate (Khodadadi et al., 2010). Nowadays, the misuse of poisons and pesticides in Iran is serious trouble (Mostafalou and Abdollahi 2013). There are different ways to isolate and recognize poisons and pesticides including extraction of the solid phase of microbe, extraction by solid-phase, extraction of liquid-liquid, and the extraction of micro liquid-liquid which are the most famous and useful ways to extract poisons and pesticides in water matrices. Extraction by solid phase is a way to prepare samples in which condensation and purification of the sample from the solution are done by its absorption on a solid phase which then can be assessed by an appropriate solution. Many low-cost adsorbents have been reported to absorb pesticides from an aqueous solution that results indicate that sheet silicate shows the highest adsorption ability, with the saturated adsorption capacity. In the environment, silicate minerals, behave differently in surface characters and adsorption ability that Biotite is favorable adsorbent in with low levels of toxins. Ions could penetrate the interlayer of biotite, this ion-exchange process is pH-dependent and only favorable under acidic condition (Arthur and Pawliszyn 1990; Barceló 1993; Ceolin et al., 2015; Duan et al., 2018; Ma, X. et al., 2020; Wu et al., 2018; Zhou et al., 2020). Biotite is commonly found in almost all types of granitic rocks and some metamorphic rocks and this research composition of Biotite from Boroujerd granitoids in Sanandaj-Sirjan Zone has been investigated to study its geochemical nature and naturally absorber for pesticides. Separated Biotites were analyzed by XRF and SEM. The present paper describes the use of natural Biotite for the removal of pesticides from aqueous environments. Permethrin, diazinon, and malathion are a pesticide that is widely used in agriculture in the study area that can contaminate water through runoff from treated plants and soil. Contamination of soil and water by pesticides is widespread in the Lorestan province. Aim of this research in the present study, Biotite, as a natural absorber for poisons (permethrin, diazinon, and malathion), is used by the extraction of the solid phase from water solutions. Absorption examinations have been done in various conditions to find the highest absorption and experimental data have been assessed by isotherm Freundlich and Langmuir models.

2. Materials and Methods

Boroujerd is located on the west of Iran and the east of Lorestan Province. A granite containing Biotite was gathered in 25 km, east of Boroujerd, in eastern longitude 48^0 56’ and northern latitude 33^0 53’ (Fig. 1). The studied area is located in the northeast of the Khoramabad and is a small part of the Sanandaj -Sirjan metamorphic belt in Iran. The area is chiefly constituted of quartz-diorite, granodiorite, monzogranite, Mesozoic schists, and pegmatites. The oldest rocks are Precambrian, but the intrusives are emplaced into metasediments of early Mesozoic age. Biotite is a phylloclade mineral with the formula $K (Mg, Fe)_3(AlSi_3 O_{10}) (OH, F)_2$ which can be seen in a wide range of igneous and metamorphic rocks. In fact, Biotite is the dominant ferrozine mineral in granitoid mass in Broujerd (Ahmad nejad et al., 2017; Jafari et al., 2018). In the present study, scanning electron microscope (SEM), MIRA3-LMU model was used to investigate the morphology and uniform absorption of Biotite. SEM picture of Biotite is presented in figure 2 in which the particles have a sheet form. Biotite compound is determined by the XRF machine whose chemical compound is shown in table 1. According to table 1, the silicate is the major component of Biotite forming more than 30% of this absorber. Gathered from the Boroujerd region, granite samples were prepared and moved to the laboratory of Lorestan University where they were chopped by the crusher. Biotite was extracted from the samples by a strong magnet. Before being used as an absorber, Biotite was dried in an oven with the temperate of 105^0 C for an hour then it was powdered in a porcelain mortar. It was screened by a 60-mesh sieve to make the sample size to 60 mesh. It should be said that the grading absorbers were kept in a closed container to the time it was used. In the current study, permethrin with the purity of 25% and molecular weight of 1/14 g/m, diazinon with the purity of 95% and molecular weight of 1/16 g/m, and malathion with the purity of 95% and molecular weight of 1/23 g/m were bought from Khoram Shimi Razi to make the main solution, while methanol (99/9%), dihydrogen phosphate diphtheria, sodium hydroxide, and hydrochloric acid were bought from Merck

Company (Kurdi and Eslamkish 2017; Goldstein et al., 2017; Batista et al., 2018).

2.1. Chromatography Conditions

Gas chromatography machine, model GC-17A, Shimadzu which is equipped with mass spectrometry detector model MS-QP5050, was applied to isolate, measure, and recognize the compounds (Rahimi et al., 2014). Separation of the compounds was conducted by a capillary column of fused silica (Polydimethy 1 Siloxane: 95% phenyl 1: 5% Bp-5), with an internal diameter of 25micrometer, the length of 30 meters, and a thin film with 25-micrometer thickness. Helium with the purity of 99.999% was applied as the carrier gas. The primary temperature of the column in the GC machine was 60^0 C which was maintained fixed for 1 minute. Then, it was increased to 200^0 C with a speed of 20^0 C min^{-1} and it was kept unchanged for 1 minute. It again was increased to 280^0 C with a speed of 8^0 C min^{-1}, although it was kept fixed for 5 minutes at this temperature. During the separation, the temperature of the injection place was 250^0 C, the temperature of transition way to the detector was 280^0 C. Besides, the speed of carrier gas in the column was 1ml min^{-1}. The injection system was set without fissure in order to guide enalite completely to GC column. The qualitative recognition of chromatography compounds (MS-GC) is based on inhibition time. Standard injection to the machine, peak inhibition time of diazinon, regarding laboratory condition, was 12/6 minute, while 14/2 minute for malathion and 23/19-23/48 minute for permethrin.

2.2. Drawing Calibration Diagram for Standard Solutions

The standards of the mixture of these compounds with different concentrations are made and directly injected to GC-MS to find out the linear border of the extracted compounds and their high and low limitation in measurement. Concentration changes are drawn based on the surface under the peak presented in figure 3.

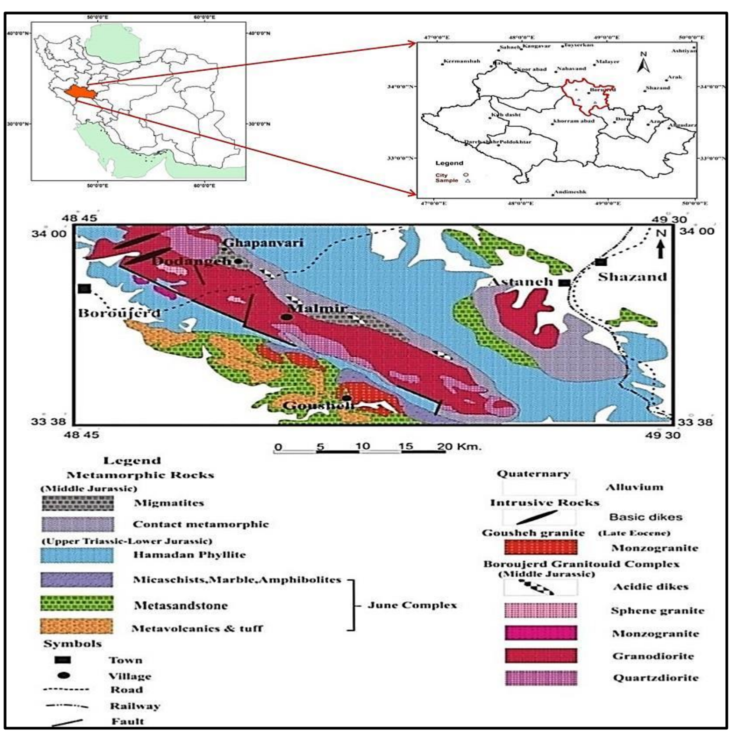


Fig. 1. The location and geological map of the study area

Table 1. Results of XRF analysis of Biotite

Composition	Mg0	MnO	Fe_2O_3	FeO	Al_2O_3	TiO_2	SiO_2
Wt%	6.21	0.44	3.95	23	18.60	2.58	32
Composition	-	H_2O	Cl_2	F	K_2O	Na_2O	CaO
Wt%	-	3.97	0.33	0.27	10.50	0.15	0.15

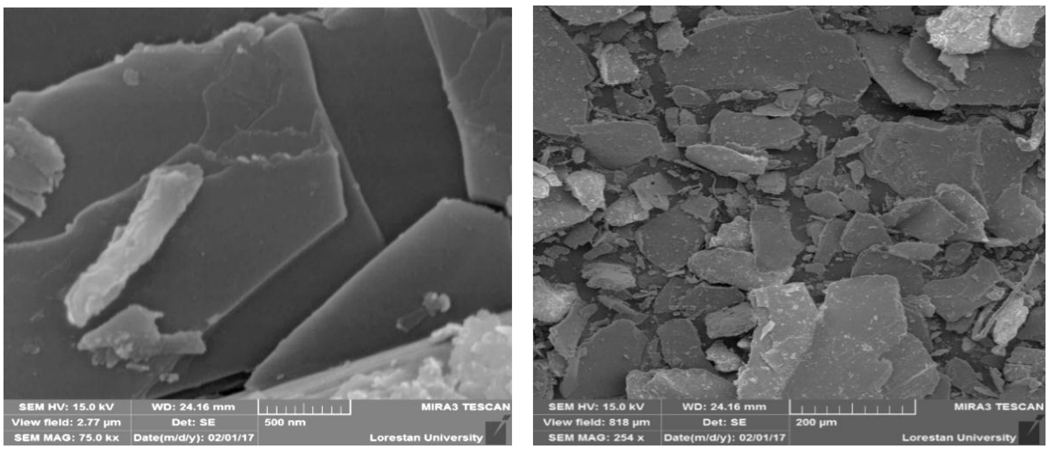


Fig. 2. SEM of Biotite silicate

3. Methodology

All the examinations were conducted by the extraction of the solid phase, patch, in which two stock solutions with high concentration and working solution with low concentration are needed. The stock solution with 100 ppm concentration is prepared by mixing 9 microliter diazinon, 8 microliter malathion, and 33.6 microliter permethrin taken by HPLC and poured in volumetric flask 100 and the solution is volumized by methanol. Besides, the solution was kept in the freezer during the testes. The following formula was applied to make a working solution in the examination:

$$M1V1 = M2V2 \quad (1)$$

M_1 stands for the concentration of the stock solution, M_2 for primary concentration, V_1 the volume taken from the stock solution, V_2 for the capacity of the solution dish. At first, buffer phosphate salt 0.02 molar ($NaH_2PO_4H_2O$) has been used to fix pH through the test. Moreover, sodium hydroxide 0.2 Molar and hydrochloric acid 0.5 molar were applied to regulate pH through the test. Primary concentration (2-4-6-8-10 ppm), pH (3-5-7-9-11), and contact time of the reaction (10-20-30-40-50 min) are the factors investigated in the present study. The amount of the absorber is considered 2g in the temperature of 25^0 C for all tests. Primary concentration was determined in fixed condition (pH -3 and contact time 30 min). However, determining optimal primary concentration by Biotite, it was first taken from two 50ml flasks to make the concentration of (2-4 ppm) and then from three 25ml flasks to make the concentration of (6-8-10 ppm). 1 ml and 2 ml of stock solution were added to 50 ml flasks and 25 ml flasks respectively and each flask was volumized by pH-3. For the next step, 2 g Biotite absorber was poured to five 50 ml beakers, and then 20 ml of pesticide (2-4-6-8-10 ppm) was added to each beaker covered by parafilm. The beakers were kept in a shaker and water bath with 150 revolutions, with a temperature of 25^0 C for 30 minutes. For the next step, taking out the beakers, the upper solution was taken and then 7 ml methanol was added to the remaining Biotite in each beaker. The samples were again put in the shaker and water bath with a temperature of 25^0 C for 30 minutes to be shaken. In the last step, the beakers were taken out of the machines and their solutions were filtered by filter paper. The volume of the diluted samples was measured by pipette. Then, 1 lµ of each diluted sample was injected into the GC-MS machine. Absorption is found by the following relationship.

$$\text{Absorption Percentage} = \frac{\text{Drop volume} * \text{Concentration (malathion,permethrin ,diazinon)}}{\text{Primary volume} * \text{Primary volume}} * \times 100 \quad (2)$$

The examinations were conducted in fixed conditions (the concentration of 4 ppm and contact time of 30 minutes) to determine the optimal pH of absorption. Biotite was taken from three 50ml flasks and a 25 ml flask to make 4 ppm concentration. 1 ml and 2 ml of stock solution were added to the 50 ml and 25 ml flasks. Each flask was volumized by pH (5-7-9-11). In the next step, four 50 ml beakers were selected filled by 2 g Biotite absorber, then 20 ml of the pesticide with 4ppm concentration was added. They were covered by a parafilm sheet and kept in the shaker and water bath with 150 revolutions with a temperature of 25^0 C for 30 minutes in order to be shaken. When the beakers were taken out from the shaker and rotary machines, the upper solution was removed and 7 ml methanol was added to the remaining Biotite. They were again moved to the shaker and water bath machines with a temperature of 25^0 C for 30 minutes to be shaken. In the last step, the beakers were taken out from the shaker and rotary machines, and the solutions were filtered by filter paper. The volume of each diluted solution was measured by pipette. 1 lµ each diluted solution was injected to GC-MS. The amount of absorption is found out in the following relationship. The examinations were conducted in fixed conditions (pH-7 and 4 ppm concentration) to determine the optimal contact time of absorption. As the first step, Biotite was taken from three 50 ml and one 25 ml flasks to make 4ppm concentrations and then 1 ml and 2 ml of stock solution were added to 50 ml and 25 ml flasks respectively. Each flask was volumized by pH-7. In the next step, four 50 ml beakers were chosen and 2 g Biotite absorber was added to each beaker. 20 ml of the pesticide with 4ppm concentration was added to each beaker covered by a parafilm sheet. They were moved to the shaker and water bath machines with 150 revolutions and a temperature of 25^0 C for (10-20-40-50 minutes) to be shaken. In the next step, taken out from the machines, the upper solution was removed, and then 7 ml methanol was added to the remaining Biotite in each beaker. They were again moved to the machines with a temperature of 25^0 C to be shaken. In the last step, the beakers were taken out and filtered by filter paper. The volume of diluted samples was measured by pipette and 1 lµ of each diluted solution was injected to GC-MS. Using the relationship (2), absorption was calculated. Concentration examinations (2-4-6-8-10 ppm) were applied to determine absorption isotherm tests. Moreover, The Langmuir and Freundlich models have been widely used to characterize the adsorption of solutes from aqueous solutions. This study was aimed at applying a combined Langmuir–Freundlich model to describe the multi-component adsorption of organic compounds such as Permethrin - Diazinon- Malathion using Biotite. The results of the study well fitted with the model developed. Langmuir and Freundlich models were used to describe the data.

4. Results

4.1. Determining the Optimal Concentration of Pesticides, including Permethrin - Diazinon- Malathion

According to figure 3, the best results in 4 ppm concentration are found from permethrin. As can be seen, when permethrin concentration increases, absorption decreases. However, in high concentrations, as the weight of the absorber increases, the absorption increases. It can be due to the fact that the molecules of the pesticide are absorbed fast on the absorption surface in a low concentration of pesticides. As a result, the increase of the primary concentration of the pesticide leads to the saturation of the absorber surface shortly. Besides, it can be due to the repulsion among the molecules of pesticide leading to absorption decrease. Probably, as the concentration of permethrin increases, a force of attraction is made among the molecules decreasing their tendency to be absorbed on a solid surface. The best results for diazinon are observed in the concentration range from 4 ppm to 8 ppm (Fig.4), although the concentration of 4 ppm is more plausible. As can be seen, when the concentration of diazinon increases, absorption decreases. According to figure 4, malathion has less tendency for absorption than permethrin and diazinon. The best results for malathion is observed in the concentration of 2 ppm. However, for more coordination with other findings, it seems that it is better to consider the concentration of 4 ppm as the reference. As it is seen, the increase in malathion concentration leads to absorption decrease.

4.2. Determining the Optimal pH of the Pesticides Permethrin - Diazinon- Malathion

According to figure 5, the results for permethrin -diazinon-malathion are observed in neutral pH (pH=7). As it is clear, absorption decreases, when pH either increases or decreases.

4.3. Determining the Optimal Contact Time of the Pesticides Permethrin - Diazinon- Malathion

Based on figure 6, it can be seen that the best results for permethrin are observed in a contact time of 20 minutes. As a matter of fact, when the contact time of permethrin increases, absorption decreases which can be due to the despondent of adsorbed molecules from the Biotite surface. According to figure 6, the best results for diazinon are found in a contact time of 30 minutes. Moreover, as figure 6 reveals, the best results for malathion are seen in a contact time of 40 minutes due to the presence of available empty sites for absorption which used to be a lot. After this time, absorption is descending and despondent happened. Obviously, as the contact time of malathion increases, absorption increases.

4.4. The Investigation of Balance Isotherms of Surface Absorption

4.4.1. Determining Adsorption Isotherm of Diazinon

Absorption isotherms indicate that absorption is a function of absorber balance concentration. Langmuir and Freundlich models are applied to fit surface absorption of diazinon (Fig. 7). Based on the findings in table 3, it is perceived that the findings are in accordance with the isotherm models; Langmuir with R^2=0.99 and Freundlich with R^2= 0.99.

4.4.2. Determining the Adsorption Isotherm of Permethrin

Absorption isotherms reveal that absorption is a function of balance concentration of the absorber. Langmuir and Freundlich's models are applied to fit the surface absorption of permethrin (Fig. 8). According to the findings in table 4, it is figured out that the results have more adaptation with the Langmuir model; R^2=0.98. Therefore, the maximum amount of permethrin surface absorption on Biotite is as equal as 2.19 mg/g. Since the Langmuir model can justify the findings, it seems that surface absorption is a kind of monolayer.

4.4.3. Determining Adsorption Isotherm of Malathion

Absorption isotherms demonstrate that absorption is a function of balance concentration of the absorber. Langmuir and Freundlich's models are used to fit the surface absorption of Malathion (Fig. 9). Based on the findings in table 5, it is found that the results have more adaptation with the Freundlich model; R^2= 0.55.

5. Conclusions

The contamination from pesticides has become a tremendous concern in producing freshwater. Agricultural poisons can always be found in water sources, so it intensifies the concerns of wastewater and freshwater filter. The most common pesticides are kinds of phosphate. In the present study, permethrin, diazinon, and malathion have been used due to their destructive effect on the environment. A majority of researchers are trying to find cheaper and more appropriate methods to filter industrial wastewaters in order to replace the costly ways to filter wastewater such as chemical treatment, the methods of ionic exchange, reverse smash, solution extraction, and other common methods. In the current study, Biotite was applied as an absorber to absorb the pesticides, including permethrin, diazinon, and malathion. The findings indicate the acceptable return of the absorber. Furthermore, the results reveal that as concentration increases, the absorption of permethrin, diazinon, and malathion decreases. In fact, permethrin has the highest absorption, 40.38%, in 4 ppm concentration. It can also be increased by the increase of absorber volume and the concentration of the pesticides. It is also found that as contact time increases, permethrin absorption decrease; in the contact time of 20 minutes it has 100% absorption which can be due to the respondent of the absorbed molecules from Biotite surface. Besides, diazinon had the highest absorption in the contact time of 30 minutes, 98/86%. In fact, as the contact time increases or decreases, the diazinon absorption decreases. Malathion had the highest absorption in the contact time of 40 minutes, 22%. After this time, the absorption is descending leading to despondent. According to the findings from concentration, PH, and time, permethrin has the highest absorption, while malathion has the lowest absorption whose absorption and filter depend on the amount of the absorber. In other words, more pesticides can be filtered by the increase of the absorber. The process of diazinon surface absorption by Biotite follows Langmuir, R^2=0.99, and Freundlich, R^2=0.99, in a balanced mood. According to the Langmuir model, the maximum surface absorption of diazinon on Biotite has been 6.497 mg/g. Surface absorption of permethrin using Biotite follows Langmuir isotherm, R^2=0.98, in a balanced mood. Since the maximum surface absorption of permethrin on Biotite has been 2.19mg/g, the Langmuir model can justify the findings. Surface absorption is a monolayer. Surface absorption of malathion by Biotite follows Freundlich isotherm, R^2=0.55, in balance mood. Based on the examinations, it is concluded that Biotite is a natural absorber with a high return which is cheap having the highest efficiency in neutral pH. Moreover, it is affordable enough which can be used to filter contaminated surface and ground waters and industrial wastewaters. Since it is strong enough to absorb pesticides, it is concluded that Biotite has a considerable role in environmental self-purification.

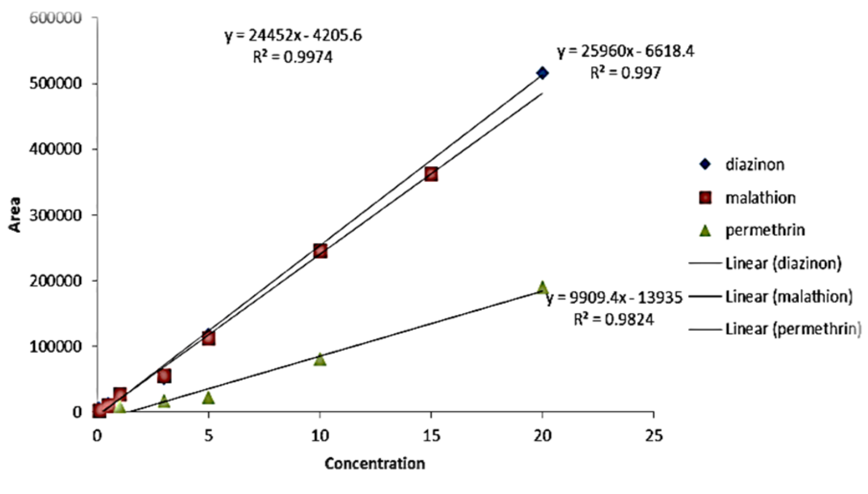


Fig. 3. The calibration carve for measurement of pesticides including permethrin, diazinon, and malathion with GC-MS

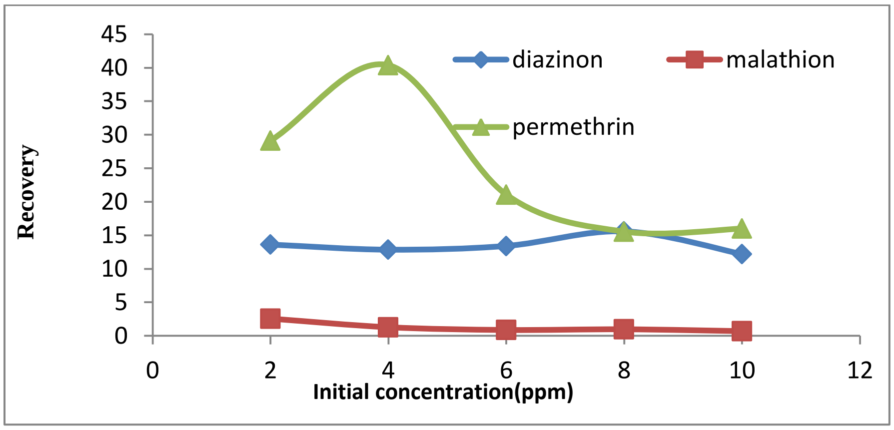


Fig. 4. The effect of the initial concentration of the pesticides Permethrin - Diazinon- Malathion absorption (pH=3, T=30 min)

Table 2. The Isotherms Langmuir and Freundlich models

Langmuir	$\frac{1}{C_e}$ vs. $\frac{1}{q_e}$	$\frac{1}{q_e} = (\frac{1}{k_l\, q_m})(\frac{1}{C_e}) + \frac{1}{q_m}$
Freundlich	Ln(q_e) vs. Ln (C_e)	Ln q_e =Ln k_f + n^{-1} Ln C_e

Table 3. Langmuir and Freundlich Isotherm model parameters for Diazinon

Model	Value	Parameter
Langmuir	6.497	q_m
	40.01	K_l
	0.9916	R^2
Langmuir	29.8624	K_f
	1.5742	1/n
	0.9979	R^2

Table 4. Langmuir and Freundlich Isotherm model parameters for Permethrin

Model	Value	Parameter
Langmuir	2.1915	q_m
	3.9114	K_l
	0.9855	R^2
Langmuir	2.0360	K_f
	0.5428	1/n
	0.9605	R^2

Table 5. Langmuir and Freundlich Isotherm model parameters for Malathion

Model	Value	Parameter
Langmuir	0.0704	q_m
	0.7879	K_l
	0.4231	R^2
Langmuir	23.8360	K_f
	0.23	1/n
	0.5503	R^2

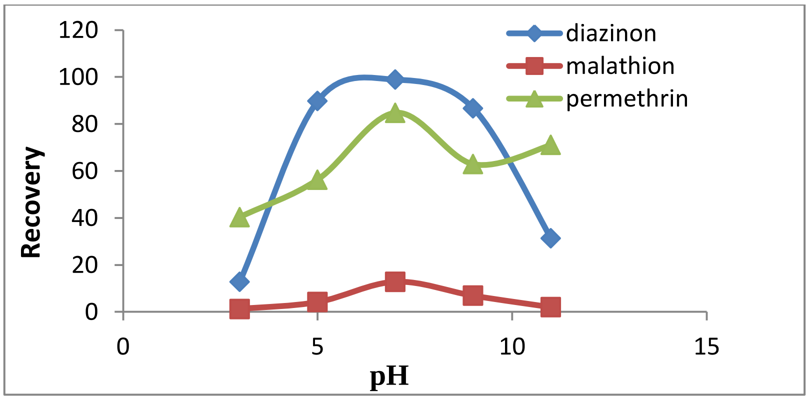


Fig.5 The effect of pH in the pesticides Permethrin-Diazinon-Malathion absorption (Concentration= 4ppm, T=30 min)

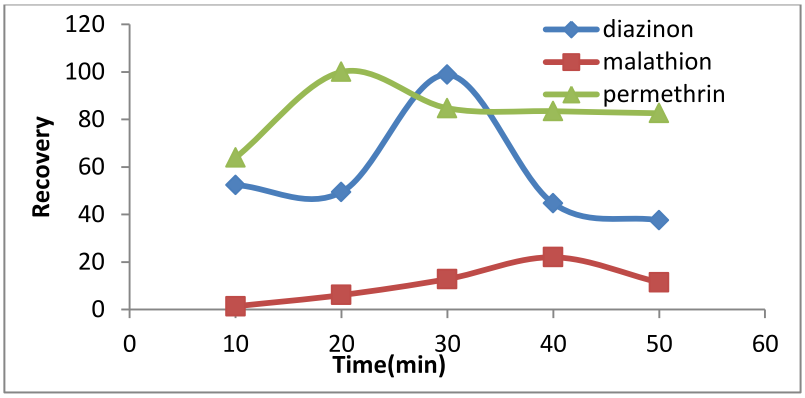
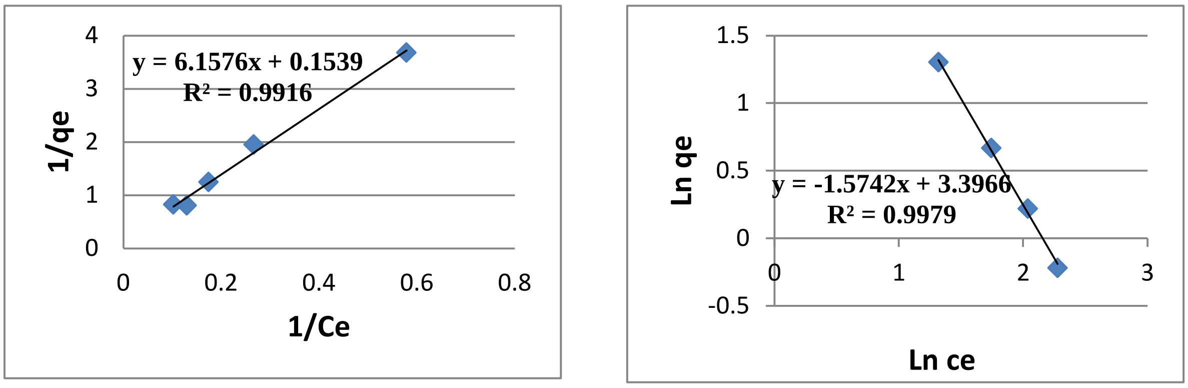


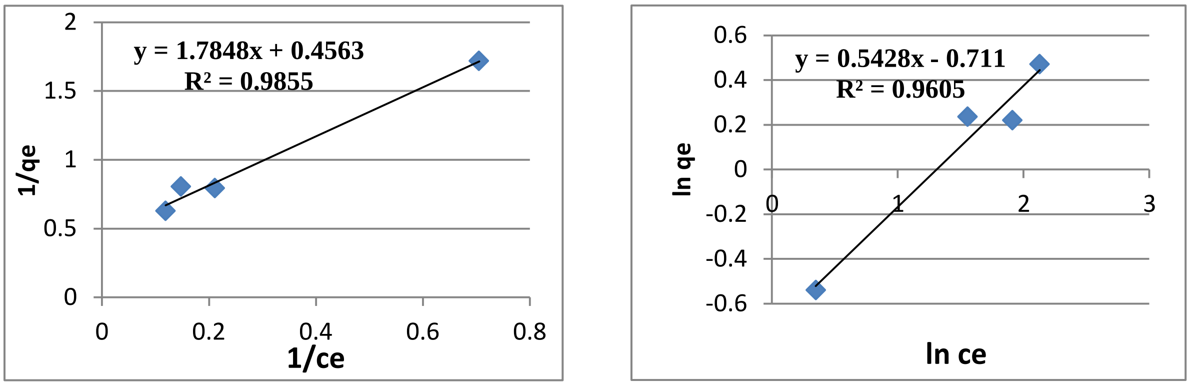
Fig. 6. The effect of contact time in the pesticides Permethrin-Diazinon-Malathion absorption (Concentration= 4ppm, pH=7)



a

b

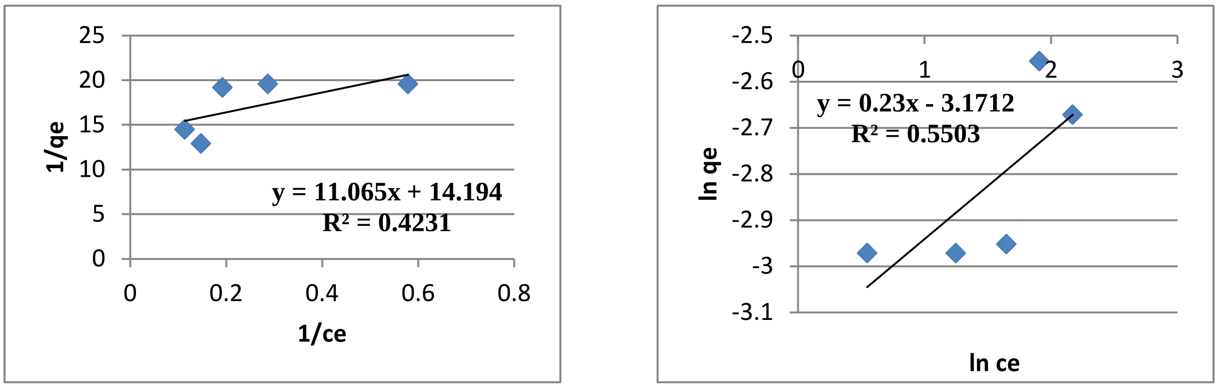
Fig. 7. Isotherm diagrams due to the Diazinon absorption (a: Langmuir model, b: Freundlich model)



a

b

Fig. 8. Isotherm diagrams due to the Permethrin absorption (a: Langmuir model b: Freundlich model)



a b

Fig. 9. Isotherm diagrams due to the Malathion absorption (a: Langmuir model b: Freundlich model)

References

Abdel-Raouf, N., Al-Homaidan, A. and Ibraheem, I., 2012. Microalgae and wastewater treatment, Saudi journal of biological sciences, 19, 257-275.

Ahmadnejad, F., Zamanian, H. and Sameti, M., 2017. Geochemistry and economic potential of the Samen Granitoid Intrusion, Northwestern Iran: Implications for skarn mineralization, Neues Jahrbuch für Mineralogie-Abhandlungen: Journal of Mineralogy and Geochemistry, 194, 175-203.

Arjmandi, R., Tavakol, M. and Shayeghi, M., 2010. Determination of organophosphorus insecticide residues in the rice paddies, International Journal of Environmental Science & Technology,7, 175-182.

Arthur, C. L., and Pawliszyn, J., 1990. Solid-phase microextraction with thermal desorption using fused silica optical fibers, Analytical Chemistry. 62, 2145-2148.

Barceló, D., 1993. Environmental Protection Agency and other methods for the determination of priority pesticides and their transformation products in water, Journal of Chromatography A,463,117-143.

Batista, A. H., Rate, A. W., Gilkes, R. J., Saunders, M. and Dodd, A., 2018. Scanning and transmission analytical electron microscopy (STEM-EDX) can identify structural forms of lead by mapping of clay crystals, Geoderma. 310, 191-200.

Blair, A., Ritz, B., Wesseling, C., and Freeman, L. B., 2015. Pesticides and human health. BMJ Publishing Group Ltd.

Ceolin, L. P. W., Junior, T. R. A., Morais, M. M., Rosado, J., Veloso, A. D., Paulino, B. F. and Martins, L. L.,2015. Biotite (Black Mica) as an Adsorbent of Pesticides in Aqueous Solution, Water, Air, & Soil Pollution. 226, 231-238.

Duan, W., Wang, N., Xiao, W., Zhao, Y. and Zheng, Y., 2018. Ciprofloxacin adsorption onto different micro-structured tourmaline, halloysite and biotite, Journal of Molecular Liquids. 269, 874-881.

El Bakouri, H., Morillo, J., Usero, J. and Ouassini, A., 2008. Potential use of organic waste substances as an ecological technique to reduce pesticide groundwater contamination, Journal of Hydrology. 353, 335-342.

Goldstein, J. I., Newbury, D. E., Michael, J. R., Ritchie, N. W., Scott, J. H. J. and Joy, D. C., 2017. Scanning electron microscopy and X-ray microanalysis. Springer.

Goudie, A. S., 2018. Human impact on the natural environment. John Wiley & Sons.

Jafari, A., Fazlnia, A. and Jamei, S., 2018. Geochemistry, petrology and geodynamic setting of the Urumieh plutonic complex, Sanandaj–Sirjan Zone, NW Iran: New implication for Arabian and Central Iranian plate collision, Journal of African Earth Sciences. 139, 421-439.

Jayaraj, R., Megha, P. and Sreedev, P., 2016. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment, Interdisciplinary Toxicology.9, 90-100.

Khodadadi, M., Samadi, M., Rahmani, A., Maleki, R., Allahresani, A. and Shahidi, R., 2010. Determination of organophosphorous and carbamat pesticides residue in drinking water resources of Hamadan in 2007, Iranian Journal of Health and Environment.2, 250-257.

Kurdi, M. and Eslamkish, T., 2017. Integration of SEM/WDX elemental mapping and micromorphology to determine mineralogical traits of peat soils (case study: Northern Iran), Acta Geochimica. 36, 298-315.

Ma, X., Ma, H., Yuan, J. and Guo, R., 2020. Synthesis of K2O–MgO–SiO2 compounds as slow-release fertilisers from acid-leached biotite residues, Ceramics International, 46, 1403-1410.

Mostafalou, S. and Abdollahi, M., 2013. Pesticides and human chronic diseases: evidences, mechanisms, and perspectives, Toxicology and applied pharmacology. 268, 157-177.

Pirsaheb, M., Dargahi, A., Hazrati, S. and Fazlzadehdavil, M., 2014. Removal of diazinon and 2, 4-dichlorophenoxyacetic acid (2, 4-D) from aqueous solutions by granular-activated carbon, Desalination and Water treatment. 52, 4350-4355.

Rahimi, A., Hashemi, P., Talei, G. R., Borzuei, M., and Ghiasvand, A. R., 2014. Comparative analyses of the volatile components of Citrus aurantium L. flowers using ultrasonic-assisted headspace SPME and hydrodistillation combined with GC-MS and evaluation of their antimicrobial activities, Analytical and Bioanalytical Chemistry Research. l.1, 83-91.

Wu, H., Qiang, S., Fan, Q., Zhao, X., Liu, P., Li, P., Liang, J. and Wu, W., 2018. Exploring the relationship between Th (IV) adsorption and the structure alteration of phlogopite, Applied Clay Science.152, 295-302.

Zhou, W., Xian, D., Su, X., Li, Y., Que, W., Shi, Y., Wang, J. and Liu, C., 2020. Macroscopic and spectroscopic characterization of U (VI) sorption on biotite, Chemosphere, 126942.