

Tetrachloroethylene Removal Rate from Aqueous Solutions by Pumice Doped with Copper: An Evaluation of the Effect of pH

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Abstract

Tetrachloroethylene (TCE) is a chlorinated aliphatic hydrocarbon, used in many industries. Effective and efficient treatment of industrial wastewater, containing TCE, is one of the environmental requirements. The purpose of this study was to determine the role of alkaline environments in TCE removal rate from aqueous solutions, using copper-doped pumice. This experimental study was performed, using granulated pumice stones with a mesh 4 (8.4 mm) in alkaline conditions; the samples were coated with copper. Copper-doped pumice was prepared as a bed at doses of 1, 2, and 3 g/L; the study was performed at pH ranges of 3, 7, and 11. Based on the results, copper-doped pumice showed good efficacy in TCE removal; in addition, its performance increased in alkaline conditions. Therefore, use of this stone for the treatment of wastewater, containing TCE, is effective due to its availability and low cost. Besides, it can be considered a good option, given its high efficiency in the adsorption process.

Keywords: Pumice, Copper, Tetrachloroethylene Removal, Alkaline Environments

1. Introduction

Halogenated aliphatic compounds are considered as the most hazardous materials in the environment (soil and water resources). These compounds may be discharged into groundwater and surface water through disposal of sanitary landfill and hazardous wastes. Tetrachloroethylene (TCE) or perchloroethylene (PCE) is a hazardous compound, categorized as a chlorinated hydrocarbon (1-3). This compound is widely used as a cleaning solvent for grease, oil, and other industrial fluids in dry cleaning and textile industries. Consequently, it may enter aquatic environments through different industries and domestic wastewater (4).

PCE compounds are potentially hazardous for human health and the environment (5). Oncology research experiments on mice liver tissues have confirmed the increasing risk of human liver cancer due to inhaling or swallowing PCE (6). This compound has been shown to be resistant to aerobic degradation and convert to vinyl chloride isomers in anaerobic conditions, thereby increasing health hazards for humans.

Regarding the abovementioned points, researchers have attempted to find suitable strategies to remove PCE

compounds from hazardous effluents. Therefore, among remediation methods, those incorporating available, cost-effective adsorption, are more desirable (7-9). In fact, since these types of pollutants are present in trace amounts in water resources, the adsorption process can be applied as a reasonable physicochemical method of removal.

Various adsorbents, such as granular and powdered activated carbon, silica, and activated alumina, are employed for adsorption. Also, pumice is a material with a porous structure. It is a light, highly porous stone, which is formed during volcanic activities. The low cost, availability, low density, and high surface-to-volume ratio of pumice make it a good candidate for the elimination of hazardous compounds (10).

The principal methods are commonly modified in research programs, ie, the adsorption capability can be greatly improved through doping with catalysts. Various combinations of metals and surfactants are used in this context. There are many elements which are doped with other compounds, such as titanium, platinum, rhodium, copper, zinc, iron, and aluminum. Among these components, copper has been extensively studied due to its flexibility and solubility in water.

Divalent copper ion has the ability to create a complex coordination number of 4 - 6. Different groups of ligands are placed around copper ions, which can act as factors of catalytic activity (11, 12); therefore, use of pumice-supported copper as a catalyst should be further investigated. On the other hand, it should be noted that this compound has no hazardous effects on the environment.

Several studies have been performed on the removal of organic compounds, using pumice doped with different metals, such as zinc, iron, aluminum, manganese, and copper. In these studies, performance of pumice in the removal of organic compounds enhanced when it was doped with various metals. In this regard, Asgari et al. performed a study on the removal of phenol from aqueous solutions, using copper-doped pumice by considering different parameters, including pH (three different levels), contact time (six different levels), and adsorbent dosage (four different levels). Based on the results, phenol removal efficiency was directly proportional to the increase in contact time, the initial concentration of phenol, and the dose of doped pumice (yield: 93%); on the other hand, removal efficiency was inversely proportional to pH level (13).

Furthermore, Guzzi et al. studied the elimination of phenyl acetylene, using copper-doped pumice and palladium and showed that the catalyst behavior, rate of phenyl acetylene elimination, and its alteration into different isomers are affected by temperature variations (14). Also, Kitis et al. performed a study on the removal of organic compounds from water, using iron-doped pumice. The results revealed that removing organic compounds from water increases dramatically when iron-doped pumice is used (15).

Moreover, Bardakci in a study on the removal of monochlorophenols using copper- and zinc-doped pumice revealed that the absorption process via metal cations increases on the surface of pumice. The findings also indicated that metal oxides can loosen the link between chlorophenol molecules if the contact area is increased (16). Several other investigations have been conducted on the effects of PCE and biological methods, while none of them have studied non-biological removal. In most studies, the used reactors were expensive; as a result, it was necessary to adopt a cost-effective procedure to remove PCE.

Undoubtedly, removal methods should be based on an accurate understanding of the current conditions and facilities and have minimum environmental risks; also, it should be noted that PCE is scarcely observed in water resources. With this background in mind, in this study, we aimed to determine the efficiency of copper-doped pumice in PCE removal. Development of new alkaline, high-pH conditions is considered as the novelty of this study.

2. Methods

2.1. Preparation of the Adsorbent

Sufficient amounts of mineral pumice were provided from construction material sale stores in Kermanshah, Iran. The process of adsorbent preparation was carried out in the laboratory of Public Health School of Kermanshah University of Medical Sciences. The required amounts of natural mineral pumice were aggregated by a standard-size mesh 4 filter (8.4 mm) and then rinsed with distilled water until the powder was completely washed away. Afterwards, the granules were dried at 103°C for 6 hours.

The copper-doping process included submerging the granular pumice in hydrochloric 1% acid solution for 24 hours, washing with distilled water, and drying at 103°C; the samples were then placed in 0.01 M of copper sulfate solution (Merck, Germany) for 72 hours at ambient temperature. The reinforced granular pumice was dried in the oven at 103°C. Finally, the coated pumice was washed with distilled water and placed at a temperature of 103°C for 24 hours in order to be stabilized and tested (13).

In order to determine the amount of stabilized copper on pumice and its compounds, X-ray diffraction (XRD; APD-2000 Model, Italy) and X-ray fluorescence (XRF; Belec GmbH, Germany) techniques were used. Structural and morphological features of copper-doped pumice were determined through scanning electron microscope (SEM; JSM-840, JEOL, Japan). All the chemicals were purchased from Merck Company.

2.2. Effect of pH on the Removal Process

In this descriptive-analytical study, in order to investigate the effect of solution pH on the removal process, PCE solutions with concentrations of 25, 75, and 125 mg/L were prepared and their pH was normally set in the range of 3, 7, and 11, using HCl and NaOH (Merck, Germany). In this manner, 1, 2, and 3 g of natural and copper-doped pumice were added to 1000 mL of the solution and kept for 80 minutes. A pH meter (Hanna pH 211) was used to measure the pH readings. Finally, after the extraction of PCE with normal pentane, the area under the curve of PCE was read by gas chromatography-mass spectrometry (GC-MS; Agilent 6890N GC and 5975C MS, Mode EI) with a Chrompack capillary column (DB-5 MS; length: 30 M, diameter: 0.25 mm, film thickness: 0.5 μ).

The concentrations were analyzed by a GC device (Agilent 6890N GC and 5975C MS, Mode EI) with a Delsi DI-200 chromatograph, fitted into a direct injection port and a flame ionization detector, both set at 340 8 °C; He (0.8 bar) was the carrier gas, and the column was a CP-Sil 5 CB capillary column (Chrompack; 50 m \times 0.32 mm, film thickness: 0.5 mm). All the samples were injected to the device, using

the non-headspace technique. Temperature programming was 100 - 280°C to 40°C/min.

The sample size was determined according to 3 pH ranges by two absorbent forms (raw granulated and doped pumice at 3 levels) in Design-Expert 8 software environment with 3 replicates and blanks. A total of 32 samples (16 blanks and 16 samples) were calculated in total. Data analysis was performed using ANOVA and Kruskal-Wallis tests at a significance level of 0.05, using SPSS version 16.

2.3. Kinetics of Absorption Reactions

The kinetic constants of reactions can be calculated by the following equations: Lagergren's pseudo-first order and Ho pseudo-second order (17, 18).

2.3.1. Pseudo-First Order Kinetics

The equation of pseudo-first order kinetics is as follows:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (1)$$

Equation 1 is changed to Equation 2 via integration ($t = 0$ to $t = t$ and $q_e = 0$ to $q_e = q_t$):

$$\log \left(1 - \frac{q_t}{q_e} \right) = -\frac{k_1}{2.302} t \quad (2)$$

Where q_e and q_t are the amounts of the adsorbate at time t and equilibrium (mg/g), respectively, and K_1 denotes the constant of the first-order kinetic rate (min^{-1}).

2.3.2. Pseudo-Second Order Kinetics

The Equation of pseudo-first order kinetics is as follows:

$$\frac{dq}{dt} = k(q_e - q)^2 \quad (3)$$

Equation 3 is changed to Equation 4:

$$\frac{1}{q_e - q_t} = \frac{1}{q_e} + kt \quad (4)$$

Also, Equation 4 can be rewritten as Equation 5 as follows:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (5)$$

Where q_e and q_t are the amounts of the adsorbate at time t and equilibrium (mg/g), respectively, h denotes the rate of initial adsorption at $t \rightarrow 0$ ($\text{mg.g}^{-1}.\text{min}^{-1}$), and K is the constant of second-order kinetic rate ($\text{g.mg}^{-1}.\text{min}^{-1}$).

2.3.3. Determination of Reaction Kinetics

In order to determine the kinetics of reaction adsorption, experiments were performed at different contact times (20, 40, 60, and 80 minutes), while other variables remained constant. In each run, a fixed dose (2 g) of the two adsorbents was added. Then, 100 mL of TCE solution (75 mg/L) was added, and the samples were well mixed with a magnetic stirrer. Next, the constants of reaction adsorption were determined. Finally, the obtained data were analyzed by the first and second-order equations.

3. Results and Discussion

3.1. Structural Characteristics of Copper-Doped Pumice

The SEM results of copper-doped pumice samples with 10 and 100 μM scales (Figure 1 and Table 1) showed structural capacity within the cavity to establish and enhance the chemical, physical, and mechanical concentrated capability of more levels of cavities with dense units, using copper sulfate. It is worth mentioning that such a structural pattern within the cavities leads to greater strength and increases the repeatability of PCE absorption on copper-doped pumice (recycling possibility of doped pumice).

Table 1. The Spectrum of Pumice Components Based on the XRF Analysis

Composition	Percent
SiO ₂	64.05
Al ₂ O ₃	23.72
K ₂ O	5.66
Na ₂ O	2.65
Fe ₂ O ₃	0.98
CaO	3.16
MgO	0.32
Total	100

XRF results also showed that the major portion of pumice structure is comprised of quartz (SiO₂). Moreover, the XRD results of pumice samples doped with copper revealed that 4 different structures of copper compounds can be found on pumice. The greatest copper content was related to Bonattite with a blue color (58.3%), while the lowest was attributed to chromite (1.45%). Figure 2 presents the results of XRD analysis.

The related forms with 10 μM accuracy showed the existence of crystals with dimensions of less than 20 - 30 μM . Also, the mechanical properties indicated interesting changes in the process of reducing the particle size from microscopic scale to nano-scale and micrometer ranges.

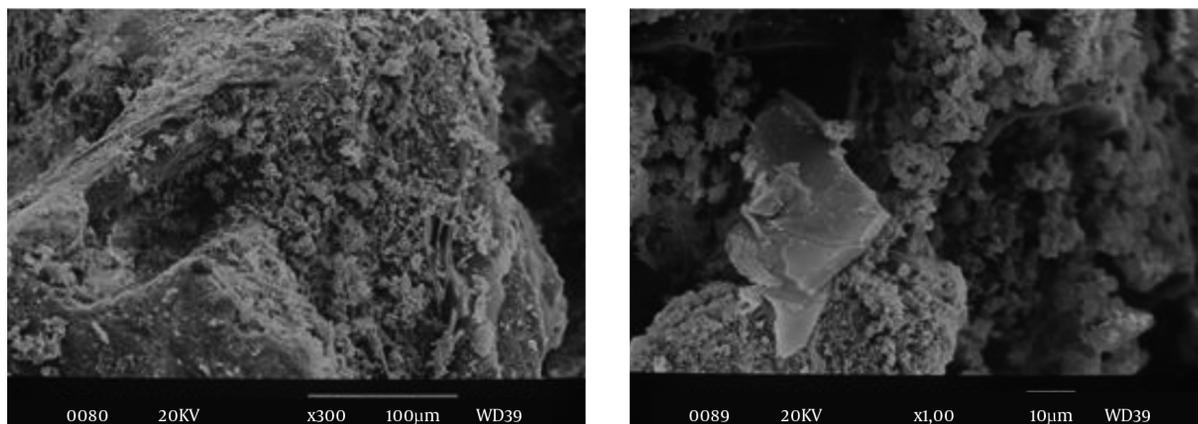


Figure 1. SEM Images of Pumice Doped with Copper in 100 and 10 Micron Scales

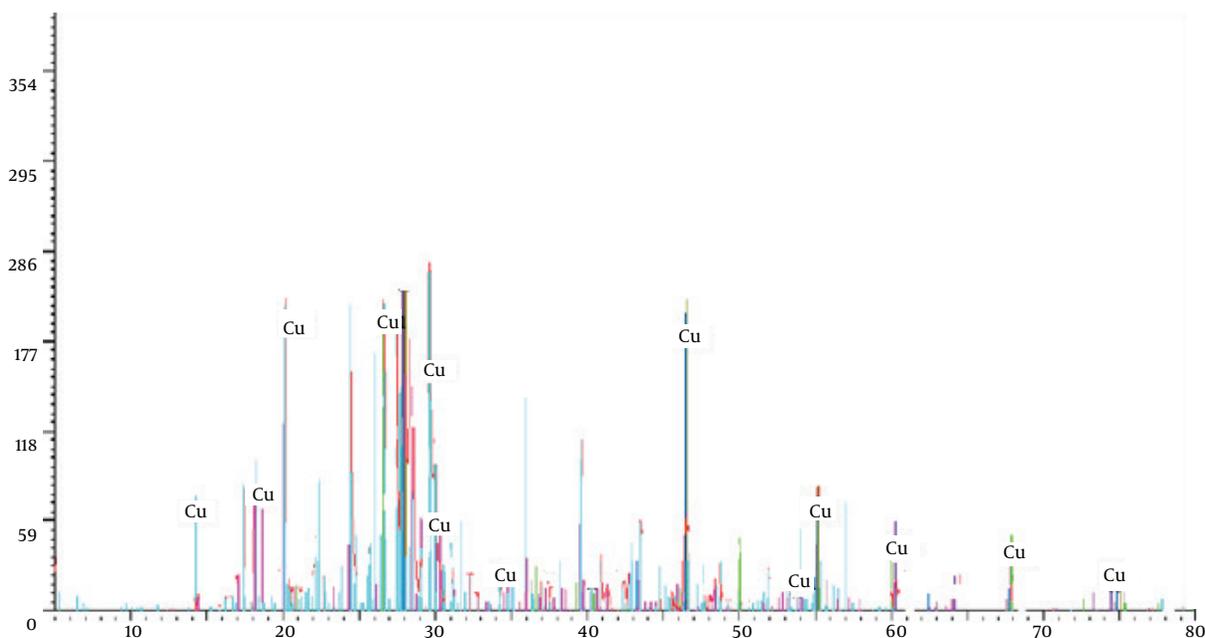


Figure 2. Copper Compounds Placed on Pumice Based on the XRD Analysis

Primary studies have generally shown behaviors such as lower elastic modulus, greater hardness and strength, and less steep in the curve of hardness for microstructure materials, compared to coarse-grained materials.

The structural forms of pumice and copper sulfate surfaces, which are usually in crystal forms, justify the possibility of mechanical strength, leading to the greater ability of pumice covered with copper sulfate in absorbing PCE. The reactivity and selectivity of microstructural catalysts can be enhanced by changing the form of small crystals

(nano-and micro-scales).

Additionally, form and summation of atoms, located at the edges and corners, are effective in catalytic efficiency. In many cases, nano-catalyst surfaces are highly active, and their shape, size, and life cycle change during catalytic reactions. Therefore, regarding the role of catalytic copper in pumice, which leads to dimmer, trimmer, or tetramer PCE, the output signals of GC-MS set should appear in the mass spectra of 498, 415, and 332 M/e (Figure 3). Regarding the absence of the mentioned signals, presence of PCE oligomers

by copper in pumice is ruled out, even if such a reaction has occurred; therefore, no patterns were observed in the GC-MS results.

Identification of the composition of absorbent structure is one of the most important points in the removal process. In this study, considering the components in the pumice structure, the dominant component was quartz (SiO_2), which constitutes around 64% of its structure. Existence of such oxides in an aqueous environment leads to the formation of surface functional groups, which are very effective in the removal of contaminants from water (10, 19). Also, in studies by Ozturk Akbal et al. and Kitis et al. SiO_2 was reported as the major component of pumice (20); the results of these studies are compatible with the present research.

Based on the present results, the absorbent structure is a very important factor in mechanical and extensive adsorption capability; in other words, such structures have a significant surface-to-volume ratio. This feature enhances the selective absorption of pumice, compared to its natural form; in this regard, a study by Kitis et al. reported a similar finding. Another interesting point is that the structural conditions of pumice, as well as the experimental conditions applied during the process of covering pumice surface with copper sulfate, provided the setting for making some micron copper sulphate crystal structures. It has been revealed that mechanical, chemical, physical, and crystalline properties of materials, including their catalytic properties, in nano- and micro-scales differ from their bulky scale.

The remarkable performance of copper-doped pumice in PCE removal under the created conditions can be justified with respect to the behavior of the mentioned structural patterns. This finding is in line with the results presented by Kitis et al. who concluded that coating with iron can be considered an effective factor for enhancing the interaction of pumice surface and increasing the extent of organic matter removal from water (15).

Additionally, Bardakci showed that metal oxide interactions on pumice surface and addition of copper to pumice are effective in removing monochlorophenols. Based on these results, removal of monochlorophenol in 824, 1092, 1494, and 1591 cm^{-1} bands was attributed to metal cations in Fourier transform infrared spectroscopy (16). Although the conditions of this study were different from the present research, a similar mechanism of action can be still considered.

As a heterogeneous catalyst, copper can lead to the oligomer breaking phenomenon through decreasing the activation energy, followed by breaking carbon double bands. This compound can also eliminate PCE molecule links through increasing the contact surface of pumice. It

can be concluded that the PCE-copper complex in pumice was so strong that it did not lead to the withdrawal of copper-pumice structure.

3.2. Effect of pH on PCE Removal

Removal of functional PCE groups on the surface of pumice is primarily affected by pumice surface load, which is influenced by the solution pH (21). The results regarding the effect of pH on PCE removal are presented in Figure 4. The findings indicated that increasing the solution pH from acidic to neutral and even alkaline ranges could decrease the PCE removal efficiency of granulated pumice from 98% to 10.7%; also, it reduced the PCE removal efficiency of copper-doped pumice from 99.7% to 93.8%. The comparison between different pH environments showed a considerable difference in PCE removal rates in case of granular pumice.

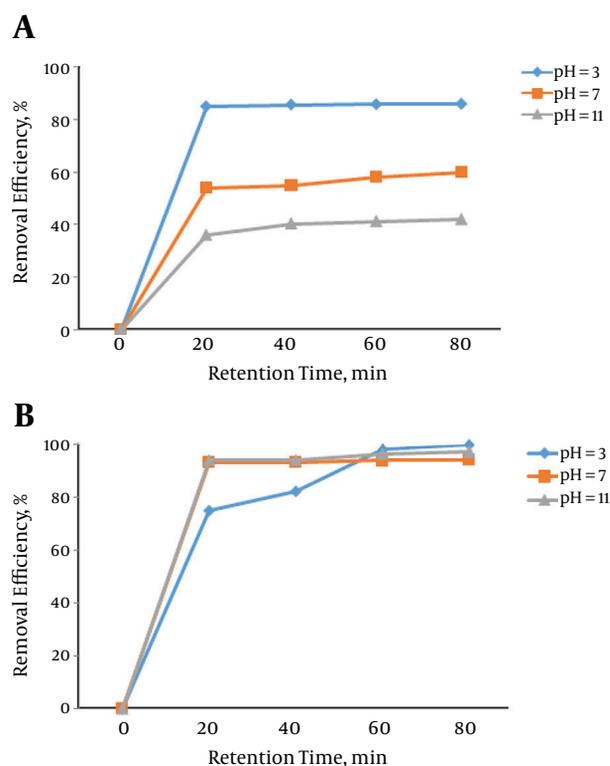


Figure 3. Efficiency of A, Granulated Pumice; B, Pumice Doped with Copper in Removing PCE at Different pH Levels (3 g/L of sorbent and 75 mg/L of PCE)

The lowest rate of PCE removal (10.7%) by granulated pumice was reported at pH = 11 with PCE concentration of 125 mg/L, 1 g of pumice, and 20 minutes of contact time. On the other hand, the highest removal rate was observed

at pH = 3 with PCE concentration of 75 mg/L, 3 g of granulated pumice, and 80 minutes of contact time (98.4%). Nevertheless, PCE removal rate by copper-doped pumice was remarkably higher at pH = 11. In other words, the increase in pH solution resulted in a decline in PCE removal. Also, PCE removal rate at pH = 11 by copper-doped pumice was more significant than granular pumice. Considering the average rate of PCE removal, there was no significant difference, based on the results of Kruskal-Wallis test ($P > 0.05$).

According to the literature, pH and consequently alkaline conditions are important factors, which affect the absorption process via influencing the structure of pollutants and adsorbent surface load (22). Some researchers, including Kitis et al. (15), Qeadeer and Rehan (23), and Asgari et al. (13) consider the presence of metal oxide on the adsorbent surface as influential factors for electrostatic forces and increased absorption amount. Also, the solution pH plays an important role in the surface adsorption process, especially absorption capacity (q_e). This can be due to surface adsorption load, ionization of substances existing in the solution, as well as the separation of functional groups placed in adsorption locations on the adsorbed surface.

Considering the mentioned factors and the results of previous investigations, PCE removal by pumice can be related to the non-ionic property of PCE. Therefore, a repulsive force exists on the surface of granulated pumice, containing SiO_2 . Also, pumice has a negative charge, which is increased by the positive charge of copper in the adsorbent, leading to greater electrostatic removal. Overall, increase of pH from acidic to neutral or alkaline ranges can reduce the PCE removal rate in granulated pumice. However, the rate of PCE removal by copper-doped pumice in the alkaline range is significantly higher than that of granulated pumice ($P = 0.01$).

The decrease in PCE removal rate in alkaline conditions is due to the weaker electrostatic bond between the adsorbent and PCE in environments with a higher pH. The results of this study are consistent with the findings reported by Asgari et al. (13), Banat et al. (24), and Varghese et al. (20). These researchers have also attributed the effect of pH on increasing pollutant removal to reduced electrical charge on the adsorbent surface in high pH conditions (Tables 2 and 3).

3.3. Investigation of the Kinetics of Reaction Adsorption

The results of reaction adsorption kinetics are presented in Tables 4 and 5. Figure 4 shows the adsorption kinetics of PCE by using copper-doped pumice. The findings illustrated that the kinetics of PCE removal by granular and copper-doped pumice were well fitted with the first-order model ($R > 0.99$). Also, a direct relationship was

Table 2. The Spectrum of Copper Compounds Placed on Pumice Based on the XRD Analysis

Composition	Formula	Percent
Bonattite	$\text{CuSO}_4 \cdot 3(\text{H}_2\text{O})$	58.3
Paderaitite	$\text{Cu}_7((\text{Cu}, \text{Ag})_6/33\text{Pb}_1/33\text{Bi}_{11}/33)\text{I}_3\text{S}_{22}$	32.05
Mgriite	$(\text{Cu}, \text{Fe})_3\text{AsSe}_3$	8.2
Chromite	Cu_3SnS_4	1.45

found between the removal rate and the initial concentration of PCE. Therefore, it can be concluded that the removal of PCE by the adsorbents occurs at a high rate.

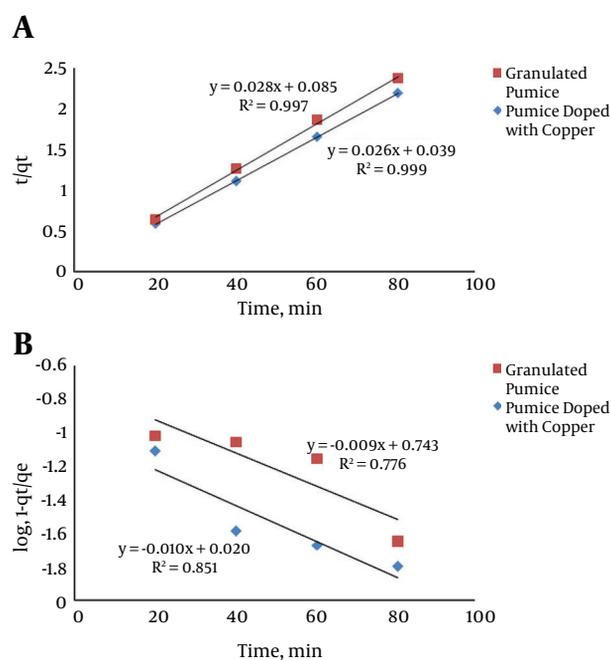


Figure 4. A, Pseudo-First Order Reaction; B, Pseudo-Second Order Reaction of the Performance of Granulated Pumice and Pumice Doped with Copper

4. Conclusions

Considering the non-ionic nature of PCE, the electrostatic attraction between the adsorbent and pollutant increases, thereby raising the removal efficiency. The increase in the removal rate in alkaline conditions by copper-doped pumice implies that copper deposits on pumice, and its positive charge escalates the removal rate in high pH conditions. In addition to increasing the efficiency of PCE removal process, the removal capacity of the system increases for a rather long time without the need for recycle-

Table 3. Comparison of the Efficiency of Two Forms of Pumice in Removing PCE at Different pH Levels

Absorbent Form	pH	Mean Rank	Test	P Value
Granulated pumice	3	22.83	Mann-Whitney U and Wilcoxon W	0.886
Pumice doped with copper	3	22.27		
Granulated pumice	7	26.75	Mann-Whitney U and Wilcoxon W	0.305
Pumice doped with copper	7	22.60		
Granulated pumice	11	24	Mann-Whitney U and Wilcoxon W	0.01
Pumice doped with copper	11	14.75		

Table 4. Kinetic Parameters of Pseudo-First and Pseudo-Second Order Reactions Based on Different Forms of Pumice at a Constant Adsorbent Dose of 2 g

Absorbent Form	Time, min	q _e , mg/g	t/q _e	Log (1-q _e /q _e)
Pumice doped with copper	20	35.15	0.56899	-1.12494
	40	37.033	1.080118	-1.59436
	60	37.2	1.612903	-1.67669
	80	37.4	2.139037	-1.80163
Granulated pumice	20	32.19	0.621311	-1.09536
	40	32.45	1.232666	-1.13753
	60	33.07	1.814333	-1.25851
	80	34.67	2.307138	-2.03218

Table 5. The Calculated Constants of Pseudo-First and Pseudo-Second Order Reactions Based on Different Forms of Pumice

Absorbent Form	Pseudo-First Order Kinetics		Pseudo-Second Order Kinetics	
	K ₁	R ²	K ₂	R ²
Granulated pumice	0.06494	0.9977	0.000129	0.7768
Pumice doped with copper	0.060339	0.9999	0.00011	0.8515

wash or absorbent reactivation. However, no similar conclusion has been made in other research studies; therefore, the authors believe that the results of this study are quite distinctive.

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