

Removal of Ortho- chlorophenol from Aqueous Solutions Using Zero-Valent Iron Nanoparticles Modified Clay (Case Clay Soils of ShahMorad Mountains in Rafsanjan)

*Shima Rezaei¹, Hooshyar Hossini², Majid Hashemi^{*3}*

1) Department of Environmental Health Engineering, Environmental Health Research Center, Research Institute for Health Development, Kurdistan University of Medical Sciences, Sanandaj, Iran

2) Department of Environmental Health Engineering, School of Health, Kermanshah University of Medical Sciences, Kermanshah, Iran

3) Environment Research Center and Department of Environmental Health Engineering, School of Health, Isfahan University of Medical Sciences, Isfahan, Iran,

*Author for Correspondence: mhashemi120@gmail.com

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ABSTRACT

Chlorophenols as priority pollutants are toxic. These acidic organic compounds cause digestive disorders, liver damage, and cancers. The aim of this study is Ortho- chlorophenol removal using zero-valent iron nanoparticles modified clay. In this experimental study, the clay soil was sampled from the mountains of Shah Murad, Rafsanjan, Iran. Then it was treated with hydrochloric acid. In the next step, the clay was modified with ferrous sulfate in the presence of the N₂ gas to prepare magnetic clay. Then, the prepared adsorbent was used to remove o-chlorophenol as a function of pH, adsorbent dose and contact time. In addition, adsorption isotherms and kinetics were determined. The findings of the present study showed that the removal efficiency obtained by the iron nanoparticles carrying clay was higher than that of the raw clay. The highest removal efficiency (91.3 %) was obtained for pH 4. The o-CP removal efficiency by the modified clay increased from 35.9 to 82.7 as the adsorbent dosage is increased from 0.05 to 1 g after 120min contact time. The Langmuir isotherm model and the second-order kinetic model provided the best fit to the experimental data compared to other studied models. The results showed that the modified adsorbent could be used an effective and readily available low-cost adsorbent for the removal of chlorophenols in industrial applications.

Key words: Chlorophenols, Adsorption, Clay, Iron nanoparticle

INTRODUCTION

By acute toxicity and stability of carbon-halogen bond, Chlorophenols have been known as most common organic pollutants that contaminate soil and water resources [1-3]. Chlorophenols are produced as a byproduct of the reaction hypochlorite with phenolic acids during the disinfection of water and wastewater with chlorine. As well, these remain in the environment as products of phenoxy herbicides decomposition [4]. Industrial wastewater of pharmaceutical, color and plastics, insecticides, fungicides, wood protections, coal processing, paper and petrochemical refineries are chlorophenols input sources to the environment [5]. In the classification of toxic organic pollutants, chlorophenols are in acidic compounds category and can cause very unfavorable taste and odor in 0.01 ppm in the drinking water [6-7]. Chlorophenol toxicity has been increased with increasing degree of chlorination [5].

Due to cause skin irritation, digestive problems and cancer, their compounds are considered environmental concerns. Chronic toxicity effects of phenolic compounds in humans include vomiting, difficulty swallowing, and loss of appetite, liver, and kidneys damage, headaches, weakness and mental disorders [8].

Ortho-chlorophenol (o-CP) was introduced as priority substances in the list published by EPA in 1976. According to the EPA Standard, o-CP concentrations should not exceed 200µg/L in drinking water (9). Therefore, it is necessary to remove them from the aquatic environment [10]. Biodegradation, biosorption, adsorption on activated carbon, solvent extraction, chemical oxidation, injected into deep wells, burning, optical dispersion, coagulation, and flocculation are the most commonly used methods for the removal of phenolic compounds from sources water and wastewater [11, 12].

Adsorption process because of simple and low-cost operation is used to remove contaminants as a suitable method. Many researches have been done on the development of application low-cost adsorbents [14, 13]. Clay is used to adsorbing many pollutants due to the high surface area and adsorption capacity [15].

Lacasa *et al.* showed the clay contains a lot of bentonite minerals could do favorable removal nitrate under optimal conditions. The clay can act as a catalyst in pollutant reducing, and also done both ion exchange and adsorption processes [16]. Recently, many researchers have tried to produce more efficient absorbers by right apply activation or modification methods [15-17]. The use of chemical reducing agents could improve the efficiency of the adsorbent. In between, some nano scale metal such as aluminum, zinc, and iron are appropriate metal used in water decontamination. Among these metals, iron is a priority because of the cheapness, availability, rapid reaction, high ability and efficiency in adsorption process and non-toxicity [17]. Reduce the surface area in zero-valent iron particles leads to increasing the contact area of pollutant with an adsorbent, therefore, the adsorption efficiency increases [17]. Because of their high level of adsorption, zero-valent iron nanoparticles (NZVI) has been widely used [18]. The aim of this study was to evaluate the effectiveness of clay modified NZVI in the removal of o-CP from aqueous solutions.

MATERIALS AND METHODS

Materials and reagents

All materials and chemical reagents used in this study were of analytical grade and purchased from Sigma Aldrich. All experiments were carried out on synthetic and in laboratory scale using a standard batch system. Then, o-CP removal efficiency from real samples in the optimal conditions was determined by the modified adsorbent.

Preparation of adsorbent

Clay used in this research was obtained from Shah Murad mountain, Rafsanjan, Kerman province, Iran, and its mineral constituents were determined by SEM analysis.

The natural clay samples were screened with a 2-1 mm sieve and then washed three times with distilled water, and were dried in an oven at 105°C to obtain a constant weight. In the next step, the clay samples were immersed in 20% hydrochloric acid for 24 hours. Afterwards, the acidified samples were filtered, washed, and dried in an oven at 70°C [19]. Then, the clay was modified with ferrous sulfate. For this purpose, 1g clay was added to ferrous sulfate solution (30mL, 1M) in the presence of N₂ gas. After that, the

suspension was diluted with ethanol and distilled water 5 times at an equal ratio. The 100mL sodium borohydride solution was drop wise added (1ml in every drop) at 25°C on a magnetic stirrer in the presence of N₂ gas and was stirred for 30 minutes. Zero-valent iron was obtained according to the following equation:



Finally, zero-valent iron nanoparticles deposited on clay were separated from the solution and then were washed three times with acetone at 60°C by injecting dry N₂ gas and were stored in a desiccator. (20) The modified clay was characterized using Emission Scanning Electron Microscope (SEM) and powder X-ray diffraction (XRD) analyses.

Adsorption process

To measure the impact of iron nanoparticles deposited on clay, o-CP removal efficiency was determined at neutral pH, o-CP concentration 50mg/l, contact time 90min by adding different dosages of the raw clay and iron nanoparticles modified clay.

Effect of adsorbent dose and contact time

In order to evaluate the effect of two factors, adsorbent dose and contact time, on the o-CP removal, various doses of the modified clay in the range of 0.05 to 1g were added to 100 mL solution containing 50mg/l o-CP at pH 7. The contact time ranged from 30 to 120 minutes, and at specific time intervals, a sample was taken from the solution and analyzed for the remaining concentration of o-CP.

Effect of pH

To investigate the effect of pH on o-CP removal efficiency, the initial pH of the solutions was adjusted from 2 to 11 using 0.1M NaOH and HCl. The adsorbent dosage and contact time were in the optimal conditions. The experiments were carried out at room temperature.

Effect of o-CP concentration

To study the impact of initial concentration on o-CP removal efficiency, solutions with initial concentration ranging from 30-200mg/l was prepared. Then, the adsorption process was performed under optimum conditions with respect to adsorbent dosage, contact time and temperature.

Adsorption isotherms and Kinetics

The Freundlich and Langmuir isotherm models and the first-order kinetics and second-order kinetic models were used to study the isotherms and kinetics of o-CP adsorption on the zero valent nanoparticles modified clay.

Physico-chemical characteristics of raw wastewater

The physicochemical characteristics of raw wastewater are presented in Table 1.

Table 1: Physico-chemical characteristics of raw wastewater of Zarand coal washing plant

Pollutant	Value	Pollutant	Value
pH	7.3	DO	2.7 mg/l
EC	3040 $\mu\text{s}/\text{cm}$	BOD	15 mg/l
TSS	136 mg/l	COD	291 mg/l
TDS	2893 mg/l	Alkalinity	51 mg/l
Turbidity	33 NTU	Ca	236 mg/l
Mg	146 mg/l	K	44 mg/l
Na	341 mg/l	Cl ⁻	367 mg/l
Sulfate	952 mg/l	Phosphate	Trace
Nitrate	1.5 mg/l	Oils and Fats	Trace
Nitrite	0.21 mg/L	Detergent	0.07 mg/l

Removal of o-CP from real wastewater

Raw wastewater (concentration about 8.64 mg o-CP/l) was sampled from Zarand coal washing plant under the standard conditions. After determining its physicochemical quality, the efficiency of the adsorbent for the removal of o-CP from the wastewater was tested under optimum conditions obtained by the previous experiments (synthetic samples). The remaining concentration of o-CP in the sample was read by a spectrophotometer (model UV-1800 SHIMADZU) at a wavelength of 274nm.

Adsorbent recycling

To determine the reusability of the iron nanoparticles modified clay, the o-CP laden adsorbent was separated and washed with distilled water and dried. After thermal desorption of o-CP from the surface of the adsorbent, its removal efficiency was again tested in the adsorption process.

Desorption study

Desorption of O-CP was determined at the end of the sorption experiment using an initial o-CP concentration of 100mg/l. After the adsorbate solution was abandoned for 24 hours in the laboratory for desorption rate check.

RESULTS AND DISCUSSION

Characterization of the Adsorbents

Fig.1 illustrates SEM images of clay samples before (a) and after (b) modification.

SEM images showed that iron nanoparticles are loaded onto the clay. This is very important for the re-use of the modified clay without losing iron nanoparticles. The images show the size of the iron particles deposited on the adsorbent is between 10-50nm.

Fig.2 illustrates XRD images of clay, NZVI and modified clay. The XRD measurement showed the formation of iron nanoparticles on clay at 45.3°

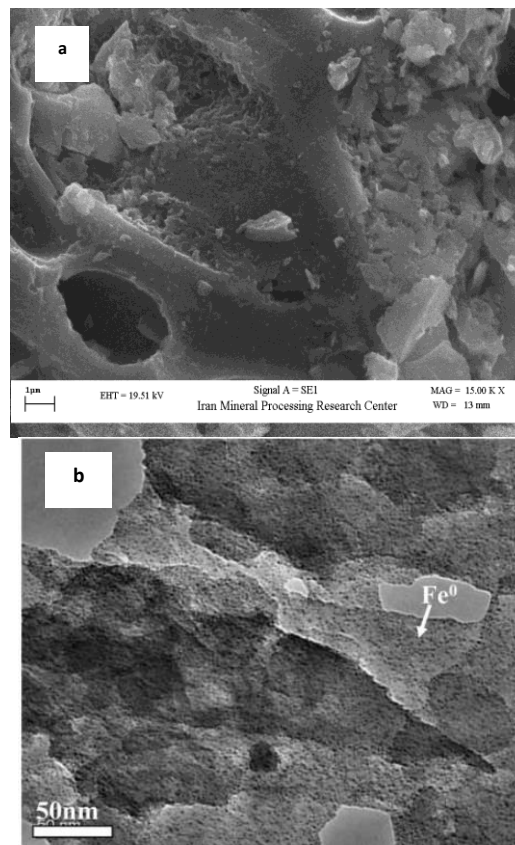


Fig. 1: SEM images a) raw clay b) Modified clay

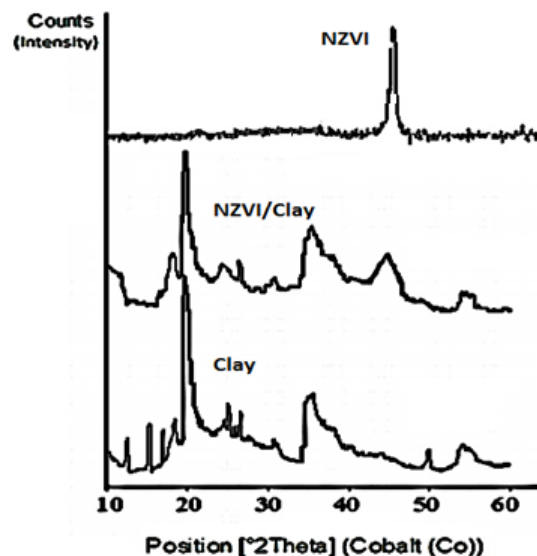


Fig.2: XRD pattern of clay, NZVI and modified clay.

Adsorbent modification

The results of comparing the removal efficiency of raw and modified clay are shown in Fig. 3.

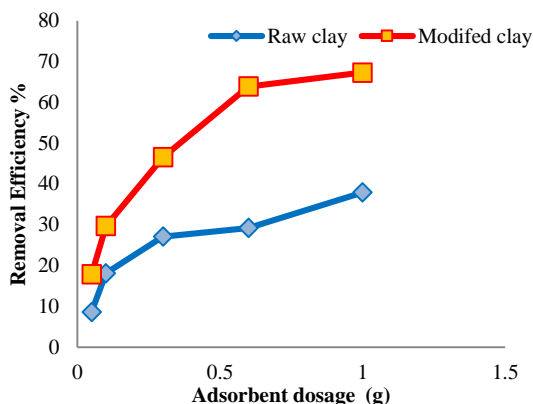


Fig. 3: The effect of adsorbent dosage on the removal of o-CP (contact time: 90min, pH: 7, adsorbent dose: 1g, solution volume: 100cc, o-CP concentration: 50mg/l).

According to Fig. 3, the removal efficiency of o-CP by raw clay increased from 8.6 to 37.91% with increasing adsorbent dosage from 0.05 to 1g. As can be seen from Fig. 3, the o-CP removal efficiency by all dosages of the modified clay was higher than the raw clay, that this indicates the presence of iron nanoparticles onto clay had a positive impact. This suggests that the dechlorination reaction occurs simultaneously with adsorption. Meanwhile, the dechlorination reaction is slow compared to adsorption and thus o-CP can be observed to accumulate on clay (as for clay system with no dechlorination, which showed accumulation of o-CP). It is thereby indicated that most of the o-CP is firstly adsorbed into the clay interlayers followed by ZVI dechlorination. The study of Hanzhong *et al.* in showed similar results [20]. The results of our study are consistent with Wang *et al.* [21].

Effect of pH and Adsorbent dose

Figs 4 and 5 present the variations in o-CP adsorption efficiency as a function of adsorbent dosage and pH value.

As can be seen from Fig. 4, by increasing the contact time and adsorbent dose, the o-CP removal efficiency increased. For instance, o-CP removal efficiency by the modified clay increased from 35.9 to 82.7 as the adsorbent dosage is increased from 0.05 to 1 g after 120 min contact time. This can be ascribed to the availability of more adsorption sites and increased adsorbent surface area caused by the increased adsorbent. It can be concluded that the rate of phenolic compounds adsorption with adsorbents rises more rapidly in the initial steps and after becomes almost a steady. Our study is consistent with Ghaffari *et al.* results. [22]. It is evident from Fig. 4 that as pH is increased, the removal efficiency decreases. The highest removal efficiency (91.3 %) was obtained for pH 4. This is due to the diminution of o-CP ionization in acidic pH. In Effect of pH, Namasisvayam *et al.* reported raising in ionized chlorophenol concentration

has been observed about 0% at pH 2.2 to 99% at pH 10.4. [23].

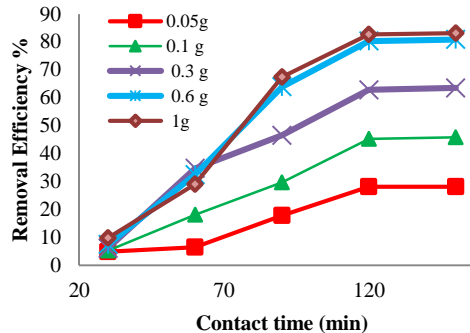


Fig.4: Variation in o-CP removal efficiency by different time and adsorbent dosages (solution volume:100cc, o-CP concentration: 50mg/l, pH:7).

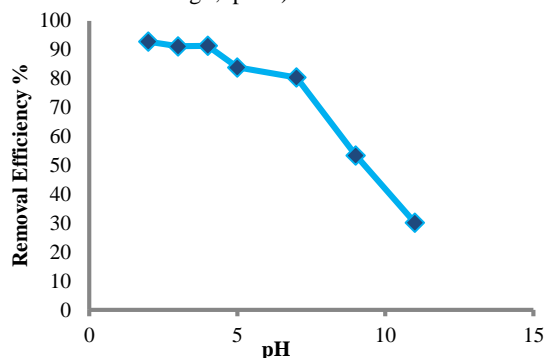


Fig. 5: pH effect on o-CP removal efficiency (solution volume: 100cc, o-CP concentration: 50mg/l, contact time: 120min, adsorbent dose: 0.6mg/l)

The adsorbent surface is positively charged in an acidic environment (less than pHzpc). Therefore, the removal efficiency increased at acidic pH, because there is no electrostatic repulsion between chlorophenol non-ionizing species and positively charged adsorbent surface. At alkaline pH, increases in the o-CP ionized species and increase in a number of negatively charged sites on the adsorbent surface lead to reduced adsorption. Also, despite the electrostatic repulsion at pH 11, the reduction in the o-CP concentration revealed chemical adsorption [5, 23-26]. Baker *et al.* have obtained similar results in the case of pH. The results achieved from this research indicated that the adsorption rate at pH 1 to 5 was constant and with increasing pH to 10, adsorption rate decreased [27]. The increase in the removal efficiency by increasing adsorbent dosage could be due to the increase in adsorbent surface area and availability of more adsorption sites. Our Findings are in good agreement with the results obtained by Sarkar *et al.* and Anbia *et al.* [5, 28].

Initial concentrations

The effect of different initial o-CP concentrations on the removal efficiency (R%) and adsorption capacity (q_e) is shown in Fig. 6

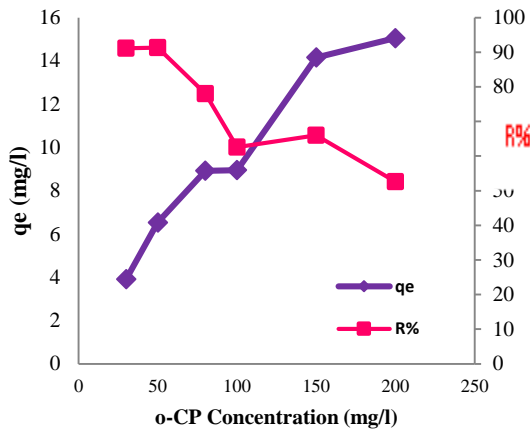


Fig. 6: Variation in o-CP removal efficiency and q_e by increasing of o-CP concentration.

Increasing o-CP concentration leads to the reduced efficiency and increased the adsorption rate. The increase in adsorption capacity with increasing o-CP concentration could be caused by the higher probability of clash between adsorbent surface and o-CP molecules. In addition, this might be attributed to

the increase in the number of o-CP molecules (or ions) competing for the available binding sites on the surface of the adsorbent [22].

Desorption study and Reusability of the adsorbent: After the adsorbate solution was abandoned for 24 hours in the laboratory for desorption rate check, it became clear and no release of analyte from the sorbent surface was detected. Also, in reusability check, after washing and drying the o-CP saturated adsorbent and consecutively applying to adsorb pollutants, the results showed that the adsorbent is re-usable.

o-CP removal from real wastewater sample: Zero-valent iron nanoparticles modified clay could remove 76.7% o-CP from the real waste water of Zarand coal washing plants.

Adsorption Kinetics and Isotherms

The Freundlich and Langmuir isotherm models and the first-order kinetics and second-order kinetic models were used to study the isotherms and kinetics of o-CP adsorption on the zero valent nanoparticles modified clay. Isotherm equations and their parameters showed in Table 2.

Table 2: Isotherm equations and their various forms.

Isotherm	Nonlinear	Linear	Parameter	value
Freundlich isotherm	$q_e = K_F C_e^{1/nF}$	$\log(q_e) = \log(K_F) + \frac{1}{nF} \log(C_e)$	$\frac{1}{nF}$	0.335
			$K_F(\text{mg/g})$	3.28
			R_2	0.8978
Langmuir isotherm	$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	$q_m(\text{mg/g})$	16.39
			K_a	0.0776
			R_2	0.933

Where C_e is an equilibrium concentration of the adsorbate (mg/l), q_e is the amount of o-CP adsorbed per unit mass of sorbent (mg/g), q_m is the maximum amount of o-CP adsorbed per unit mass of sorbent at complete monolayer on the surface-bound, and K_a (mg/l) is a constant related to the affinity of the binding

sites. K_F is a Freundlich adsorption constant related to the adsorption capacity of the adsorbent (mg/g) (mg/l) $1/n$ and $1/n$ is adsorption intensity.

Kinetic equations, their parameters, and values showed in Table 3.

Table 3: Kinetic equations and their various forms.

Type	Nonlinear	Linear	Parameter	value
Pseudo-first order	$q = q_e(1 - e^{-tk_1})$	$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t$	$q_{e(\text{cal})} \frac{\text{mg}}{\text{g}}$	0.335
			k_1	3.28
			R_2	0.8978
Pseudo-second order	$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e^2 t}$	$\frac{t}{q_t} = \frac{1}{k q_e^2} + \frac{t}{q_e}$	$q_{e(\text{cal})} \frac{\text{mg}}{\text{g}}$	7.81
			k_2	0.0048
			h	0.2941
			R_2	0.9932

Where K_1 is the pseudo first-order adsorption rate constant, K_2 is the pseudo-second order adsorption rate constant, q_t is the amount of o-CP adsorbed at any time t (mg/g), q_e is the pseudo-second order

adsorption rate constant (g/mg/min). The Langmuir and Freundlich isotherms models and first and second-order kinetics models were used to investigate the adsorption isotherms and kinetics of o-CP onto the

magnetically modified clay, and the results of these models are presented in Fig. 7 and 8, respectively.

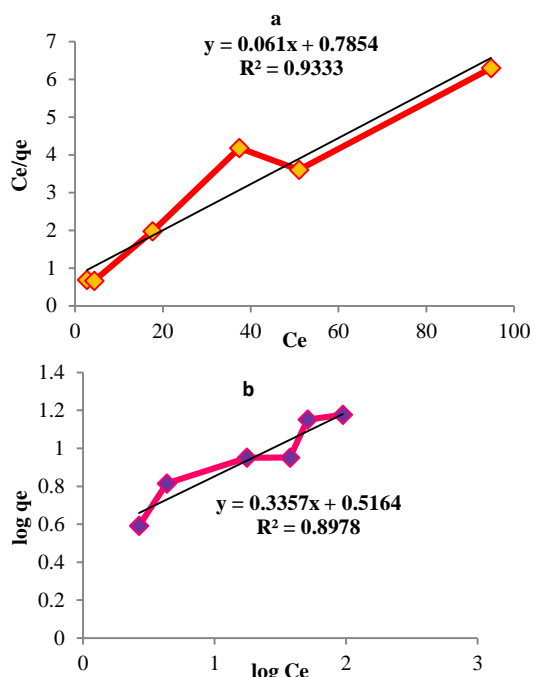


Fig. 7: a) Langmuir and b) Freundlich isotherms of o-CP adsorption

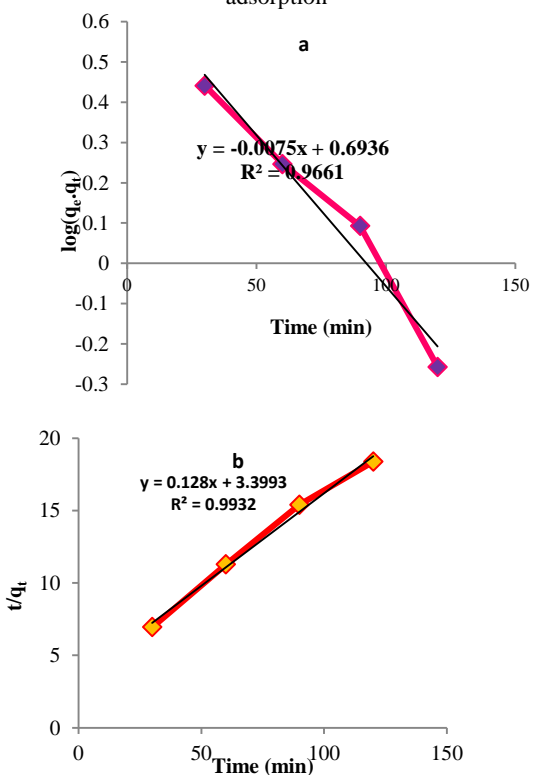


Fig.8: a) First and b) second order kinetics of o-CP adsorption

The adsorption process followed the Langmuir isotherm with $R^2 = 0.933$ and second-order kinetic

model with the correlation coefficient equal to 0.0993. The adsorption process reached equilibrium after 120min at 50mg/l o-CP concentration, and adsorption capacity was calculated to be 6.5mg/g. Also, in adsorption kinetics and isotherms, we found that by increasing the initial concentration of pollutant, adsorption capacity enhanced and removal efficiency reduced. So that, at 200mg/l concentration, removal efficiency and q_e were 52% and 15.02mg/g, respectively; because a constant mass of adsorbent can only adsorb a certain amount of pollutants. With an increase in o-CP concentration for a fixed number of adsorption sites, the number of molecules adsorbed increased due to the competition between molecules to occupy the available adsorption sites. The position of -Cl group in benzene ring has great impact relation to the capacity and ability to adsorb. The initial concentration led to creating a large driving force to overcome Mono-chlorophenol mass transfer resistance between aqueous and solid phase. Also, higher adsorbate to adsorbent ratio enhances the attaching speed of analyte to adsorbent [12].

Ncibi *et al.* have observed that by increasing in adsorbate concentration from 10 to 50mg/l, adsorption capacity increased from 0.42 to 4.64mg/g and removal efficiency decreased [29]. Results obtained in the present study are consistent with other studies [8, 22].

CONCLUSION

In this research, the zero-valent iron nanoparticles modified clay used for other- chlorophenol removal. The highest removal efficiency (91.3 %) was obtained for pH 4. The o-CP removal efficiency by the modified clay increased from 35.9 to 82.7 as the adsorbent dosage is increased from 0.05 to 1g after 120min contact time. The Langmuir isotherm model and the second-order kinetic model provided the best fit to the experimental data compared to other studied models. A modification process carried out on the clay leads to improve the adsorption efficiency. So that can reach a suitable adsorbent for wastewater treatment in industrial scale, with this simple and economic modification method.

ETHICAL ISSUES

Hereby, it is declared that this work and obtained results are original experimental work of authors and it has neither been published, nor is it under review in another journal, and it is not being submitted for publication in any other journals.

CONFLICT OF INTEREST

The authors declare that they have no competing interest.

AUTHORS' CONTRIBUTION

This work is the result of the full cooperation of all mentioned authors.

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