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Research Article

REMOVAL PARAQUAT FROM AQUEOUS SOLUTIONS WITH ZEOLITE NANOPARTICLES OPTIMIZED USING THE BOX-BEHNKEN DESIGN

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Abstract

Nowadays, much attention for using chemicals as adsorbent for removal herbicide from aqueous solution has been aroused. Zeolite as low-cost adsorbent was used in this paper for removal paraquat from water. Iran has a variety resources of zeolite. Zeolite was collected from Semnan region and after modification, zeolite nano-particles was used for adsorption. Box-Behnken experimental design was used for simplifying and optimizing the experiment condition. Three factor was studied in this paper; pH (6-8), temperature (25-45°C) and the amount of adsorbent (0.5-2 g). The residue of paraquat after each experiment was determined by injection of 250 µl of each sample to HPLC equipped with column (150mm×4.6mm, ODS (C18)-H-OL), UV-detector at 258 nm. The mobile phase composition was a mixture of tetramethylammonium hydroxide pentahydrate and ammonium sulphate in ultra-pure water and adjusted to pH 2 with sulphuric acid. According to BBD the optimum condition was pH 6, temperature 45°C and 2 g of adsorbent. At this condition the removal efficiency was about 80%. The results of this study showed thatby increasing the pH, the percentage of removal was decreased. However, the higher temperatureslead to more removal capacity of zeolite nano-particles but it was not statistically significant.

Keywords: Paraquat, Zeolite, Box-Behnken design, HPLC.

Introduction

With the explosion of population in the past few decades demand for food has increased; pests are the main problem for crop production. There’s limited physical methods for controlling pests; hence the use of agrochemical compounds is inevitable. Presence of herbicides in water has numerous deleterious effects on aquatic organisms and humans. One of the most hazardous herbicides is Paraquat (Aramendía et al. 2006; Dores et al. 2008; Maya et al. 2011; Pinto and Jardim 2000).

Paraquat a biperidylium herbicide is one of the most widely used herbicides in the world especially in developing countries (Nanseu-Njiki et al. 2010; Shahrtash et al. 2011). It is a potent, fast acting, nonselective, broad-spectrum contact herbicide(El Mhammedi et al. 2010; Samai et al. 2010). Paraquat reduces the amounts of NADPH in cells and subsequently produces highly reactive oxygen species (ROS) that cause lipid peroxidation, degradation of cholrophile, denaturation of proteins and inhibition of photosynthesize (Hong et al. 2002; Okolonkwo and Nwachuku 2013; Spanier et al. 2009). Adverse effects of PARAQUAT are accidental toxicity for plants and aquatic organism and also toxicity in humans. Thousands of deaths occurred after ingestion or dermal exposure to PARAQUAT, both in acute and chronic intoxication(Nagami et al. 2005; Sittipunt 2005).Paraquat cause multiple organ dysfunction and to date there is no known pharmacological antagonist for Paraquat (Tan et al. 2015; Wei et al. 2014).

Due to harmful effects of herbicides on environment and human; removingthose from aquatic systems isnecessary (Nur et al. 2005; Yao et al. 2013). The removal of herbicide at low levels from water always consume as a problem (Konstantinou et al. 2000).There are several methods for removal of pesticide from contaminated water such as oxidation process (ozonolysis, electro-Fenton process, and electro-oxidation), microfiltration and adsorption on porous materials (Dehghani et al. 2014; Garcia et al. 2013; Ibrahim and Jbara 2009). There is great interest in adsorption nowadays because it is fast, cost effective and is a major separation technique(Ali and Gupta 2006).Different porous materials such as activated carbon, zeolites, fly ash and clays are used for removing herbicides from water and wastewater(Bhatnagar and Minocha 2006).

Natural Zeolites are crystalline, highly ordered structures of hydrated aluminosilicates. They have high ion-exchange and adsorption capacity (Sprynskyy et al. 2005).

An important feature of zeolites is their microporousity(Tan et al. 2012). Many zeolites contain a multi-dimensional micro-porous system. The micro porous system also adds another important feature to the zeolites, namely shape-selectivity (Jae et al. 2011; Osmundsen et al. 2013; Smit and Maesen 2008).

Natural zeolites due to their high cation-exchange ability and molecular sieve properties show especial potential in water purification (Suppes et al. 2004). The advantage of zeolite over other porous materials is because of its significant permeability (Sprynskyy et al. 2005).

Materials and Methods

Reagents and solutions

Paraquat and Tetra methyl ammonium hydroxide pentahydrate were purchased from Sigma. Methanol, sulphuric acid, ammonium hydroxide, ammonium sulphate and sodium sulphate from Merck. 690mg sep-pak silica cartridges were purchased from Waters.

Instruments and Characterizations

The mineralogical composition of the zeolite was determined by a Philips PW 1840 X-ray diffractometer, and the semi-quantitative analysis was based on the XRD pattern of disoriented powder sample using the method described by Schultz(Schultz 1964). The X-ray fluorescence spectrometer, Bruker S4 Pioneer was used to analysis total elemental in the zeolite. Planetary ball mill (Nano Shat PBM-210 model, IRAN) was used to prepare the zeolite nano-particles. Transmission electron microscope (LEO 906E model, Germany) and Scanning electron microscope (LEO 1455VP model, Germany) were used to determine the size and the surface morphology of zeolite nano-particles. The specific surface area and cation exchange capacity of the zeolite sample were measured by N2-BET sorption analysis and NH4-acetate method. Also the size of zeolite nanoparticles was measured with a dynamic light scattering particle size analyzer (Scatter scope 1 Codex model, Korea). Paraquat concentration was measured according to the published method Rial-Otero(Rial-Otero et al. 2006). A Shimadzu HPLC system (Kyoto, Japan) equipped with an injector with a 250 µm loop, LC-10ADVP pump, UV–Vis absorbance detector (SPD-10AVPmodel), column (150mm×4.6mm, ODS (C18)-H-OL 5-34174model) and guard column was used to separate and determinate the concentration of Paraquat in water solutions.

Determination PARAQUAT was performed by isocratic elution at a constant flow rate of 0.7 mL/min. The mobile phase composition was a mixture of tetramethylammonium hydroxide pentahydrate (10 g) and ammonium sulphate (30 g) in 1 L of ultra-pure water and adjusted to pH 2 with 5M sulphuric acid. Quantitation was done at 258 nm.

The mobile phase was passed through filter membrane (0.45ìm) with a Millipore system (Sartorius, Germany). A BEL engineering analytical balance (M124A model, Italy) was used to measure the amount of chemicals. A Metrohm pH-meter from Switzerland was used for measuring pH of solutions. Incubator-shaker Vision Scientific.LTD. (Model: VS-8480) used for shaking the samples.

Extraction PARAQUAT from samples

For each sample one 690mg Sep-Pak silicaCartridge was assembled onto the vacuum manifold. Cartridges were conditionedby passing 2.5 ml sulphuric acid 0.5M aqueous solution, 5 ml ultra-pure water, 2.5 ml ammonium hydroxide 2% (v/v) in water and 5 ml ultrapure water respectively. 25 ml of each spiked water sample was loaded onto the conditioned cartridge at rate of2.5 mL/min and dried by blowing nitrogen for a period of 15 minutes. Finally the bonded paraquat was eluted by 2.5 ml of the mixture of 0.1M sodium sulphate solution in water–methanol (1:1, V/V) adjusted to pH 2 with 1M sulphuric acid aqueous solution. This eluate was evaporated to approximately 1 mL under a gentle stream of nitrogen and adjusted to the volume of 1.0 mL(Rial-Otero et al. 2006).

Preparation of zeolite nanoparticles

Semnan province in Iran is a very rich resource of zeolites so the used zeolite in this paper was collected from there. Sufficient quantity of Zeolite was reduced to a moderately fine powder by mortar and pestle. Then the powder passed through the analytical sieves (270 mesh, 53 micron), for separating the particles. Scanning electron microscope was used to evaluate the surface morphology of the zeolite micro-particles .Then the zeolite nanoparticles were prepared by mechanical method with planetary ball-mill equipment (350 rpm, 120 h) of zeolite micro- particles. The zeolite nanoparticles were stored in a desiccator(Mohammad Javad khodayar and Nazari Khorasgani 2015).

Paraquat Removal

For carrying out the study, four liters of deionized water was spiked by Paraquatat 1500 ppb concentration. The adsorption experiments were performed by mixing certain amounts of zeolite nanoparticles with 25 mL of the mentioned prepared solution. The pH was adjusted to the desired values using 0.01 M NaOH or 0.01 MH_2SO_4 solutions. For each experiment certain amount of sorbent was added to 25mL of paraquat solution and shaken at 250 rpm for 30 minutes at appropriate temperature. Then the solution was centrifuged at 5000 rpm for 15 minute and supernatant was transferred carefully to a micro-tube and then by injection of 250µl of the prepared sample to HPLC, the paraquat content was determined. All measurements were carried out with two replications. The Paraquat removal percentage was calculated by the following equation:

$$\text{Percentage of Removal} = (C_i - C_{eq})/C_i \times 100$$

Where $C_i$and C_{eq} (mg/L) are the initial and equilibrium concentration of Paraquat in each setup experiment solution, respectively.

Box-Behnken experimental design and optimization by RSM

Box-Behnken experimental design has been preferred over the conventional statistical design because it can reveal the interaction between variables, is more inexpensive due to the numbers of runs is lesser and the designs are also rotatable. Hence, the Box-Behnken statistical design was selected to optimize parameters in this study.

The design for 3 variables and 3 levels has only 15 experimental runs, instead of having 27 experimental points if the run was done in 3^3 complete factorial design.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j + \varepsilon$$

Where Y is the response (dependent variable), k is the number of the patterns, i and j are the index number for patterns, $\beta_0$intercept term, X_1, X_2, …, X_k, are the independent variables, β_i, $\beta_{ii}$and β_{ij} are the regression coefficient (Dayal et al. 2005; Kousha et al. 2012; Ragonese et al. 2002; Sayyad et al. 2007; Solanki et al. 2007; Yetilmezsoy et al. 2009).

The Box-Behnken equation for paraquat adsorption on zeolite nano-particles is as follows:

$$Y = 170.226 - 59.282X_1 + 85.896\ X_3 + 5.918X_1X_1 - 9.222\ X_1X_3$$

Where X_1, X_2 and X_3 are pH, temperature and amount of adsorbent, respectively.

Results and Discussion

Particle size analysis, XRD, XRF, SEM and TEM study for zeolite nanoparticles

Particle size analyzing showed that distribution of particles was about 10-9 m, that D (50) and D (90) were 5.94 and 9.34 nm. Figure 1A shows the SEM image of zeolite micro-particles before modification. The TEM image of the zeolite nano-particles has showed that the surface structure of the samples was changed after modification (Figure 1B). According to the images zeolite nanoparticles are spheroidal and their sizes are between 1-100 nm.

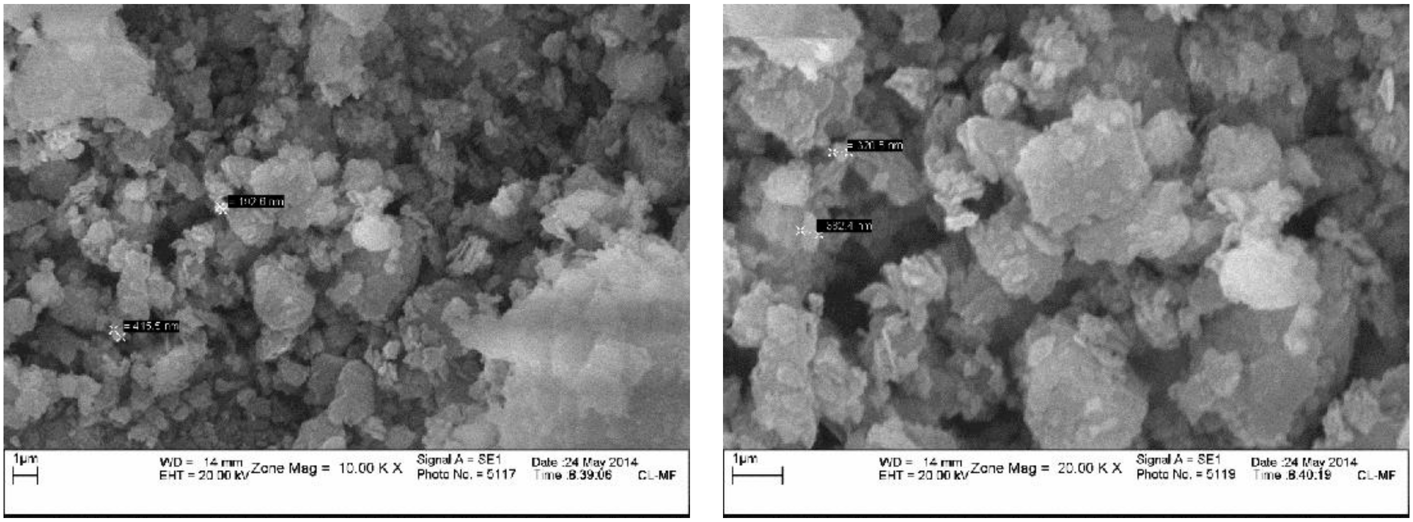

Fig 1-a, Scanning electron microscope (SEM) image of zeolite micro-particles

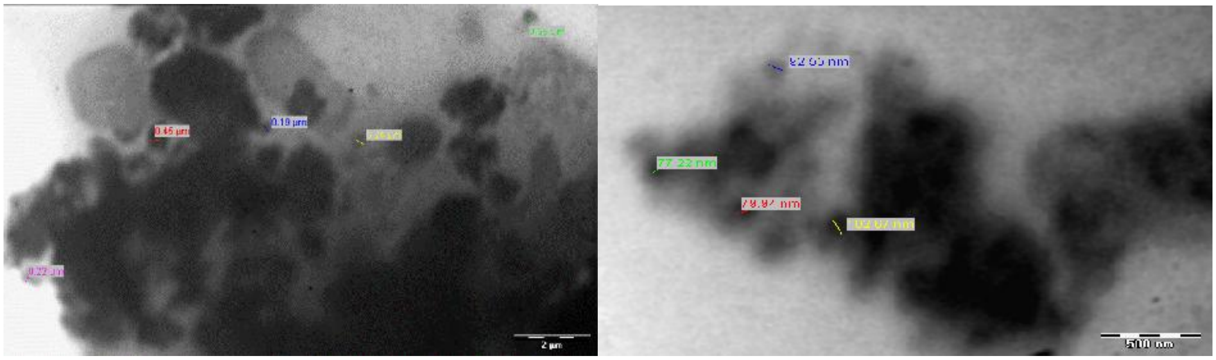

Fig 1-b,Transmission electron microscope(TEM) image of zeolite nano-particle

According to The result from XRD pattern (figure 2) clinoptilolite is the major component of zeolite (80%). Quartz and calcite are other components in the sample. XRF analysis shows that the zeolite sample contains 62.78% SiO_2 and 9.02% Al_2O_3. The cation exchange capacity and the specific surface area of zeolite were 85 cmol (+) kg−1 and 34 m2 g-1, respectively (Mohammad Javad khodayar and Nazari Khorasgani 2015).

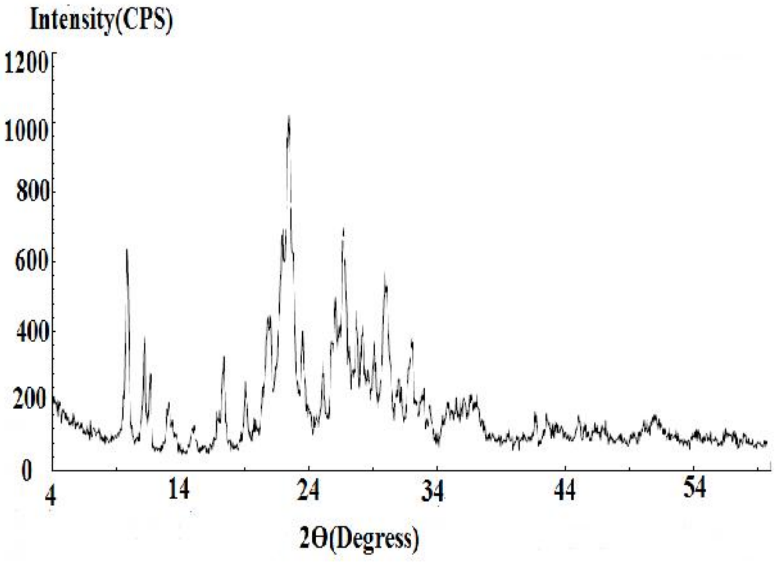

Fig2-a, XRD pattern of zeolite

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d(0)    1.50 nm / 1.75 um    ° d(5)    3.23 nm / 3.83 um    ° # of Peaks   2
d(10)   3.71 nm / 4.34 um    ° d(25)   4.62 nm / 5.40 um       5.90 nm       6.90 um
d(50)   5.94 nm / 6.93 um    ° d(75)   7.50 nm / 8.76 um
d(90)   9.34 nm / 10.9 um    ° d(95)   10.7 nm / 12.5 um
d(100)  23.1 nm / 27.0 um
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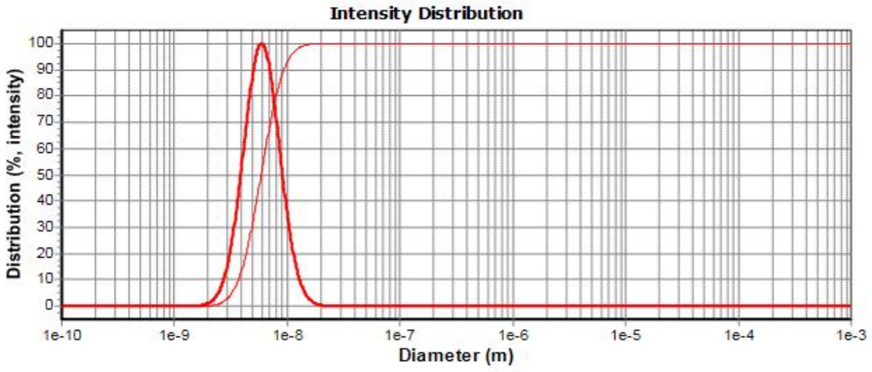


Fig 2-b, particle size distribution

Effect of Parameters on Paraquat Removal

A contour plot indicates the relationship between two variables and response. The most important factors that effect on the removal efficiency of paraquat on the zeolite nano-particles are pH, temperature and amounts of adsorbent. Based on the result of Response optimizer of BBD, the optimum conditions was pH 6, temperature 45°C and 2 g of adsorbent.

pH Effect

Due to effect of acidity on the adsorption process; removal of Paraquat was performed at different pH ranging from 6 to 8.Results showed that pH effect on the surface charge of thesorbent in the solution. According to the results Paraquat adsorption capacity of zeolite nanoparticles has a reverse trend with increasing pHand maximum sorption efficiency was obtained at pH 6.In acidity pH, the alkali and alkaline earth cations such as sodium and calcium in the zeolite structure leave the aluminosilicate networks, so the aluminosilicate charge becomes negative andconsidering that the paraquat is a cation, it seems that in acidity pH paraquat adsorbed on the surface of zeolite by mechanism of cation-exchange(Demir et al. 2002; Tsitsishvili et al.). Figure 3 shows that with increasing pH from 6 to 8 the removal efficiency has decreased. Based on the Response optimizer pH 6 is the optimum value.

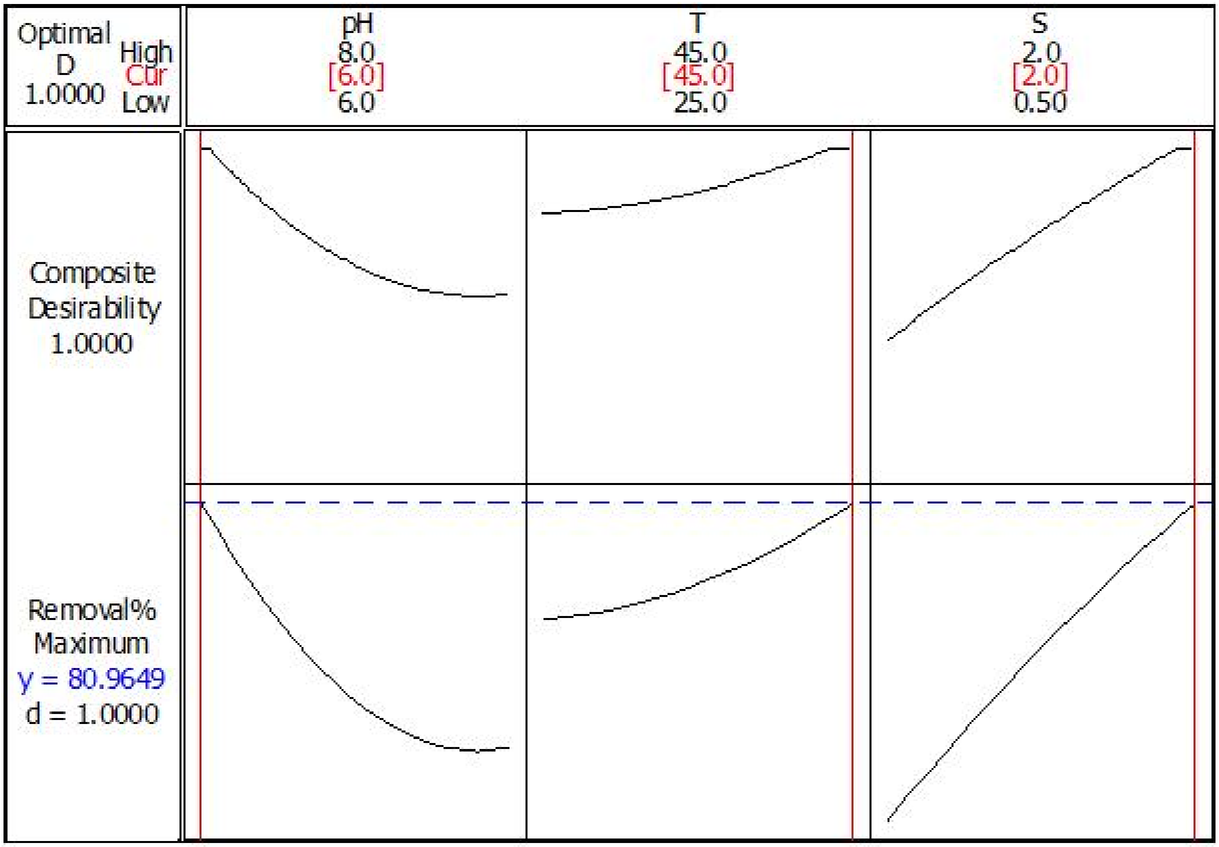


Fig 3 Response optimizer image for paraquat adsorption on zeolite nano-particles

Temperature

For evaluating thermal effect on the adsorption of Paraquat on the zeolite; experiments was done at temperature varying from 25°C to 45°C. The results show that there is direct trend between temperature and removal percentage of Paraquat. The maximum removal of Paraquat was obtained at 45°C as the optimum value. Figures 3-a and 3-c show the countor plots for adsorbent-temperature and pH-temperature respectively.

Adsorbent

Figure 3B and 3C show the relationship among the amount of adsorbent, pH and temperature. The figures showed that increase in the amount of adsorbent, while other variables are constant, cause higher adsorption. Based on Response optimizer the optimum amount of adsorbent is 2 g.when the amounts of sorbent has increased, the number of sorbent sites,functional groups and adsorption capacity increased in the solution.

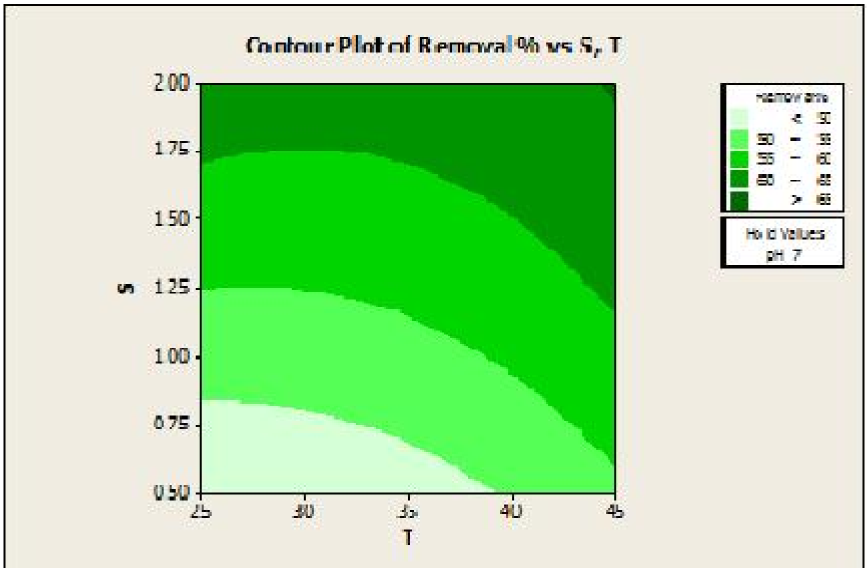


Fig 3-a

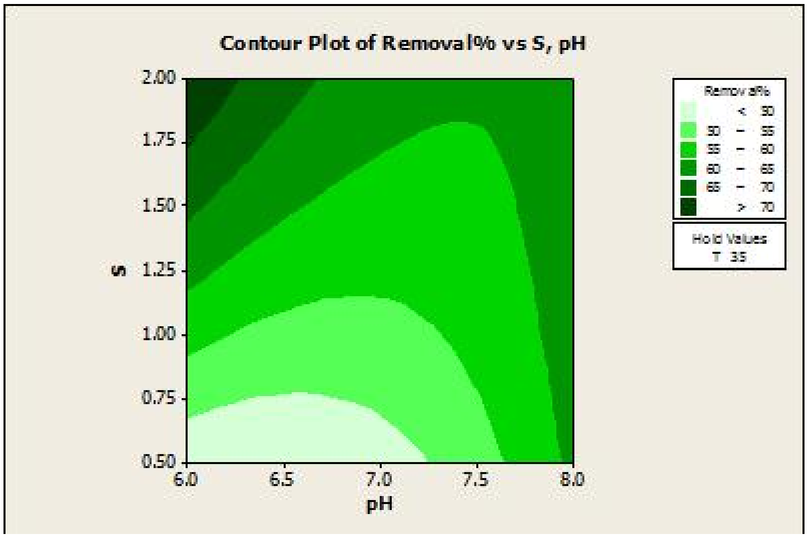


Fig 3-b

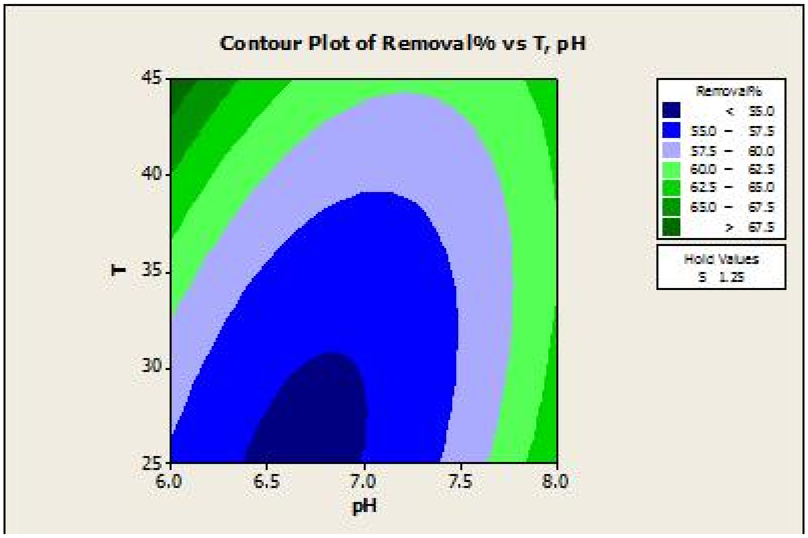


Fig 3-c

Kinetic Studies

Kinetics study help us to predict the rate that adsorption takes place. Therefore In this part of study, we investigated in the kinetic aspect of the adsorption of Paraquat on the zeolite. The experiment include time necessary for the adsorption process to reach the equilibrium. The effect of contact time on the adsorption of Paraquat under optimal conditions (pH 6, temperature 45°Cand amount of adsorbent 2g) was studied. To describe the adsorption process of Paraquat on zeolite, three kinetic models including pseudo- first-order, pseudo-second-order, and intra-particle diffusion were investigated.

Pseudo-first-order-kinetic equation is as follows:

$$log(q_e - q_t) = logq_e - \frac{k_1 t}{2.303}$$

Where q_e and q_t are the amount of Paraquat adsorbed per mass of adsorbent (µg/g) at equilibrium and time t (min) respectively. K_1 is the equilibrium rate constant of pseudo-first-order adsorption.

The pseudo-second order model which can be formulated as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/µg).
The intra-particle diffusion equation is the following:

$$q_t = k_i t^{0.5} + C$$

Where k_i is the intra-particle diffusion rate constant.

According to the results the pseudo-second-order model is the best fitted kinetics model. The plot of t/qt against t (Figure 4) yielded a very good correlation coefficient (R2 =0.999). According to this finding, adsorption paraquat on the zeolite is dependent on the number of occupied active site on the surface of zeolite. The results showed that the high rate of adsorption was achieved at the first 10 minutes (63.75% of the Paraquat was adsorbed), and after 120 minutes80.63%of the Paraquat was adsorbed.(Ho 2006; Yuh-Shan 2004).

Adsorption Isotherms

An equilibrium isotherm model explains that how adsorbate react with adsorbent. Therefore isotherm models are invaluable graphs that play important role for explanation of mechanism of adsorption, describing characteristics of surface adsorption, adsorbent capacity and designing an appropriate adsorption systems. In this study the Langmuir and Freundlich isotherm model were used.

The Freundlich equation is commonly expressed as follows:

$$\frac{x}{m} = k_f.C_e^{1/n}$$

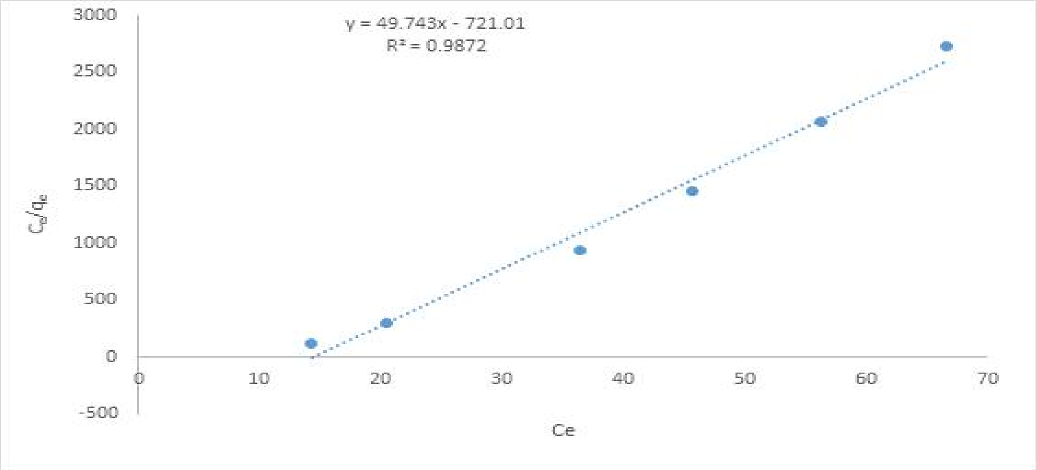
Where $\frac{x}{m}$ is the amount of Paraquat adsorbed per unit of mass of adsorbent (mg/g) C_e is the equilibrium concentration (mg/L) and K_f and $\frac{1}{n}$ are the Freundlich isotherm constant (L/mg) and intensity of adsorption, respectively.

The Langmuir isotherm model expressed as follows:

$$\frac{x}{m} = \frac{abc_e}{1+ac_e} or \frac{1}{x/m} = \frac{1}{abc_e} + \frac{1}{b}$$

Table 1, the Langmuir isotherm model

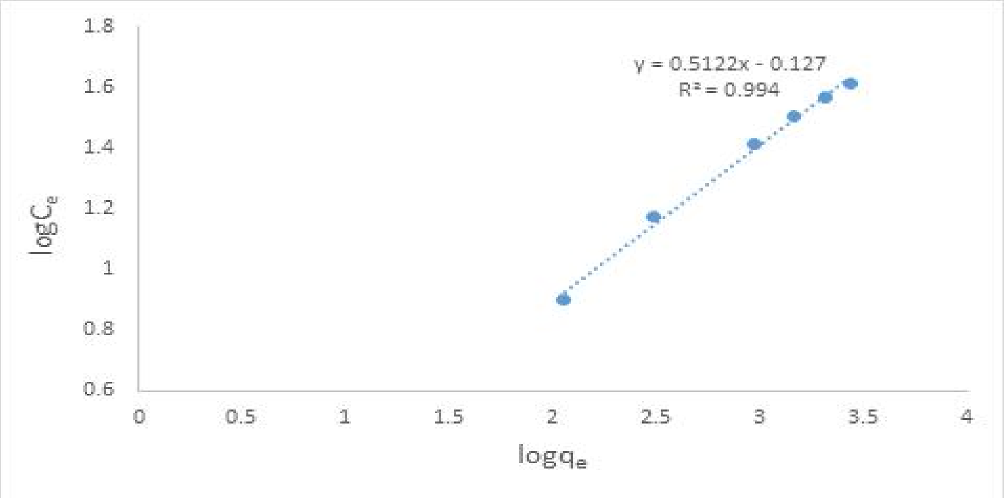
log C_e	logq_e
2.056153	0.900502
2.485519	1.173966
2.972439	1.411091
3.162461	1.502827
3.315145	1.56436
3.435489	1.612019



Graph 1, the Langmuir isotherm model

Table 2, the Freundlich isotherm model

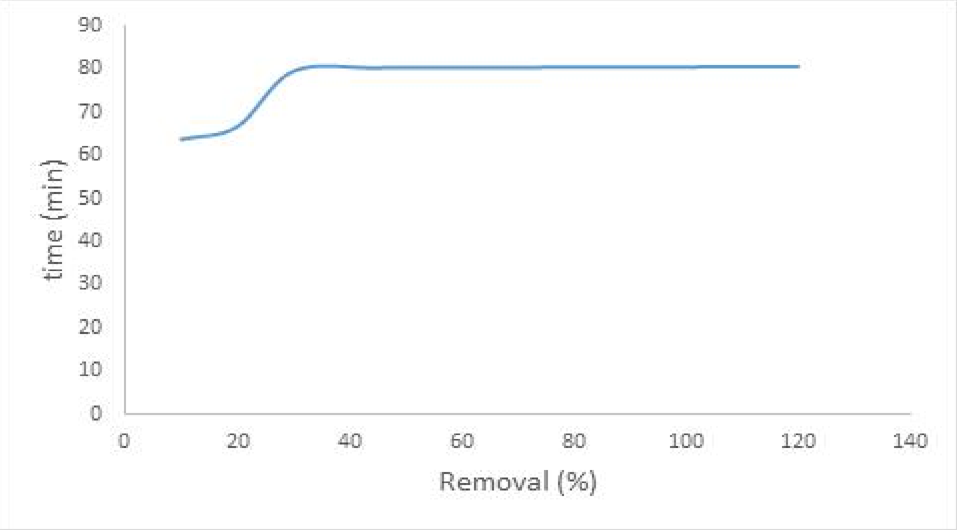
Ce/Qe	Ce
14.31039	113.8028
20.49054	305.8578
36.42066	938.5102
45.6703	1453.655
56.33594	2066.071
66.59935	2725.77



Graph 2, the Freundlich isotherm model

Table 3, effect of contact time

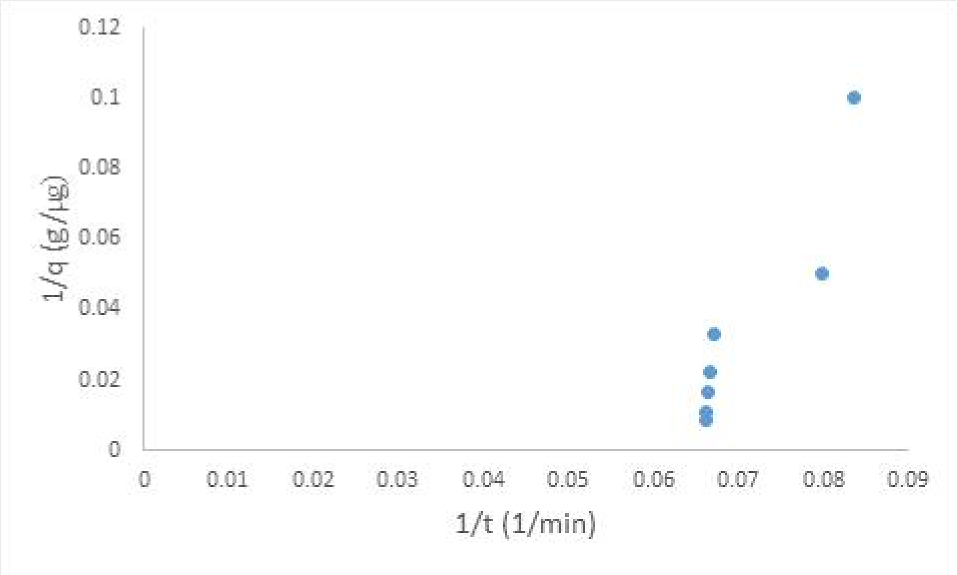
time	R%
10	63.75482
20	66.722715
30	79.588462
45	80.338777
60	80.397654
90	80.514982
120	80.635976



Graph 3, effect of contact time

Table 4, pseudo-first-order kinetics

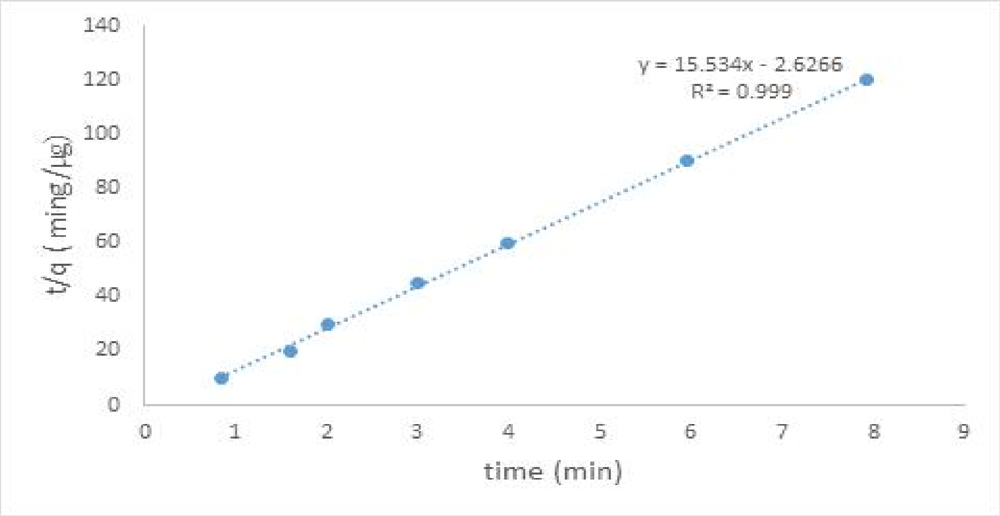
1/q	1/t
0.083654	0.1
0.079933	0.05
0.067011	0.033333
0.066568	0.022222
0.066418	0.016667
0.06624	0.011111
0.066141	0.008333



Graph 4, pseudo-first-order kinetics

Table 5, pseudo-second-order kinetics

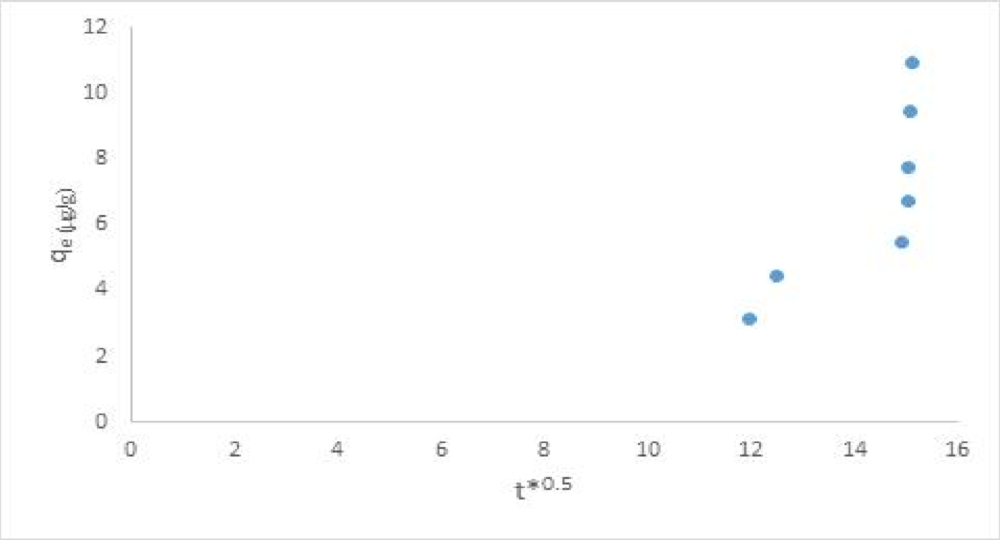
t/q	time
0.836538	10
1.598656	20
2.010342	30
2.995547	45
3.985089	60
5.961623	90
7.936904	120



Graph 5,pseudo-second-order

Table 6, intra –particle diffusion

qe	t*0.5
11.95403	3.162278
12.51051	4.472136
14.92284	5.477226
15.0223	6.708204
15.05612	7.745967
15.09656	9.486833
15.11925	10.95445



Graph 6, intra –particle diffusion

Table 7, Box-Behnken experimental design for paraquat adsorption on zeolite (3 factors, 3 level)

pH (X_1)	T (X_2)	Adsorbent (X_3)
7	45	2
7	45	0.5
8	45	1.25
6	35	2
7	35	1.25
8	35	0.5
8	35	2
7	25	2
7	35	1.25
8	25	1.25
6	25	1.25
7	25	0.5
6	35	0.5
6	45	1.25

Table 8, the measured responses for paraquat adsorption on zeolite

pH	T	S	Removal%
7	45	2	66.0749
7	45	0.5	55.56859
8	45	1.25	64.5233
6	35	2	76.73032
7	35	1.25	56.55056
8	35	0.5	58.87786
8	35	2	60.29733
7	25	2	61.18624
7	35	1.25	55.15733
8	25	1.25	67.72373
7	35	1.25	56.29438
6	25	1.25	56.47729

Langmuir model assumes monolayer and homogenous adsorption whereas Freundlich model explains the multi-layer, non-ideal, and reversible heterogeneous adsorption. To study the adsorption capacity of zeolite nanoparticles for Paraquat adsorption; the initial Paraquat concentrations were 750, 1500, 3000, 4000, 5000 and 6000ppb under optimal conditions (pH 6, the amount of adsorbent 2 g,temperature 45°C and time 45 min). The correlation coefficients R2 for the Langmuir and Freundlich isotherms are 0.9872and 0.994, respectively which indicate that the sorption of Paraquat onto zeolite nanoparticles can be better explained by the Freundlich model. The value of n (1.95), between 1 and 3,and the value of K (1.34 mg/g) show the good sorption of Paraquat onto zeolite nano-particles (Al-Asheh et al. 2000; Allen et al. 2004; Hamdaoui and Naffrechoux 2007; Malek and Farooq 1996).

Hadi nur et al, used NaY zeolite covered with alkylsilane for adsorption of paraquat. The result showed the high percentage of removal (about 95-99%)(Nur et al. 2005).

Khalil M.Ibrahim et al, used zeolite as adsorbent for removal paraquat from wastewater and the average removal efficiency was 59%.the Langmuir isotherm model was not fitted for the adsorption process$^($Ibrahim and Jbara 2009).

A.walcarius et al were studied on the paraquat removal in In-vitro condition by using zeolite. The zeolite was suitable for acute paraquat ingestion and has a long-term retention capability of the toxic herbicide$^($Walcarius and Mouchotte 2004).

Jovan levic et al. used the organo-zeolite for removal of atrazine, lindane and diazinone from water. The results showed the good adsorption efficiency. Well fitted isotherm model for diazinone was Langmuir and the well fitted model for atrazine and lindane was Freundlich (Lemić et al. 2006).

K.S.Hui et al. investigated on removal of mixed metal ions from wastewater by zeolite. The result showed that the pseudo-second-order model is well fitted for most of the ions (co^{2+}, cr^{2+}, Cu^{2+} and zn^{2+}), the pseudo-first-order model was just fitted for $Ni^{2+(}$Hui et al. 2005).

The results of this study are consistent with aforementioned studies.

Conclusion

In this study the ability of Semnan zeolite as a low-cost adsorbent for remova lParaquat from aqueous solutions was investigated. The Box–Behnken statistical experimental design was used to optimize the adsorption of Paraquatonto zeolite nano-particles. The optimum conditions were pH 6, temperature 45°C and amount of adsorbent 2g. Adsorption isotherm models was fitted to the Freundlich model rather than the Langmuir isotherm model. Kinetic studies have shown that the adsorption of Paraquat onto zeolitenano-particles was relatively rapid process and can be described well withthe pseudo-second-order model. This study indicated that the surface of zeolite nanoparticles have a high density of active sites for Paraquat uptake. The mechanism of removal Paraquat by zeolite nanoparticles is the surface adsorption and may be explained by cation-exchange mechanism. This study show that the zeolite from Semnan, because of its low cost and rich resource in Iran,is a good alternative adsorbent for removal of Paraquat from the aqueous solutions.

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References

Al-Asheh S, Banat F, Al-Omari R, Duvnjak Z (2000) Predictions of binary sorption isotherms for the sorption of heavy metals by pine bark using single isotherm data Chemosphere 41:659-665

Ali I, Gupta V (2006) Advances in water treatment by adsorption technology Nature protocols 1:2661-2667

Allen S, Mckay G, Porter J (2004) Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems Journal of Colloid and Interface Science 280:322-333

Aramendía MA et al. (2006) Determination of diquat and paraquat in olive oil by ion-pair liquid chromatography–electrospray ionization mass spectrometry (MRM) Food Chemistry 97:181-188 doi:http://dx.doi.org/10.1016/j.foodchem.2005.05.005

Bhatnagar A, Minocha A (2006) Conventional and non-conventional adsorbents for removal of pollutants from water-A review Indian journal of chemical technology 13:203-217

Dayal P, Pillay V, Babu RJ, Singh M (2005) Box-Behnken experimental design in the development of a nasal drug delivery system of model drug hydroxyurea: characterization of viscosity, in vitro drug release, droplet size, and dynamic surface tension Aaps Pharmscitech 6:E573-E585

Dehghani M, Naseri S, Karamimanesh M (2014) Removal of 2, 4-Dichlorophenolyxacetic acid (2, 4-D) herbicide in the aqueous phase using modified granular activated carbon J Environ Health Sci Eng 12

Demir A, Gunay A, Debik E (2002) Ammonium removal from aqueous solution by ion-exchange using packed bed natural zeolite Water SA 28:329-336

Dores EF, Carbo L, Ribeiro ML, De-Lamonica-Freire EM (2008) Pesticide levels in ground and surface waters of Primavera do Leste Region, Mato Grosso, Brazil Journal of chromatographic science 46:585-590

El Mhammedi M, Achak M, Bakasse M, Bachirat R, Chtaini A (2010) Accumulation and trace measurement of paraquat at kaolin-modified carbon paste electrode Materials Science and Engineering: C 30:833-838

Garcia LLC, Figueiredo-Filho LCS, Oliveira GG, Fatibello-Filho O, Banks CE (2013) Square-wave voltammetric determination of paraquat using a glassy carbon electrode modified with multiwalled carbon nanotubes within a dihexadecylhydrogenphosphate (DHP) film Sensors and Actuators, B: Chemical 181:306-311 doi:10.1016/j.snb.2013.01.091

Hamdaoui O, Naffrechoux E (2007) Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon: Part I. Two-parameter models and equations allowing determination of thermodynamic parameters Journal of Hazardous materials 147:381-394

Ho Y-S (2006) Review of second-order models for adsorption systems Journal of hazardous materials 136:681-689

Hong S-Y et al. (2002) Effect of vitamin C on plasma total antioxidant status in patients with paraquat intoxication Toxicology letters 126:51-59

Hui K, Chao C, Kot S (2005) Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash Journal of Hazardous Materials 127:89-101

Ibrahim KM, Jbara HA (2009) Removal of paraquat from synthetic wastewater using phillipsite–faujasite tuff from Jordan Journal of Hazardous Materials 163:82-86 doi:http://dx.doi.org/10.1016/j.jhazmat.2008.06.109

Jae J, Tompsett GA, Foster AJ, Hammond KD, Auerbach SM, Lobo RF, Huber GW (2011) Investigation into the shape selectivity of zeolite catalysts for biomass conversion Journal of Catalysis 279:257-268

Konstantinou IK, Albanis TA, Petrakis DE, Pomonis PJ (2000) Removal of herbicides from aqueous solutions by adsorption on Al-pillared clays, Fe–Al pillared clays and mesoporous alumina aluminum phosphates Water research 34:3123-3136

Kousha M, Daneshvar E, Dopeikar H, Taghavi D, Bhatnagar A (2012) Box–Behnken design optimization of Acid Black 1 dye biosorption by different brown macroalgae Chemical Engineering Journal 179:158-168

Lemić J, Kovačević D, Tomašević-Čanović M, Kovačević D, Stanić T, Pfend R (2006) Removal of atrazine, lindane and diazinone from water by organo-zeolites Water Research 40:1079-1085

Malek A, Farooq S (1996) Comparison of isotherm models for hydrocarbon adsorption on activated carbon AIChE Journal 42:3191-3201

Maya F, Estela JM, Cerdà V (2011) Improved spectrophotometric determination of paraquat in drinking waters exploiting a Multisyringe liquid core waveguide system Talanta 85:588-595 doi:http://dx.doi.org/10.1016/j.talanta.2011.04.022

Mohammad Javad khodayar FN, Saeid Hojati, Ahmad Landi, Zahra, Nazari Khorasgani SA (2015) Removal of Ametryn from Aqueous Solutions with Zeolite NanoparticlesOptimized Using the Box-Behnken Design

Nagami H et al. (2005) Hospital-based survey of pesticide poisoning in Japan, 1998–2002 International journal of occupational and environmental health 11:180-184

Nanseu-Njiki CP, Dedzo GK, Ngameni E (2010) Study of the removal of paraquat from aqueous solution by biosorption onto Ayous (Triplochiton schleroxylon) sawdust Journal of Hazardous Materials 179:63-71. doi:http://dx.doi.org/10.1016/j.jhazmat.2010.02.058

Nur H, Manan AFNA, Wei LK, Muhid MNM, Hamdan H (2005) Simultaneous adsorption of a mixture of paraquat and dye by NaY zeolite covered with alkylsilane Journal of Hazardous Materials 117:35-40 doi:http://dx.doi.org/10.1016/j.jhazmat.2004.07.015

Okolonkwo BN, Nwachuku EO (2013) The antioxidant effects of vitamin C on liver enzymes: aspartate aminotransferase, alanine aminotranferease, alkaline phosphatase and gamma-glutamyltransferase activities in rats under Paraquat insult Journal of Xenobiotics 3:e5

Osmundsen CM, Dahl S, Taarning E, Rossmeisl J (2013) Catalytic Conversion of Carbohydrates. Technical University of DenmarkDanmarks Tekniske Universitet, CenterCenters, Center for Atomic-scale Materials DesignCenter for Atomic-scale Materials Design

Pinto GMF, Jardim ICS (2000) Use of solid-phase extraction and high-performance liquid chromatography for the determination of triazine residues in water: validation of the method Journal of chromatography A 869:463-469

Ragonese R, Macka M, Hughes J, Petocz P (2002) The use of the Box–Behnken experimental design in the optimisation and robustness testing of a capillary electrophoresis method for the analysis of ethambutol hydrochloride in a pharmaceutical formulation Journal of pharmaceutical and biomedical analysis 27:995-1007

Rial-Otero R, Cancho-Grande B, Perez-Lamela C, Simal-Gándara J, Arias-Estévez M (2006) Simultaneous determination of the herbicides diquat and paraquat in water Journal of Chromatographic Science 44:539-542

Samai M, Samai HH, Hague T, Naughton D, Chatterjee PK (2010) Novel superoxide dismutase mimetics for protection against paraquat-induced acute renal injury Sierra Leone Journal of Biomedical Research 2:54-64

Sayyad SA, Panda BP, Javed S, Ali M (2007) Optimization of nutrient parameters for lovastatin production by Monascus purpureus MTCC 369 under submerged fermentation using response surface methodology Applied Microbiology and Biotechnology 73:1054-1058

Schultz LG (1964) Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre Shale.

Shahrtash M, Mohsenzadeh S, Mo-habatkar H (2011) Salicylic acid alleviates paraquat oxidative damage in maize seedling Asian J Exp Biol Sci 2:377-382

Sittipunt C (2005) Paraquat poisoning Respir Care 50:383-385

Smit B, Maesen TL (2008) Molecular simulations of zeolites: adsorption, diffusion, and shape selectivity Chemical reviews 108:4125-4184

Solanki AB, Parikh JR, Parikh RH (2007) Formulation and optimization of piroxicam proniosomes by 3-factor, 3-level Box-Behnken design AAPS PharmSciTech 8:43-49

Spanier G et al. (2009) Resveratrol reduces endothelial oxidative stress by modulating the gene expression of superoxide dismutase 1 (SOD1), glutathione peroxidase 1 (GPx1) and NADPH oxidase subunit (Nox4) J Physiol Pharmacol 60:111-116

Sprynskyy M, Lebedynets M, Terzyk AP, Kowalczyk P, Namieśnik J, Buszewski B (2005) Ammonium sorption from aqueous solutions by the natural zeolite Transcarpathian clinoptilolite studied under dynamic conditions Journal of Colloid and Interface Science 284:408-415

Suppes GJ, Dasari MA, Doskocil EJ, Mankidy PJ, Goff MJ (2004) Transesterification of soybean oil with zeolite and metal catalysts Applied Catalysis A: General 257:213-223

Tan D, Fan W, Xiong W, Sun H, Li A, Deng W, Meng C (2012) Study on adsorption performance of conjugated microporous polymers for hydrogen and organic solvents: The role of pore volume European Polymer Journal 48:705-711

Tan D, Wang Y, Bai B, Yang X, Han J (2015) Betanin attenuates oxidative stress and inflammatory reaction in kidney of paraquat-treated rat Food and Chemical Toxicology 78:141-146 doi:10.1016/j.fct.2015.01.018

Tsitsishvili G, Andronikashvili T, Kirov G, Filizova L Natural Zeolites, 1992. Ellis Horwood,

Walcarius A, Mouchotte R (2004) Efficient in vitro paraquat removal via irreversible immobilization into zeolite particles Archives of environmental contamination and toxicology 46:135-140

Wei T, Tian W, Liu F, Xie G (2014) Protective effects of exogenous β-hydroxybutyrate on paraquat toxicity in rat kidney Biochemical and Biophysical Research Communications 447:666-671 doi:10.1016/j.bbrc.2014.04.074

Yao F, Liu H, Wang G, Du L, Yin X, Fu Y (2013) Determination of paraquat in water samples using a sensitive fluorescent probe titration method Journal of Environmental Sciences 25:12 45-1251 doi:http://dx.doi.org/10.1016/S1001-742(12)60 124 -7

Yetilmezsoy K, Demirel S, Vanderbei RJ (2009) Response surface modeling of Pb (II) removal from aqueous solution by Pistacia vera L.: Box–Behnken experimental design Journal of Hazardous Materials 171:551-562

Yuh-Shan H (2004) Citation review of Lagergren kinetic rate equation on adsorption reactions Scientometrics 59:171-177