According to the results of the present study, the efficiency of phenol removal increased at the higher concentrations of the nanoparticles. At the retention time of 60 min, the process efficiency at the highest concentration of the nanoparticles reached its maximum (93%). The increased efficiency of the UV/ $S_2O_8^{2-}/Al_2O_3$ process could be attributed to the increased degradation of persulfate anions by UV rays on the surface of aluminum oxide, which in turn increased the concentration of the active sulfate radicals on the surface and in the volume of the fluid.[29,30] In this regard, Qi *et al.* examined the effects of aluminum oxide superficial properties on 2, 4, 6-trichloroanisole (TCA) ozonation, reporting that increased concentration of the catalyst resulted in the higher density of surface-active groups, thereby accelerating the decomposition of TCA. In other words, the surface-active groups in the catalytic ozonation process are the main activity sites.[31]

Effect of the initial phenol concentration

Fig. 8 depicts the effects of various concentrations of phenol (10, 20, 30, 50, and 100 mg/L) on the efficiency of the UV/$S_2O_8^{2-}$/ Al_2O_3 process. As is observed, the phenol removal efficiency increased with decreased phenol concentration. The maximum removal rate of phenol was observed at the concentration of 10 mg/L and retention time of 60 min (95%), while the minimum phenol removal rate was denoted at the concentration of 100 mg/L and retention time of 60 min (45%).

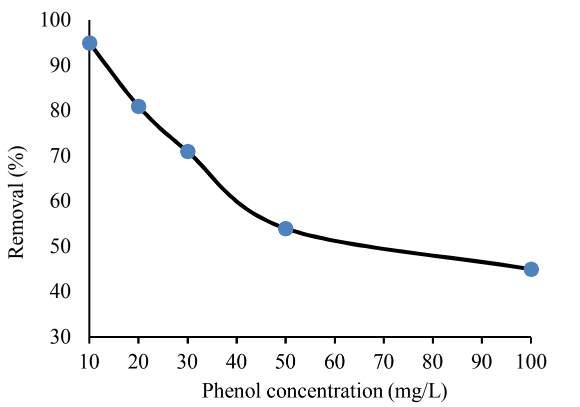

Fig. 8. Effect of initial phenol concentration on efficiency of UV/$S_2O_8^{2-}/Al_2O_3$ process (persulfate concentration: 50 mg/L, pH=5, nanoparticle concentration: 40 mg/L, reaction time: 60 min)

The findings of the current research indicated an inverse correlation between the input phenol concentration and removal efficiency in the studied system, so that the phenol removal efficiency reduced by increasing its initial concentration. This is in congruence with the results obtained by Shokoohi *et al.*[32] and Almasi *et al.*[33,34] In another study conducted by Almasi *et al.*, phenol concentration was considered to be 100-400 mg/L, with the highest phenol removal rate observed with the concentration of 100 mg/L.[35] Similarly, Shokoohi *et al.* aimed to remove bisphenol A from aqueous solutions, reporting that the removal efficiency decreased with an increase in phenol concentration. Moreover, the highest system efficiency was obtained at the concentration of 10 mg/L, while the lowest system efficiency was denoted at the concentration of 100 mg/L.[3] This is in line with the results of the present study which obtained the highest and lowest phenol removal rate at the phenol concentrations of 10 and 100 mg/L, respectively.

Effects of separated processes on phenol removal in the optimal conditions

Based on the optimal conditions, the efficiency of each process was determined separately for each intervener (Figs. 9 and 10).

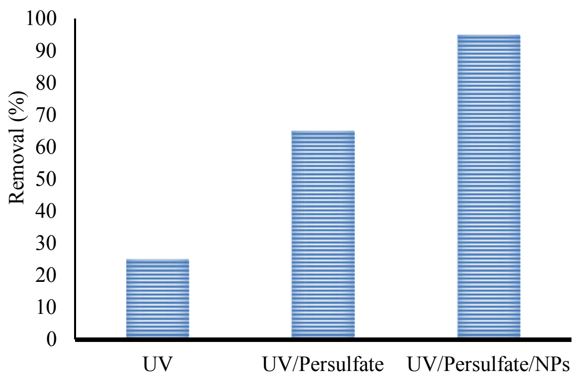

Fig. 9. Effects of separated processes on phenol removal (persulfate concentration: 50 mg/L, pH=5, nanoparticle concentration (Al_2O_3): 40 mg/L, phenol concentration: 10 mg/L)

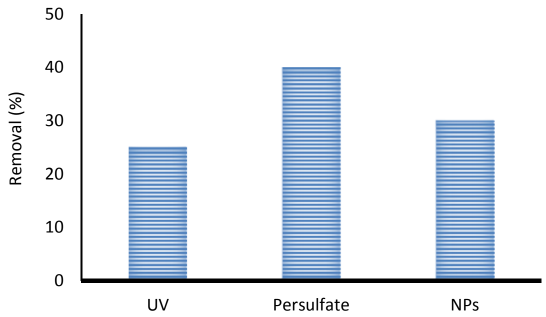

Fig. 10. Effects of separately intervening chemical agents on phenol removal (persulfate concentration: 50 mg/L, pH=5, nanoparticle concentration (Al_2O_3): 40 mg/L, phenol concentration: 10 mg/L)

Reaction kinetics

Our findings regarding the kinetics of phenol removal indicated that the pseudo-first-order kinetics had a higher regression coefficient (R^2=0.9499) compared to the pseudo- second-order model (R^2=0.7924) (Fig. 11); as such, the phenol removal process was in accordance with the pseudo-first-order kinetic model. Therefore, it could be concluded that the phenol removal process complied with the pseudo-first-order model more than the pseudo-second-order model.

According to the absorption kinetic evaluations, the correlation coefficient (R^2) in the pseudo-first-order kinetic model was significantly higher than the pseudo-second-order kinetic model. Therefore, the kinetics of adsorption followed the pseudo-first-order model. In the pseudo-first-order kinetic model, the reaction rate was direct, and a linear correlation was also observed with the reactive substances (initial concentration of the pollutant). In most of the studied processes in the literature, it has been reported that the kinetics of the process follow the pseudo-first-order kinetic model. For instance, Gao *et al.*, through the evaluation of removal of sulfamethazine from water by the UV/$S_2O_8^{2-}$ process, have concluded that the kinetics of the process followed the removal of the pollutant in pseudo-first-order kinetics.[36] Another research by Lau *et al.* demonstrated that the efficiency of the UV/ $S_2O_8^{2-}$ process was followed by the removal of butylated hydroxyanisole (BHA) from pseudo-first-order kinetics.[37]

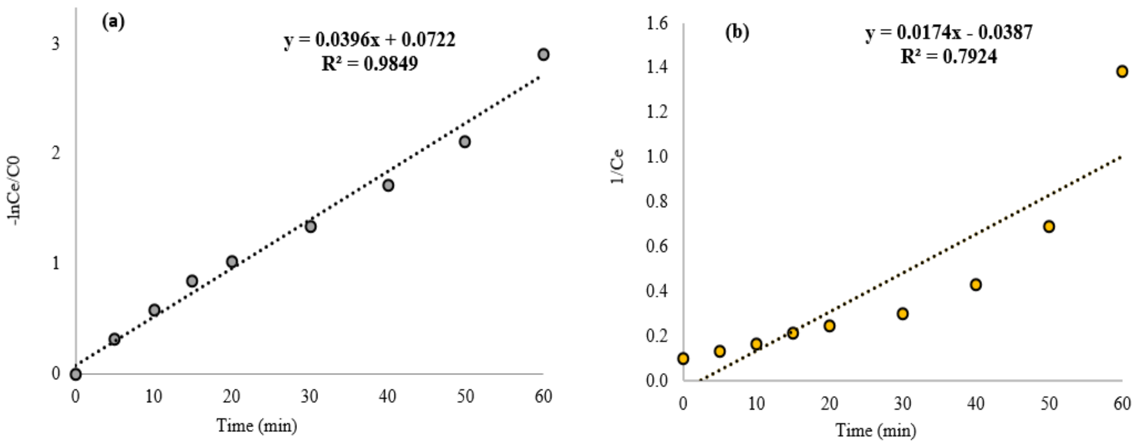

Fig. 11. a) Pseudo-first-order Kinetics and b) Pseudo-second-order Kinetics (persulfate concentration: 50 mg/L, pH=5, nanoparticle concentration: 40 mg/L, initial phenol concentration: 10 mg/L)

Conclusion

Phenol is a resistant and highly biodegradable environmental pollutant, which could cause cancer through inhalation, threatening public health. Therefore, the monitoring of phenol-contaminated aquatic environments is of utmost importance. According to the results, the process of chemical photocatalytic oxidation and other advanced oxidation methods could be used as advanced treatments for the removal of contaminants such as phenol and other pollutants in industrial refineries.

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References

1. Seidmohammadi A, Asgari G, Leili M, Dargahi A, Mobarakian A. Effectiveness of quercus branti activated carbon in removal of methylene blue from aqueous solutions. Arch Hyg Sci 2015; 4(4): 217-25.
2. Shokoohi R, Joneidi Jafari A, Dargahi A, Torkshavand Z. Study of the efficiency of bio-filter and activated sludge (BF/AS) combined process in phenol removal from aqueous solution: Determination of removing model according to response surface methodology (RSM). Desalination Water Treat 2017; 77(1): 256-63.
3. Shokoohi R, Mahmoudi M M, Aazami Ghilan R. Efficiency of magnetic nanoparticles modified with sodium alginate for removal of bisphenol A from aqueous solutions using heterogeneous fenton process. J Mazandaran Univ Med Sci 2017; 27(148): 88-99.
4. Fazelian M, Ramavandi B. Performance of activated carbon prepared from populus alba in removal of phenol from aqueous solution. J Mazandaran Univ Med Sci 2015; 24(121): 250-63.
5. Hasanoğlu A. Removal of phenol from waste-waters using membrane contactors: Comparative experimental analysis of emulsion pertraction. Desalination 2013; 309: 171-180.
6. Almasi A, Dargahi A, Pirsaheb M. The effect of different concentrations of phenol on anaerobic stabilization pond performance in treating petroleum refinery wastewater. Water wastewater 2013; 24(85): 61-68.
7. Dargahi A, Mohammadi M, Amirian F, Karami A, Almasi A. Phenol removal from oil refinery wastewater using anaerobic stabilization pond modeling and process optimization using response surface methodology (RSM). Desalination Water Treat 2017; 87: 199-208.
8. Darvishi S, Sarrafzadeh MH, Mehrnia MR. Biodegradation of phenol by using conventional activated sludge process. J Chem Pharm Res 2016; 8(5): 792-803.
9. Bazrafshan E, Kord Mostafapour F, Jafari Mansourian H. Phenolic compounds: Health effects and its removal from aqueous environments by low-cost adsorbents. Health Scope 2013; 2(2):65-6.
10. Namane A, Hellal A. The dynamic adsorption characteristics of phenol by granular activated carbon. J Hazard Mater 2006; 137(1): 618-25.
11. Busca G, Berardinelli S, Resini C, Arrighi L. Technologies for the removal of phenol from fluid streams: A short review of recent developments. J Hazard Mater 2008; 160(2-3): 265-88.
12. Bazrafshan E, Kord Mostafapour F, Heidarinezhad F. Phenol removal from aqueous solutions using Pistachio hull ash as a low-cost adsorbent. J Sabzevar Univ Med Sci 2013; 20(2): 142-53.
13. Chaichanawong J, Yamamoto T, Ohmori T. Enhancement effect of carbon adsorbent on ozonation of aqueous phenol. J Hazard Mater 2009; 175: 673-9.
14. Liotta LF, Gruttadauriab M, Carlo GD, Perrini G, Librando V. Heterogeneous catalytic degradation of phenolic substrates: Catalysts activity. J Hazard Mater 2009; 162: 588-606.
15. Jiang Y-h, Zhang J-b, Xi B-d, An D, Yang Y, Li M-x. Degradation of toluene-2, 4-diamine by persulphate: Kinetics, intermediates and degradation pathway. Environ Technol 2015; 36(11): 1441-7.
16. Shokoohi R, Dargahi A, Amiri R, Ghavami Z. Evaluation of US/$S_2O_8^{-2}$ compilative process performance in the removal of Erythrosine B dye from aqueous solution. J Adv Environ Health Res 2018; 6(1): 1-8.
17. Pizarro A, Monsalvo V, Molina C, Mohedano A, Rodriguez J. Catalytic hydrodechlorination of p-chloro-m-cresol and 2, 4, 6-trichlorophenol with Pd and Rh supported on Al-pillared clays. Chem Eng J 2015; 273: 363-70.
18. Yuan Y, Tao H , Fan J, Ma L. Degradation of p-chloroaniline by persulfate activated with ferrous sulfide ore particles. Chem Eng J 2015; 268: 38-46.
19. Kuleyin A. Removal of phenol and 4-chlorophenol by surfactant-modified natural zeolite. J Hazard Mater 2007; 144(1): 307-15.
20. Olmez-Hanci T, Dursun D, Aydin E, Arslan-Alaton I, Girit B, Mita L, *et al.* US/$S_2O_8^{-2}$/UV-C and H_2O_2/UV-C treatment of Bisphenol A: Assessment of toxicity, estrogenic activity, degradation products and results in real water. Chemosphere 2015; 119: S115-S23.
21. Cheng Z, Fu F, Pang Y, Tang B, Lu J. Removal

of phenol by acid-washed zero-valent aluminium in the presence of H_2O_2. Chem Eng J 2015; 260: 284-90.
22. Classer LS, Greenberg AE, Eaton AD. Standard method for the examination of water and wastewater. 21st ed. Washington DC: the American Water Works Association 2005; 589-691.
23. Hassan H, Hameed B. Decolorization of acid red 1 by heterogeneous Fenton-like reaction using Fe-ball clay catalyst. International Conference on Environment Science and Engineering IPCBEE IACSIT Press Singapore; 2011.
24. Nkansah-Boadu F, Srinivasan A, Liao PH, Lo KV. Effect of pre-heating on microwave enhanced advanced oxidation process. J Environ Eng Sci 2015; 10(1): 2-9.
25. Kishimoto N, Nishimura H. Effect of pH and molar ratio of pollutant to oxidant on a photochemical advanced oxidation process using hypochlorite.Environmental technology. Environ Technol 2015; 36(19): 2436-42 .
26. Saeid S, Behnajady MA. Photooxidative removal of phenazopyridine by UV/H_2O_2 process in a batch re-circulated annular photoreactor: Influence of operational parameters. Orient J Chem 2015; 31(2): 1211-4.
27. Sharma J, Mishra IM, Kumar V. Degradation and mineralization of Bisphenol A (BPA) in aqueous solution using advanced oxidation processes: UV/H2O2 and UV/$S_2O_8^{2-}$ oxidation systems. J Environ Manage 2015; 156: 266-75.
28. Zhou L, Zheng W, Ji Y, Zhang J, Zeng C, Zhang Y, *et al.* Ferrous-activated persulfate oxidation of arsenic (III) and diuron in aquatic system. J Hazard Mater 2013; 147(1-2): 105-10.
29. Xie B, Zhang H, Cai P, Qiu R, Xiong Y. Simultaneous photocatalytic reduction of Cr (VI) and oxidation of phenol over monoclinic $BiVO_4$ under visible light irradiation. Chemosphere 2006; 63(6): 956-63.
30. Kasprzyk-Hordern B, Ziółek M, Nawrocki J. Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment. Appl Catal B: Environ 2003; 46(4): 639-69.
31. Qi F, Chen Z, Xu B, Shen J, Ma J, Joll C, *et al.* Influence of surface texture and acid–base properties on ozone decomposition catalyzed by aluminum (hydroxyl) oxides. Appl Catal B: Environ 2008; 84(3): 684-90.
32. Shokoohi R, Movahedian H, Dargahi A. Evaluation of the efficiency of a biofilter system's phenol removal from wastewater. Avicenna J Environ Health Eng 2016; 3(1): e7449.
33. Almasi A, Dargahi A, Amrane A, Fazlzadeh M, Mahmoudi M, Hashemian AH. Effect of the retention time and the phenol concentration on the stabilization pond efficiency in the treatment of oil refinery wastewater. Fresenius Environ Bull 2014; 23(10a): 2541-8.
34. Almasi A, Dargahi A, Amrane A, Fazlzadeh M, Soltanian M, Hashemian A. Effect of molasses addition as biodegradable material on phenol removal under anaerobic conditions. Environ Eng Manag J 2018; 17(6): 1475-82.
35. Almasi A, Dargahi A, Pirsaheb M. The effect of different concentrations of phenol on anaerobic stabilization pond performance in treating petroleum refinery wastewater. J Water Wastewater 2013; 24(1): 61-68.
36. Gao Y-q, Gao N-y, Deng Y, Yang Y-q, Ma Y. Ultraviolet (UV) light-activated persulfate oxidation of sulfamethazine in water. Chem Eng J 2012; 195: 248-53.
37. Lau TK, Chu W, Graham NJ. The aqueous degradation of butylated hydroxyanisole by UV/US/$S_2O_8^{-2}$: Study of reaction mechanisms via dimerization and mineralization. Environ Sci Technol 2007; 41(2): 613-9.