

Efficient phenol removal from aqueous solution using iron-coated pumice and leca as an available adsorbents: evaluation of kinetics and isotherm studies

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Abstract

Searching for low cost, accessible, simple implementation, and environmentally friendly adsorbents has been one of the concern of researchers in recent years. Therefore, the aim of this study was to investigate the efficient phenol removal from a synthetic aqueous solution using iron-coated pumice and LECA as an available adsorbents. Bath adsorption experiments were carried out to evaluate the effects of the independent variables such as pH (3-5-7-9-11), initial concentration of phenol (10-50mg/L), contact time (10-60 min) and different concentrations of pumice and LECA (0.2-1 g/100 cc) on the phenol adsorption. The results of the experiments showed that there was a direct relationship between the phenol removal efficiency and increasing the contact time and the adsorbent dosage but it has reverse relationship with the increasing of pH and phenol initial concentration. The optimal condition of parameters for phenol removal were 200 rpm agitation speed, 0.6 g adsorbent dosage, 30 min contact time, and 20 mg/L initial phenol concentration. The study of isotherm and kinetic models showed that the experimental data of the phenol adsorption process were correlated with Freundlich ($R^2_{\text{pumice}}=0.9749$, $R^2_{\text{LECA}}=0.9487$) and Pseudo-second order ($R^2_{\text{pumice}}=0.9745$, $R^2_{\text{LECA}}=0.9486$) models. Based on this study's results, the modified pumice and LECA have a high ability to remove the phenol compounds from aqueous solution.

keywords: phenol removal, adsorption, pumice stone, light expanded clay aggregate, aqueous solution

1. introduction

With the rapid expansion of industries and industrialization of societies, the water resources are influenced by various pollutants. Among various water resources pollutants, the phenol and phenolic compounds are categorized as the priority pollutants, which are considered to be a serious threat to human health and aquatic organisms(1). Phenolic compounds are a large group of aromatic hydrocarbons that are flammable and can extensively dissolve in water, oil and some organic solvents(2). This compound and its derivatives are found in a variety of industries such as paint, pesticides, polymer resins, oil and petrochemical, paper, rubber, textiles, and wood (3-5). The allowable amount of phenol compounds for drinking water and wastewater discharged to the environment is 0.001 and 1 mg /L(6). For this purpose, different methods such as oxidation, adsorption, ion exchange, solvent extraction, biological treatment and precipitation have been used to remove the phenol compound from aqueous solutions(7-9). The adsorption process among these techniques has found more popularity than other methods in terms of initial cost, simplicity, flexibility, easy operation, insensitivity to toxic compounds, high potential for removal of organic and inorganic compounds even at lower concentrations (10). Various materials such as activated carbon(10), coconut shell(11), single-walled and multi-walled carbon nanotubes(12) and chitin(13) have been used for the phenol removal from aqueous solutions. However, the use of low-cost and local adsorbents for pollutant removal is highly interesting(14). For this purpose, several studies have been conducted on the use of the pumice or LECA as an local low-cost in both natural and modified forms, to remove the pollutants such as phenol and 4-chlorophenol(15), cadmium(16), fluoride(17), basic dyes(18), heavy metals(19), from aqueous solution (17). Pumice stone is a porous igneous volcanic rock, with significant accessibility, which it is abundantly found in nature and considered as an inexpensive adsorbent (17, 18). LECA has derived from the phrase of light expanded clay aggregate. It is produced in a rotary kiln and at a temperature of 1200°C, due to the expansion of a particular type of clay. Due to features such as lightness, sound insulation, temperature and moisture insulation, incompressibility against constant pressure, non-degradability, heat-resistant, its natural structure, production in the country and lower cost than industrial adsorbents, it can be used as a suitable, inexpensive and environmentally friendly adsorbent (20). According to availability the numerous pumice and LECA mines in Iran, especially in Kurdistan province of Iran, the main objective of this study was investigate the efficiency of pumice and LECA coated with iron nanoparticles in removing the phenol from aqueous

environments. Moreover, the effect of independent variables such as pH, initial phenol concentration, contact time and different dosage of pumice and LECA on the phenol removal efficiency in a batch reactor was investigated. Finally, isotherm models, i.e., the Freundlich and Langmuir models, and the kinetic models, i.e., pseudo-first-order and pseudo-second-order models were investigated to determine the equilibrium constant of reaction and the adsorption kinetic.

2. Materials and Methods

2.1. Adsorption experiments in batch conditions

In this research, the efficiency of adsorption process using pumice and LECA coated with iron nanoparticles in removing phenol from aqueous solution were studied in batch procedure and laboratory scale. Experiments were carried out in 250 ml Erlenmeyer Flask containing specific amounts of adsorbent and various concentration of pollutant at the different pH and time. To create the proper mixing between adsorbent and adsorbate in all samples studied, a shaker at 150 rpm was used. In order to optimize the experiment conditions, the effect of pH and contact time on the phenol adsorption process was investigated at pH values of 3-11 and the contact time of 10-60 min, and the optimum contact time and pH were determined. Determination of optimum pH and time was performed at the constant values of initial phenol concentration (30mg/L) and adsorbent dosage (0.6g/100 cc). In the next step, after optimizing the pH and contact time, the effect of initial phenol concentration in range of 10-50 mg/L and the adsorbent dosage of 0.1-2.0 gr on the phenol removal efficiency was studied. Finally, the isotherms and kinetics of phenol adsorption onto the pumice and LECA coated with iron nanoparticles were separately determined. All materials used in this study were provided from Merck CO and data analysis was performed by Excel software. Phenol concentrations in the studied samples were measured using the 4-Aminoantipyrine colorimetric method by a UV/VIS spectrophotometer (Shimadzo-1700, Japan) at a wavelength of 500 nm(21). All the adsorption experiments were carried out three times and their mean values were used as the final results in the calculations.

2.2. Preparation and characterizaion of Pumice and LECA adsorbents

The LECA and pumice adsorbents used in this study was obtained from Ghorveh area, Kurdistan province, Iran. In order to increase the porosity and remove the impurities, the adsorbent was exposed to 0.1M sulfuric acid for 24 h and then washed with distilled water and dried in an oven at 105°C for 24 h. Afterward, this acid-washed adsorbent was used for the coating process. The

desired particle size(mesh 80) of adsorbents was obtained from sieve pumice and LECA which had been grinded previously. In the next step, to modify the adsorbent particles, they were placed in 1M iron nitrate solution. So that, while the iron nitrate solution was stirred at 200 rpm, a 0.5 M NaOH solution was added until the pH reached 9.5 ± 1 and mixed for 5 min. The 100 gr of adsorbent was then added into the solution, and the resulting mixture was placed at 60°C and 200 rpm for 24 h and finally dried in an oven at 105°C for 24 h. After that, the resultant particles were washed with distilled water several times and were dried at 60°C . The adsorbent was kept in the polyethylene container at room temperature and kept away from light during the experiments(17, 20, 22, 23). In order to investigate the shape, the mean particle diameter and details of the modified adsorbents surface, the scanning electron microscopy (SEM) were utilized. X-ray diffraction (XRD) was also used to determine their crystalline structure and FTIR was used to study the functional groups on the surface of the particles.

3. Discussion and Conclusion:

3.1. Effect of the solution pH in the process of phenol adsorption from aqueous solution

The solution pH is one of the main parameters that influence the removal efficiency in the oxidation-reduction and adsorption process(24). In order to investigate the effect of pH in the phenol removal from aqueous solution, a concentration of 30 mg/L of the solution was studied at various pH values of 3, 5, 7, 9 and 11, the adsorbent dose of 0.6g/100cc at 150 rpm (Fig 1 and 2). Then, at different intervals (10-60 min), the sample was taken from the solution and all samples were centrifuged for 10 min at 3000 rpm with a sigma-301 centrifuge device prior to measure the residual concentration of phenol. Based on the results, the phenol adsorption onto the LECA and pumice adsorbents is increased by increasing the contact time and this increase in adsorption continues for 30 min, and then the adsorption rate remains somewhat constant. As shown in Fig 1 and 2, with increasing pH from 3 to 11, the phenol removal efficiency by pumice and LECA adsorbents decreased from 99.12% to 67.12% and from 99.12% to 76.01%, respectively. Therefore, the pH 3 and the contact time of 30 min were used as optimum values in other experiments. In this study, the highest phenol adsorption by pumice and LECA occurred at pH 3, which this is due to the effect of the hydrogen positive ions in acidic state on the adsorbents surface and the establishment of electrostatic bond between adsorbents with positive charge and the phenol which has a negative surface charge. At high and alkaline pH values, the removal efficiency is

dramatically reduced, which this reduction in the removal efficiency is due to the competition between negative ions of hydroxyl and phenol to react with adsorbents; so that, at higher pH values, the hydroxyl ions concentration is greater, and this will reduce the efficiency(25). In addition, the results indicate that the adsorption rate and the rate of equilibrium are higher in the pumice adsorbent compared to the LECA. After 30 min, it is almost possible to say that the LECA and pumice adsorbents are saturated and should be regenerated or replaced with other suitable adsorbents to remove the pollutant. The results of this study are somewhat different from the results of studies by some researchers. The study conducted by Ghader to investigate the phenol adsorption onto activated carbon showed that the equilibrium time is observed after 15 min using the activated carbon, which it is inconsistent with the results of this study(26).

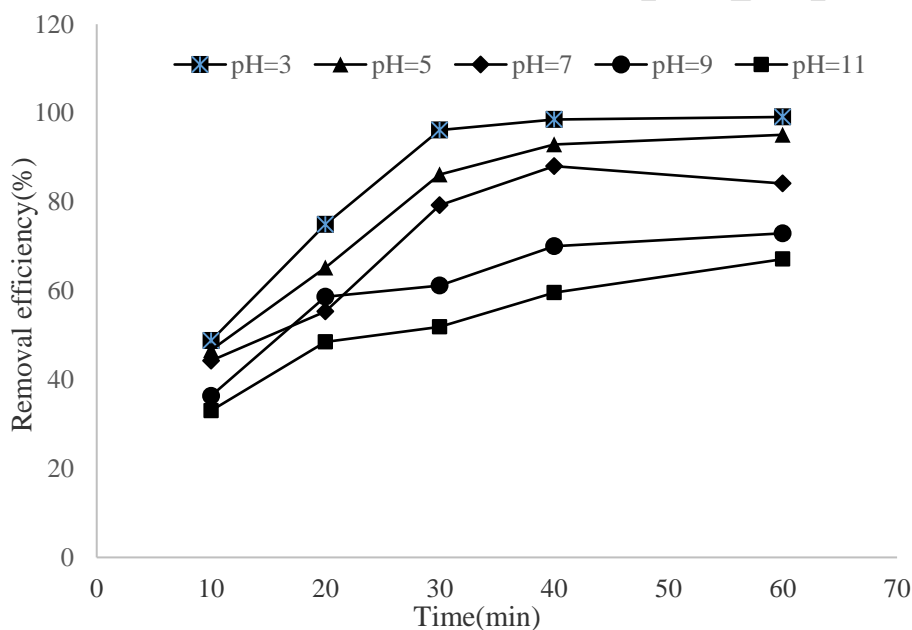


Fig. 1. Effect of solution pH on adsorption of phenol onto modified pumice stone (phenol concentration=30mg/L, adsorbent dose= 0.6g/100cc)

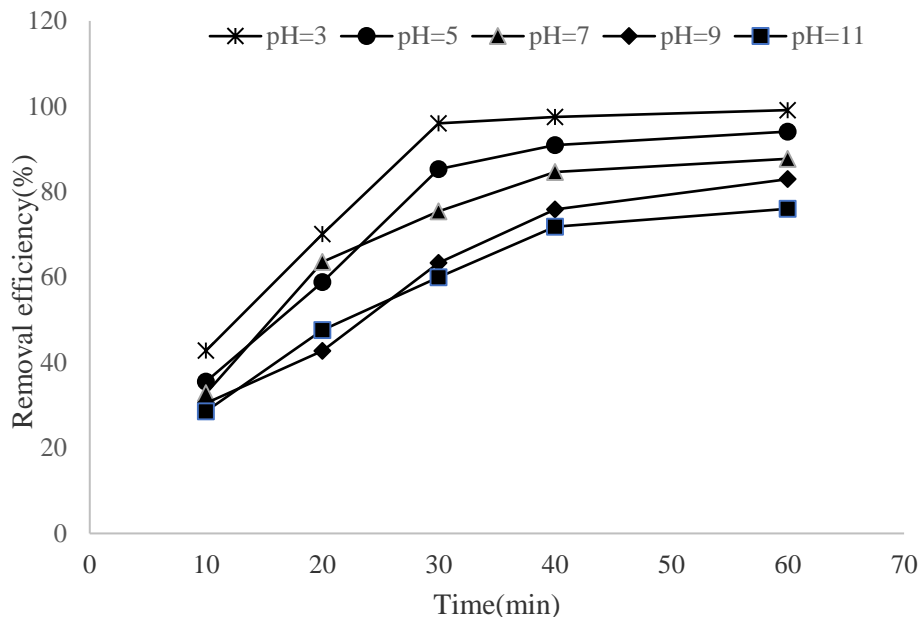


Fig. 2. Effect of solution pH on adsorption of phenol onto modified LECA (phenol concentration=30mg/L, adsorbent dose= 0.6g/100cc)

3.2. The effect of phenol initial concentration on the adsorption process

In order to investigate the effect of phenol concentration on the removal efficiency by LECA and pumice adsorbents, the concentration of 10, 20, 30, 40 and 50 mg/L of phenol were prepared and studied using adsorbent dosage of 0.6g/100cc, at contact time of 30 min and optimum pH (pH=3) (Fig 3). As can be seen in the Fig3, the phenol removal efficiency by the adsorbents increased with increasing the initial phenol concentration up to a concentration of 30 mg/L, and, subsequently, had a small reduction. The results of this study indicate that the amount of phenol adsorption onto the adsorbents depends on its initial concentration. The phenol removal efficiency is noticeable at low concentrations, but its efficiency decreases with increasing the concentrations. The reason for these conditions is due to the filling the adsorption capacity of adsorbents, which reduces the adsorbent efficiency at higher concentrations. The results of the present study are consistent with the research carried out by Varghese et al(27).

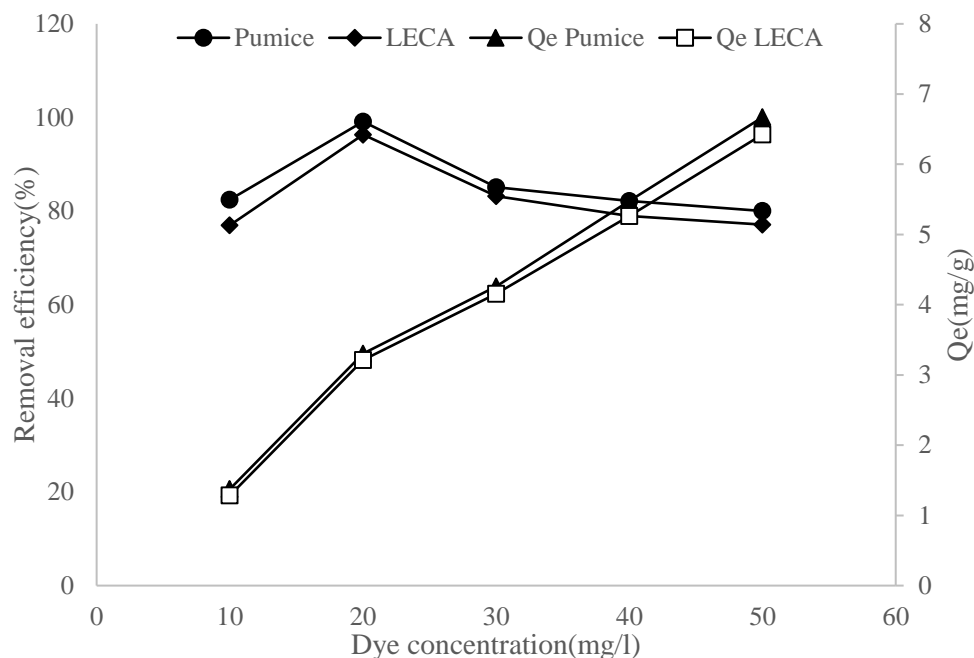


Fig3. Effect of initial phenol concentration on phenol adsorption onto pumice and LECA adsorbent (pH=3, adsorbent dose= 0.6g/100cc, contact time=30min)

3.3. Effect of adsorbent dosage on the adsorption efficiency

At this step, after optimizing pH, initial phenol concentration and contact time in the previous steps, the phenol adsorption by modified pumice and LECA with different adsorbent dosage (0.2-1 g/L) were investigated (Fig. 4). As shown in Fig. 4, by increasing the adsorbent dosage from 0.2 to 1 g in 100 ml, the phenol removal efficiency by pumice and LECA increases from 65.70% to 99.81% and from 69.94 to 99.76%, respectively. The above results were obtained at an optimal pH of 3 and an optimum time of 30 min. This increase in efficiency can be attributed to an increase in the active surface available for the pollutant. Although, increasing the adsorbent dosage is led to enhance the removal efficiency, but the amount of adsorption per unit mass (adsorption capacity) decreases due to the saturation of some of the sites on the adsorbent surface(28). The similar results were observed in a study which it was conducted by Abussaud et al for adsorption of phenol by activated carbon impregnated with iron oxide, aluminum oxide and titanium oxide(10).

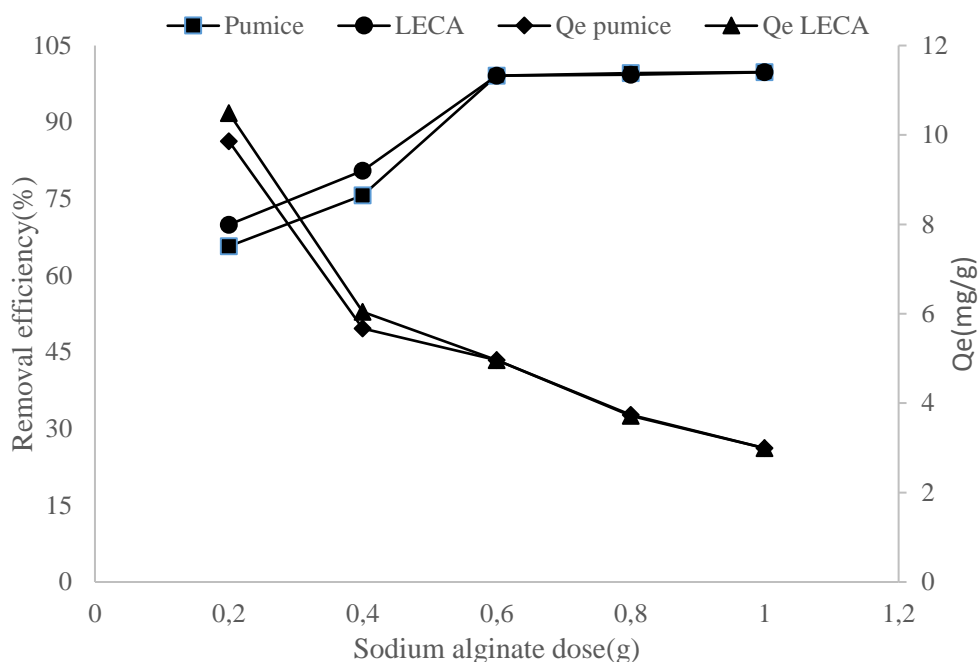
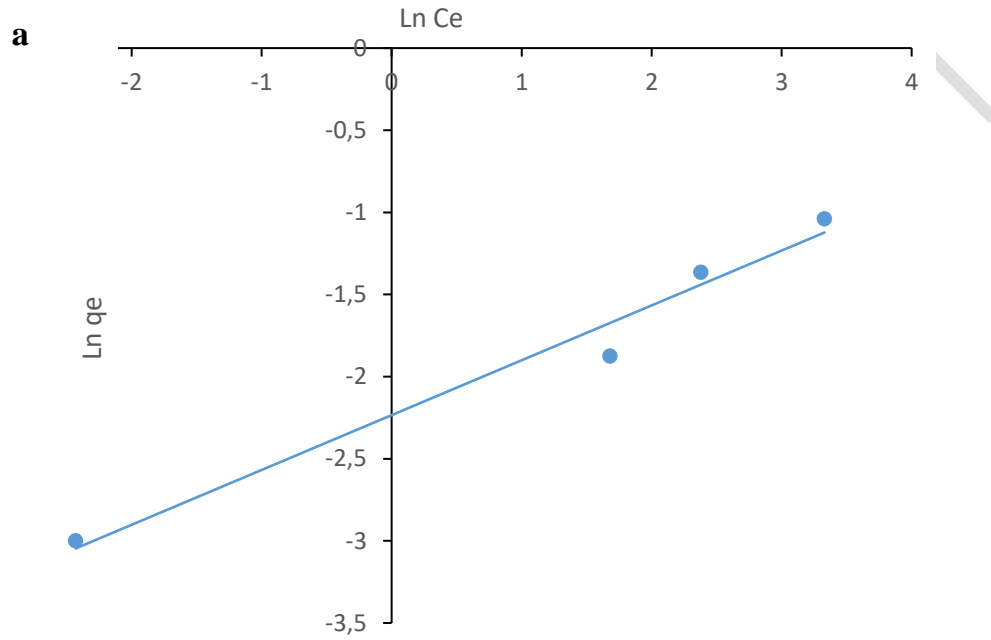


Fig. 4. Effect of adsorbent dose onto percentage removal of phenol onto (pH=3, contact time=30min, phenol concentration=20mg/L)

3.4. Isotherms of phenol adsorption onto pumice and LECA adsorbent

Two Langmuir and Freundlich isotherms are widely used to study the adsorption process. The Langmuir isotherm model is based on the single-layer adsorption in a limited number of identical sites. In this model, it is assumed that adsorption takes place in the sites with the same energy that are located on the surface of the adsorbent, while, in the Freundlich isotherm model, it is assumed that the soluble matter is adsorbed on heterogeneous and multilayer surfaces(29, 30). The adsorption isotherm parameters are expressed in terms of adsorption capacity of the adsorbents. The constant and specific values in the isotherm represent the adsorption surface properties and can be used to compare the adsorption capacity of adsorbent for different pollutants(31). Figures 5 (5a, 5b) show the results of matching the phenol adsorption equilibrium data with the isothermal models. The phenol removal reactions by pumice ($R^2 = 0.975$) and LECA ($R^2 = 0.981$) has a better correspondence with Freundlich isotherm. These results show that the phenol adsorption onto the adsorbents is multi-layer and the surface of the adsorbents is heterogeneous(29). According to Table 1, the low q_{max} values of pumice and LECA indicate that their effectiveness in removing the phenol is weak. On the other hand, the amount of R_L obtained for the reactions performed is less than 1, which indicates that phenol adsorption on the adsorbents is undesirable(32). The results of

study by Jun et al. (2017) showed that the phenol adsorption onto activated carbon derived from coal residues corresponds to the Langmuir isotherm, which it is inconsistent with results of this study(1).



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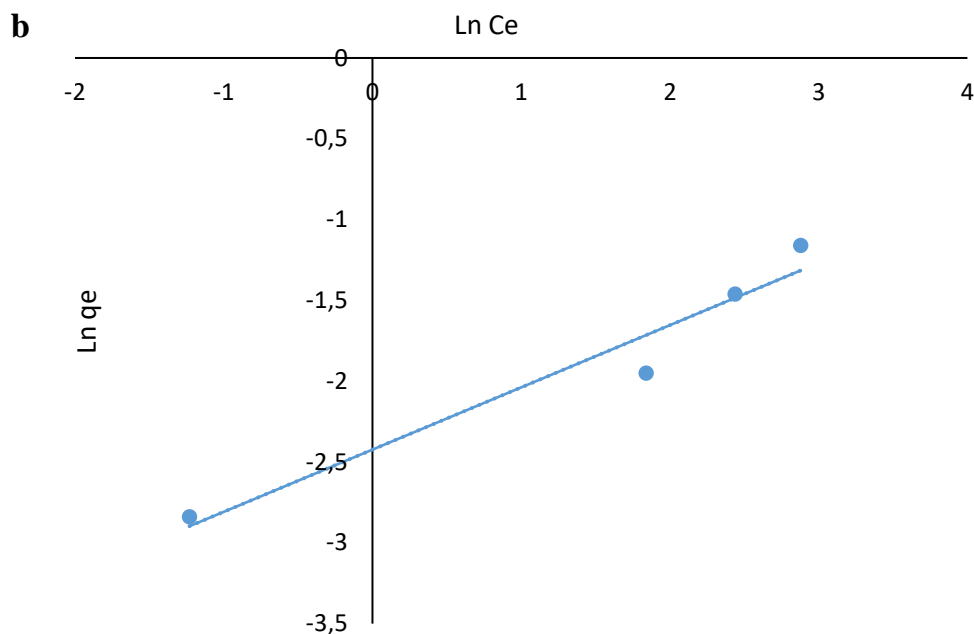


Figure5: Freundlich isotherms plot for adsorption of phenol (a: adsorption of phenol onto modified pumice stone, b: modified LECA)

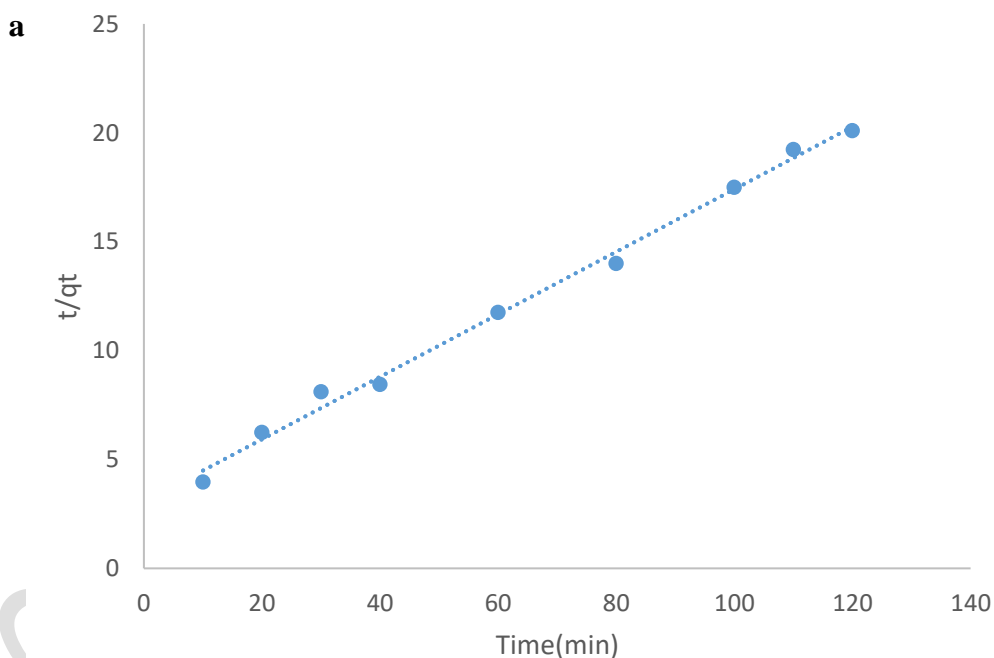
Table 1. Langmuir and Freundlich isotherm parameters

Adsorbent type	Langmuir equation			Freundlich equation		
	$q_m(\text{mg/g})$	$b(\text{L/mg})$	R^2	$k_f(\text{mg/g})$	n	R^2
Pumice stone	0.392	0.222	0.9297	0.1	2.99	0.9749
LECA	0.358	0.2	0.8007	0.09	2.6	0.9487

3.5. Kinetics of phenol adsorption by pumice and LECA adsorbents

The adsorption kinetics give important information about the adsorption mechanism, the adsorption rate of the adsorbent and the control of time in the adsorption process(33). The dependence of the reaction rate on the initial phenol concentration was evaluated by the assumption of a pseudo-first-order and pseudo-second-order model. The pseudo-first-order model assumes that adsorption occurs only by a process or mechanism and in the same type of adsorption sites.

Since, in this model, there are numerous adsorption sites and also there may be the mass transfer effect, therefore it seems that it is not appropriate for heterogeneous surfaces. The pseudo-second-order model is based on the assumption that the speed limiting may be a chemical uptake including the valence forces through the sharing or exchanging an electron between the adsorbent and adsorbate. Unlike the pseudo-first-order equation, this model can adequately predict the adsorption behavior during the adsorption time(34). As shown in Figs. 6a and 6b, the phenol adsorption process onto LECA and pumice meets the pseudo-second order kinetics with the correlation coefficients higher than 0.9. This result shows that the mechanism of phenol adsorption on the adsorbents can be physical adsorption(34). The results of this study are consistent with the study by Abdelwahab et al(35).



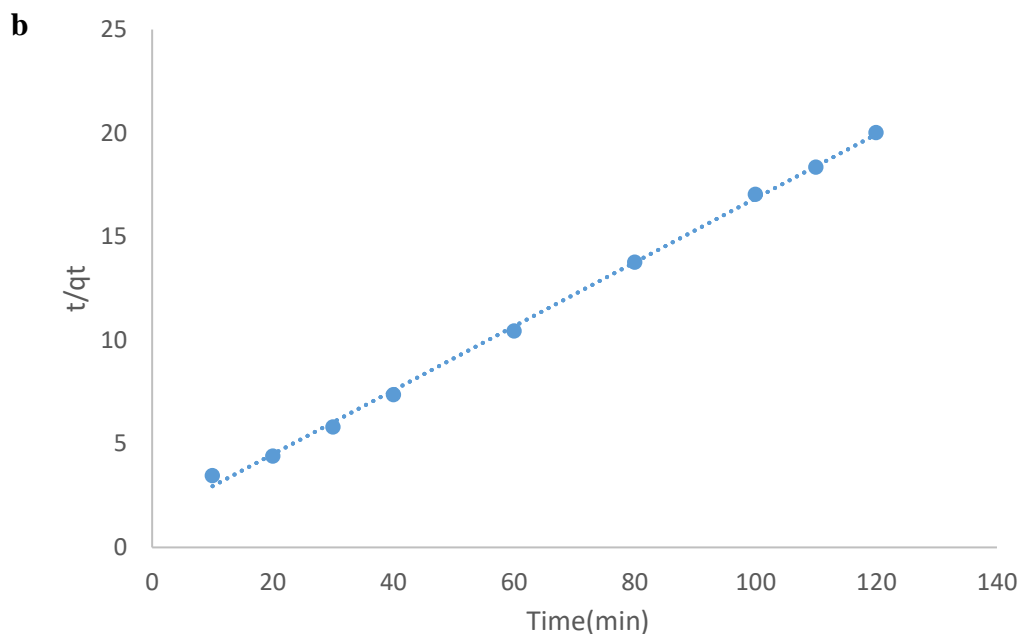


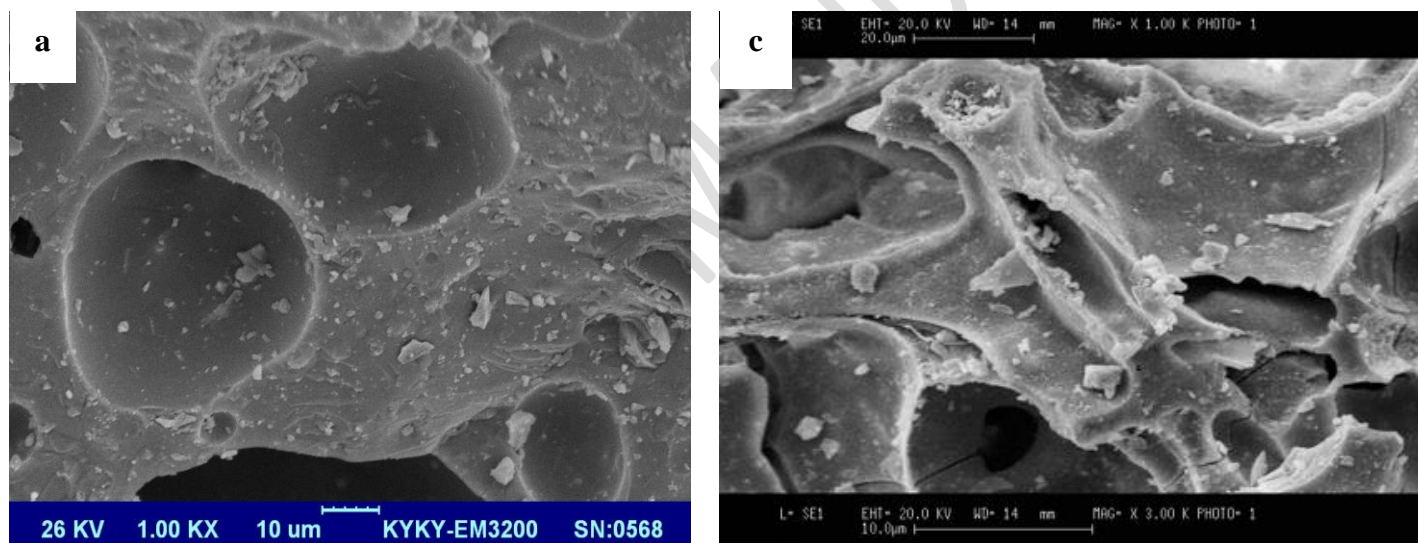
Figure 6. The fitting of obtained data onto pseudo-second-order plot for adsorption of phenol (a: adsorption of phenol onto modified pumice stone, b: modified LECA)

Table2: Obtained parameters of kinetic models for modified pumice stone and LECA

Adsorbent type	Pseudo-first-order			Pseudo-second-order		
	k_1	q_e	R^2	K_2	q_e	R^2
Pumice stone	0.0121	4.35	0.9031	0.0067	6.97	0.9745
LECA	0.0155	2.53	0.8579	0.017	6.47	0.9486

3.6. Structural characteristics of pumice and LECA

In this study, SEM was used to determine the adsorbent apparent properties. Fig. 7 (a, b, c, d) represents the SEM image of raw pumice and LECA and their modified form with iron nanoparticles. Fig. 7a is related to the raw pumice and it is clarifying that the primary raw pumice has a porous surface. After modification of raw pumice with iron nanoparticles (Fig. 7b), it is observed that the initial pumice surface has altered and the initial porous surfaces are not clearly visible. This is because the pumice outer surface has coated with iron nanoparticles (13). These changes are clearly visible on the surface of the LECA before and after modification with iron nanoparticles.



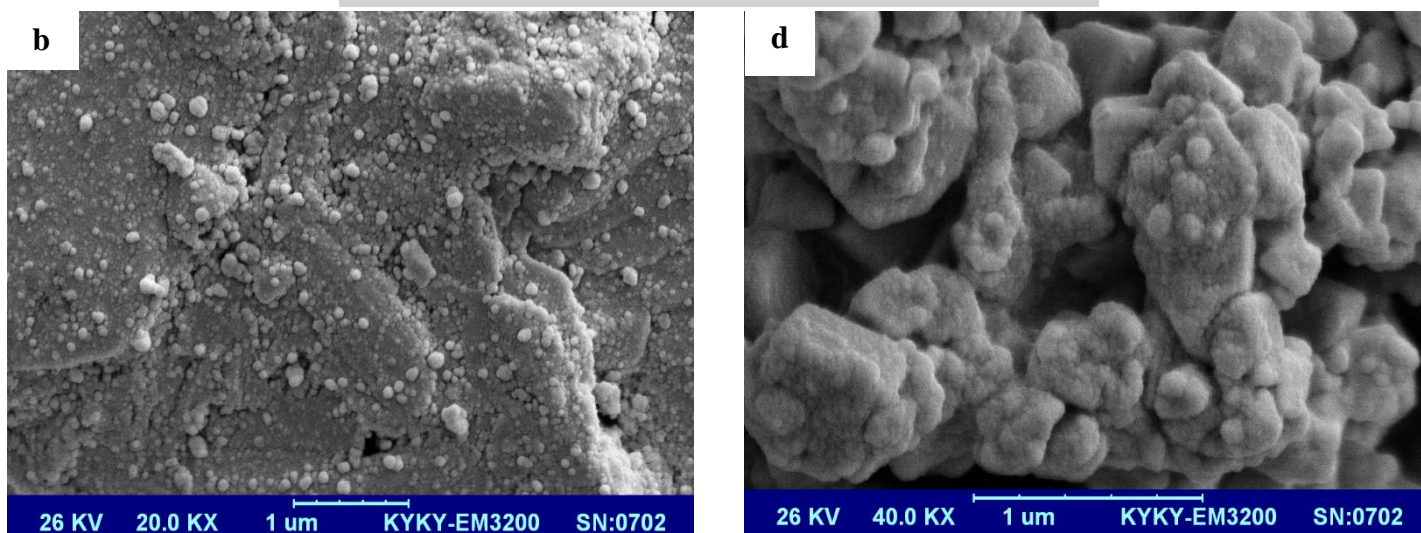


Figure 7. Scanning electron micrograph (SEM) image (a: natural pumice stone, b: natural LECA, c: modified pumice stone, d: modified LECA)

Conclusion

This study is a basic-applied study in which pumice stone and LECA were used as the effective adsorbents in phenol removal from aqueous solution. In this study, the effects of independent variables such as pH (3-5-7-9-11), initial concentration of phenol (10-50 mg/l), contact time (10-60min) and different dosage of pumice and LECA (0.2-1g/100cc) was investigated on the efficiency of phenol removal in a batch reactor. The results of the experiments showed that the removal efficiency of phenol has a direct relationship with increasing the contact time and the adsorbent dosage and has a reverse relationship with increasing the pH and the initial concentration of phenol. The study of isotherm and kinetic models showed that the experimental data of the phenol adsorption process were correlated with with Freundlich ($R^2_{\text{pumice}}=0.9749$, $R^2_{\text{LECA}}=0.9487$) and Pseudo-second order ($R^2_{\text{pumice}}=0.9745$, $R^2_{\text{LECA}}=0.9486$) models. The results of this study indicate that the modified pumice and LECA have a high ability to remove the phenol and use of this process can be considered as a suitable method for the removal of phenol in aqueous solutions because these adsorbents are inexpensive and their modification method is easy.

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