Application of Pier Waste Sludge for Catalytic Activation of Proxy-monosulfate and Phenol Elimination From a Petrochemical Wastewater

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Abstract

This investigation aimed to remove phenol from a real wastewater (taken from a petrochemical company) by activating peroxy-monosulfate (PMS) using catalysts extracted from pier waste sludge. The physical and chemical properties of the catalyst were evaluated by FE-SEM/EDS, XRD, FTIR, and TGA/DTG tests. The functional groups of O-H, C-H, CO_3^{2-} , C-H, C-O, N-H, and C-N were identified on the catalyst surface. Also, the crystallinity of the catalyst before and after reaction with petrochemical wastewater was 103.4 nm and 55.8 nm, respectively. Operational parameters of pH (3-9), catalyst dose (0-100 mg/L), phenol concentration (50-250 mg/L), and PMS concentration (0-250 mg/L) were tested to remove phenol. The highest phenol removal rate (94%) was obtained at pH=3, catalyst dose of 80 mg/L, phenol concentration of 50 mg/L, PMS concentration of 150 mg/L, and contact time of 150 min. Phenol decomposition in petrochemical wastewater followed the first-order kinetics ($k > 0.008 \text{ min}^{-1}$, $R^2 > 0.94$). Based on the reported results, it was found that the pH factor is more important than other factors in phenol removal. The catalyst stability test was performed for up to five cycles and phenol removal in the fifth cycle was reduced to 42%. Also, the energy consumption in this study was 77.69 kw.h/m^3 . According to the results, the pier waste sludge catalyst/PMS system is a critical process for eliminating phenol from petrochemical wastewater.

1. Introduction

Wastewater from various industries, including oil refineries, coke, paper, textiles, and petrochemical industries, contains phenol and its derivatives (Ganguly et al. 2020). Phenolic compounds are chemically stable and soluble in water (Honarmandrad et al. 2021, Othman et al. 2020). These compounds pose very serious risks to human health and the environment, so they must be properly disposed before discharge into the environment (Honarmandrad et al. 2021, Mady et al. 2019). Drinking phenol-containing water can disrupt the sleep system, damage the kidneys and pancreas, damage the central nervous system, and possibly cause cancer in humans (Al Bsoul et al. 2021). Given the importance of phenol on human health and the environment, the US Environmental Protection Agency has set a maximum concentration of phenol in industrial effluents for discharge to surface water sources of 1 mg/L (Ganguly et al. 2020, Othman et al. 2020).

Various methods are used to remove phenol from wastewater, including adsorption (Nirmala et al. 2021), ion exchange (Camacho et al. 2021), membrane processes (Ali et al. 2021), reverse osmosis (Al-Huwaidi et al. 2021), and biological processes (Pandian et al. 2021). Conventional treatment methods, however, face challenges such as inefficiency at high phenol concentrations, management and disposal of saturated adsorbents, high cost, and long process times (Bin-Dahman & Saleh 2020).

Sulfate radical-based advanced oxidation processes (AOPs) with the production of free radicals with high oxidation strength (2.5-3.1 eV) (Khan et al. 2017), longer half-life (30-40 μs) (Cui et al. 2017, Wang et al. 2019) and its effect on a wider pH range (2-8) as an effective and efficient method, can convert organic chemical compounds into minerals (Eslami et al. 2018, Li et al. 2021).

Removal of phenol using PMS activation by CuFe₂/MnO₂ catalysts (Liu et al. 2021), CoO@TiO₂/MXene (Ding et al. 2021), γ-Fe₂O₃/MnO₂ (Wang et al. 2021), CeVO₄ (Othman et al. 2020), Co₃O₄-Bi₂O₃ (Hu et al. 2019), and CeO₂ (Gao et al. 2021) have been performed in previous studies. However, due to the secondary contamination, high cost, and inefficiency of these catalysts, researchers are seeking to obtain inexpensive, high-performance, environmentally friendly catalysts (Zhang et al. 2020). Therefore, in this study, the pier waste sludge was used for the first time as a catalyst to remove phenol from a petrochemical wastewater. Extensive studies have been performed on the removal of phenol from synthetic wastewater by PMS systems. The challenge facing this system is its efficiency in removing phenol from real wastewater. Studies in this area are rare. Thus, the aim of this study is to remove phenol from petrochemical wastewater by pier waste sludge/PMS system. The effect of various operating parameters such as solution pH, catalyst dose, phenol concentration, PMS concentration, and reaction time were also investigated. In this study, the physical and chemical properties of the prepared catalyst before and after the reaction with real wastewater and the stability and reuse of the catalyst were presented.

2. Materials And Methods

2.1. Chemicals

Phenol (C₆H₅OH) with 99% purity, NaOH, and HCl 0.1M was prepared from Kimia Material Company, Iran. Potassium peroxy-monosulfate (2KHSO₅·KHSO₄·K₂SO₄) was purchased from Merck, Germany. Deionized water has been used to prepare a catalyst from pier waste sludge.

2.2. Catalyst preparation

The pier waste sludge as a catalytic precursor was collected from Jofreh shipping, Bushehr port, Iran (28° 58'20" N, 50° 49' 31" E). The pier waste sludge was removed from the tides and in conditions where the seawater was tidal. The pier waste sludge was placed in the oven at 105 °C for 24 h to dry. It was then ground and passed through a sieve with mesh number# 40 to produce uniform particles. The pier waste sludge in the electric furnace was optimized at 400 °C and the residence time in the furnace for 3 h (Khoshtinat et al. 2021).

2.3. Real wastewater

The actual wastewater of this study was prepared from a petrochemical company in Bandar Mahshahr, Iran. Approximately 15 liters of wastewater were taken from the outlet of the equalization pond of the petrochemical wastewater treatment plant. The sample was transferred to the laboratory in sealed containers at intervals of 5 h. The chemical properties of petrochemical wastewater are given in Table S1, which shows the presence of phenol, organic compounds, and salt in it, which are capable to consume $\text{SO}_4^{\cdot-}$ radicals. According to the range of parameters in petrochemical wastewater and in order to evaluate the efficiency of pier waste sludge catalyst/PMS system on phenol removal efficiency, pHs and initial phenol concentration of the petrochemical wastewater were set in the range of '3, 5, 7, 8, 9' and '50, 100, 150, 200, 250 mg/L', respectively.

2.4. Design of experiments

The exact amount of 0.1 g of phenol was dissolved in 100 mL of deionized water to obtain a stock solution of 1000 mg/L. This solution was prepared daily to add to the actual wastewater and spiking the phenol concentration to the desired value. All oxidation tests were performed at ambient temperature in batch mode in 250 mL Erlenmeyer flasks containing 100 mL of wastewater. All experiments were done in a shaker-incubator (Kimia Novin Company, Iran) at a speed of 200 rpm. Operating factors and their range include phenol concentration (50, 100, 150, 200, 250 mg/L), catalyst dose (0, 5, 10, 20, 30, 50, 80, 100 mg/L), pH (3, 5, 7, 8, 9), PMS concentration (0, 50, 100, 150, 200, 250 mg/L), and contact time (20, 40, 60, 100, 150 min). The effect of pH (3, 5, 7, 8, 9) was tested under constant conditions of contaminant concentration of 100 mg/L, catalyst dose of 30 mg/L, and PMS concentration of 100 mg/L, and the highest removal efficiency was selected as the optimal value. After optimizing the pH, the effect of catalyst dose (0-100 mg/L) was explored under conditions of initial phenol concentration of 100 mg/L, PMS concentration of 100 mg/L, and pH=3 (optimal value obtained from the previous step). Contaminant dose (50-250 mg/L) was evaluated at PMS concentration of 100 mg/L, pH=3, and catalyst dose of 80 mg/L. The effect of PMS concentration (0-250 mg/L) was tested under constant conditions of initial phenol content of 100 mg/L, pH=3, and catalyst dose of 80 mg/L, and the maximum removal efficiency was selected as the optimal PMS concentration. After the specified time, the reaction mixture was filtered through Whatman 42 filter paper. After determining the optimal conditions for phenol removal from petrochemical wastewater, the pollutant removal kinetics was obtained under optimal conditions. The first-order model was used to investigate the kinetic behavior of phenol removal:

$$\ln \frac{[\text{final phenol conc.}]}{[\text{initial phenol conc.}]} = -k \cdot t \quad (5)$$

If the graph $\ln C/C_0$ against time t is plotted, a line is obtained, which slope is equal to the reaction rate constant (k , min^{-1}).

In this study, the experiments were repeated three times, and the removal efficiency of phenol (%) from petrochemical wastewater was calculated by the following equation.

$$\text{Removal efficiency (\%)} = \left(\frac{\text{Initial phenol} - \text{Final phenol}}{\text{Initial phenol}} \right) \times 100 \quad (6)$$

The test of catalyst reutilization for phenol removal from the wastewater was performed under optimal conditions. After filtering the reaction mixture, the separated catalyst particles were washed with distilled water and dried at 105 °C, and used in the next cycle.

2.5. Measurements

METTLER TOLEDO pH meter from Switzerland was used to measure pH. Phenol was measured by high-performance liquid chromatography (HPLC) by the AZURA model made by KNAUER Germany. FE-SEM image analysis was performed to investigate the morphology of catalyst particles (pier waste sludge) using the electron microscope scanning device (ZEISS, Sigma VP model). Also, the elemental analysis and chemical composition of the samples were evaluated by X-ray diffraction (XRD) spectroscopy test using Oxford Instruments. XRD patterns were recorded using a detector on an advanced XRD broker with CuK α for crystal structure characterization by 'X Pert Pro, Panalytical, made in the Netherlands at 40 kV and 40 mA from 5 to 80 (2 θ). Functional groups were analyzed using the Fourier Transfer Infrared (FTIR) spectrum, Perkin Elmer Company, made in the USA in the range of 400-4000 cm⁻¹. The TGA device STA 1500 model, Rheometric Scientific Company, made in the USA was applied to investigate the temperature changes of the catalyst samples in the ambient temperature range up to 800 °C.

3. Results And Discussion

3.1. Catalyst characteristics

3.1.1. FE-SEM/EDX

To study the surface morphology of pier waste sludge catalyst particles before and after removal of phenol from petrochemical wastewater, FE-SEM test and also for elemental analysis of these particles, EDX test and elemental analysis map was used. The results of these tests are shown in Fig. S1 and S2. According to Fig. S1, pier waste sludge particles with irregular morphology and an average particle size of about 56 nm can be seen. Significant amounts of chlorine, sodium, calcium, oxygen, carbon, and magnesium was observed in the results of the EDX test and elemental analysis map of this sample (Kanimozhi et al. 2014). In the microscopic images shown in Fig. S2 of the pier waste sludge sample, after removing the phenol from the petrochemical wastewater, the morphological change compared to the fresh sample is quite evident. According to this image, the particles of pier waste sludge are completely adhered to each other and have created porous pellets with a diameter of about 3-8 μ m. Also, with increasing magnification, it is clear that the size of nanoparticles in seawater has increased due to agglomeration and the average particle size is about 109 nm, which shows an increase of about twice compared to the pristine sample. In fact, due to the presence of various compounds in petrochemical wastewater in addition to phenol, the adsorption of these compounds on the surface

of pier waste sludge has caused adhesion between the particles and clumps shown in Fig. S2 (a and b) (Mahieux et al. 2010). In the results of elemental analysis of this sample, carbon concentration has increased significantly and has accounted for more than 80% of all elements in the system, which confirms the presence of carbon-containing compounds (including phenol) on the surface of pier waste sludge particles. After the mentioned element, the elements of oxygen, chlorine, titanium, and sulfur had the highest concentration among other elements in this system. Significant sulfur concentrations in this sample can be due to the presence of PMS in the solution or to sulfur compounds in petrochemical wastewater (Rivas et al. 2012). Also, due to the relatively acidic environment of the wastewater, some calcium carbonate is probably dissolved in the solution, and therefore the amount of calcium in this sample is less than the previous sample.

3.1.2. XRD

For a more detailed study of the crystal phases in these two samples, an XRD test was performed on them and the results are shown in Fig. 1. According to the diffraction pattern of the pier waste sludge sample and by applying it to the reference diffraction patterns, it is clear that the composition of calcium carbonate (CaCO_3) in two phases of calcite (with trigonal crystal structure and reference code JCPDS 17-14743) and vaterite (with hexagonal crystal structure and code JCPDS reference 13-192) are the major crystalline phases in this sample. The presence of calcium carbonate in the structure of pier waste sludge has already been proven by Tavasol et al. (2020). Also, magnesium oxide (with reference code JCPDS 89-7746) is another phase that can be identified in the sample, the presence of which was predictable due to the significant percentage of magnesium in the elemental analysis results. In the X-ray diffraction pattern related to pier waste sludge after removal of phenol from petrochemical wastewater, it is clear that significant changes have been made in the resulting spectrum. The most important change in this sample is the removal of most of the calcium carbonate-based phases, which was previously observed in the results of elemental analysis. In fact, by placing seawater in a relatively acidic solution of petrochemical wastewater, calcium carbonate phases are dissolved and phases with more chemical stability such as titanium oxide, magnesium oxide, and iron oxide phases remain. The remaining titanium oxide (TiO_2) in the two phases of anatase (with reference code JCPDS 21-1272) and rutile (with reference code JCPDS 21-1276) both have a tetragonal crystal structure and their differences in how the single-crystal units are placed next to each other. Also, iron oxide with Fe_2O_3 structure, which is known as hematite phase, has been observed in this diffraction pattern (with reference code: JCPDS 86-055), which can be justified due to the presence of iron element in the results of elemental analysis test related to this sample. Another parameter that can be measured by XRD is the size of the crystals in the crystalline materials. The Scherrer equation (Eq. (7)) is used to calculate the crystal size (Hajipour et al. 2021).

$$D = K\lambda/B \cos(\theta) \quad (7)$$

In this equation, λ is the X-ray wavelength used (here $1.54 \text{ \AA}$), K is the shape factor (≈ 0.9), B is the peak width at half of the height and θ is the peak location.

By calculating the crystallite size of calcite in the catalyst sample before phenol removal and also titanium oxide in the catalyst after phenol removal by this relation, this value for these two samples is equal to 103.4 and 55.8 nm, respectively. From this decrease in crystal size, it can be concluded that the deposition of phenol in the solution on the catalyst during the removal process has reduced the degree of system crystallinity and therefore the crystal range of the grains in the presence of the amorphous phase of phenol has decreased.

3.1.3. FTIR

In order to more accurately study the chemical structure of the compounds in the fresh and used catalysts, the FTIR test was used and the results are shown in Fig. S3. In Fig. S3, the broad peak located at 3438 cm^{-1} wavelength corresponds to the O-H bonds in adsorbed water or other hydroxyl groups (Sivakumar et al. 2012). Also, the peaks in the wavenumber range of 2700 cm^{-1} to 3000 cm^{-1} are related to the symmetric and asymmetric tensile vibrations of C-H bonds in organic compounds and different groups containing this bond (Petrovskii et al. 2016). Tensile and flexural vibrations related to carbonate groups (CO_3^{2-}) in calcium carbonate have shown absorption peaks at 1460 cm^{-1} and 860 cm^{-1} , respectively (Vagenas et al. 2003). It has also shown the flexural vibration associated with C-H bonds and the tensile vibration associated with C-O bonds at the 1021 cm^{-1} wavenumber of overlapping absorption peaks (Jung et al. 2018). In the spectrum of the pier waste sludge sample after phenol removal from petrochemical wastewater, in addition to the peaks mentioned above, the absorption peaks related to the tensile vibration of N-H bonds in the wavenumber of about 2500 cm^{-1} and the tensile vibration of C-N bond in the wavenumber of 1285 cm^{-1} confirms the presence of amino compounds in petrochemical wastewater that sits on the surface of the catalyst (Dias et al. 2010, Patty et al. 2017). The flexural vibration of hydroxyl bonds has also shown an absorption peak at 1682 cm^{-1} (Shahmoradi et al. 2020). The reduction of intensity and bandwidth related to carbonate bonds in this sample is another confirmation of the dissolution of this compound in petrochemical wastewater. In the used sample, the presence of a peak related to the flexural vibration of aromatic rings indicates the presence of phenol residues on the surface of the catalyst. Also in this sample, peaks can be observed in the wavenumber less than 500 cm^{-1} , which is related to the tensile vibration of metal-oxygen bonds (Tavasol et al. 2020), which can be titanium, iron, and magnesium. The existence of these elements was previously confirmed by XRD. Therefore, in these results, the existence of different organic compounds such as phenol and different types of amines in petrochemical wastewater can be proven.

3.1.4. TGA/DTG

TGA/DTG test was used to investigate the thermal changes of the samples, and the results are shown in Fig. S4. As shown in Fig. S4, thermal decomposition occurred in the pier waste sludge thermogram at a temperature of about $760\text{ }^{\circ}\text{C}$, which is related to the decomposition of CaCO_3 and its conversion to calcium oxide and carbon dioxide (Li et al. 2017). Therefore, this test also confirms the predominance of the calcium carbonate phase in pier waste sludge. In the pier waste sludge sample after removal of

phenol from petrochemical wastewater, the lack of weight loss in the temperature of 760 °C is another confirmation of the dissolution of calcium carbonate in the wastewater solution. In used sample, weight loss occurred at temperatures between 300 and 400 °C, which is related to the thermal decomposition of adsorbed organic compounds on the catalyst surface (Chavan et al. 2014). Therefore, this test, like the FTIR test, confirms the presence of significant amounts of organic compounds on the photocatalyst surface.

3.2. Effect of wastewater pH

The effect of pH parameter on phenol removal efficiency was studied under constant operating conditions of phenol concentration of 100 mg/L, PMS quantity of 100 mg/L, and catalyst dose of 30 mg/L (Fig. 2). According to the results, the highest phenol removal efficiency was obtained at pH=3 (83.98%) after 150 min. With increasing pH, the removal efficiency decreased, so pH=3 was selected as the optimal pH. In the process of PMS activation at the acidic pH, the radical $\text{SO}_4^{\cdot-}$ are dominant in the reaction medium which has higher oxidation power and longer half-life (Eslami et al. 2018, Khoshtinat et al. 2021). The zero electric charge point (pHpzc) of the catalyst was 8.5 and due to the positive surface charge of the catalyst at acidic pH, it absorbs more PMS anions and increases the removal efficiency (Pang et al. 2020). Due to the radical reaction of $\text{SO}_4^{\cdot-}$ with OH^- in alkaline conditions and radical formation $\cdot\text{OH}$ which has less oxidation potential and shorter half-life than radical, so in alkaline conditions, the removal efficiency of phenol is reduced (Liu et al. 2021). In the study of activation of persulfate with pyrite for oxidation of 2,4-dichlorophenol, the highest removal efficiency was obtained at pH=5 after 120 min (He et al. 2021). In the decomposition of 4-chlorophenol by a AOP system, the highest removal rate was obtained at pH=4 and the lowest at pH=10 (Eslami et al. 2018).

3.3. Effect of catalyst mass

Effect of catalyst dose (0, 5, 10, 20, 30, 50, 80, 100 mg/L) on phenol removal at steady conditions pH=3, phenol concentration of 100 mg/L, and PMS quantity of 100 mg/L was examined (Fig. 3). Phenol removal efficiency increased with increasing catalyst dose up to 80 mg/L and 90.39% of phenol was removed after 150 min. Again, with increasing the catalyst dose to 100 mg/L, the removal of phenol decreased. Therefore, the catalyst dose of 80 mg/L was selected as the optimal dose. Also, the removal of phenol by PMS in the absence of a catalyst was obtained almost 8% after 150 min. This indicates that phenol is not easily oxidized by PMS in the absence of a catalyst. Improving the phenol removal efficiency by increasing the catalyst dose to 80 mg/L is linked to the increase of active catalyst sites for PMS activation and more production of $\text{SO}_4^{\cdot-}$ radicals (Huang et al. 2018, Li et al. 2020, Li et al. 2021, Wang et al. 2019). By increasing the catalyst dose to 100 mg/L, the active sites of the catalyst probably decreased due to clot formation and the available surface area of the catalyst, thus reducing the phenol removal efficiency at high catalyst doses (Liu et al. 2021). The results reported by researchers such as (Liu et al. 2021) and (Saputra et al. 2020) confirm our work.

3.4. Effect of phenol concentration

The effect of initial contaminant concentration (0-100 mg/L) on the removal process was investigated under constant conditions of pH=3, PMS concentration of 100 mg/L, and catalyst dose of 80 mg/L (Fig. 4). With increasing the concentration of pollutants, the removal efficiency had a decreasing trend. According to the results, the removal efficiency of phenol after 20 min for initial concentrations of 50, 100, 150, 200, and 250 mg/L were obtained 57.38, 41.36, 32.82, 20.28, and 10.47%, respectively. With increasing the reaction time to 150 min, the removal efficiencies increased to 94, 90.39, 82.78, 75.17, and 67.56% for the abovementioned concentrations, respectively. The ratio of the number of produced $\text{SO}_4^{\cdot-}$ radicals to phenol molecules at low concentrations is higher, so the removal efficiency of phenol is higher at low concentrations (Othman et al. 2020, Zhao et al. 2020). At constant amounts of $\text{SO}_4^{\cdot-}$ radicals produced with increasing phenol concentration, the amount of exposure to $\text{SO}_4^{\cdot-}$ radicals decreases, resulting in a decrease in phenol removal (Saputra et al. 2020). In the study of phenol removal from aqueous solutions by MnO_x /PMS system, the highest phenol removal efficiency was 100% at 25 mg/L for 60 min and the lowest was 75% at 100 mg/L after 120 min. (Saputra et al. 2013). In the decomposition of phenol from aqueous solutions by MnO_x /ACP/PMS system, removal of 100% phenol, at a concentration of 50 mg/L after 10 min and a concentration of 75 mg/L and 100 mg/L for a period of 30 min and 90 min were obtained (Saputra et al. 2020). Various researchers have stated that the rate of phenol decomposition decreases with increasing concentration and the solution to this challenge is to increase the reaction time. Comparisons of phenol removal efficiencies in different catalytic systems are given in Table 1. According to this table, the pier waste sludge catalyst/PMS system, in comparison with other processes, has a good efficiency for removing phenol from petrochemical wastewater.

Table 1. Comparison of phenol removal efficiency in different catalytic systems.

Studied system	Initial content of phenol (mg/L)	Removal efficiency (%)	Reference
Biochar-La/US/PS	42.25	>99	(Razmi et al. 2019)
Mn_2O_3 /PMS	50	98	(Saputra et al. 2013)
UV/PS	200	≈ 91	(Seid-Mohammadi et al. 2016)
Cu- Co_3O_4 @ MnO_2 /PMS	30	100	(Khan et al. 2017)
Ag/ZnO/PMS/Vis	30	≈ 100	(Truong et al. 2021)
MnO_x /ACP/PMS	75	100	(Saputra et al. 2020)
US/PS	17	90.92	(Moradnia et al. 2021)
Pier waste sludge /PMS	50	94	This work

3.5. Effect of PMS dose

The effect of PMS concentration (50-50 mg/L) on the phenol removal process was evaluated under operating conditions of pH=3, phenol concentration of 100 mg/L, and catalyst dose of 80 mg/L (Fig. 5). According to the results, increasing the PMS concentration to 150 mg/L increased the phenol removal efficiency and 92.98% of the contaminant was removed from the wastewater after 150 min. By increasing the concentration of PMS to 250 mg/L, a decreasing trend of phenol removal from wastewater was observed and 87.56% of the contaminant was removed. Therefore, a concentration of 150 mg/L was considered as the optimal concentration. Phenol oxidation in the absence of PMS indicated that approximately 14% of phenol was removed after 150 min and the removal of the contaminant was significantly reduced in the absence of PMS, and the major removal mechanism in the absence of PMS was probably attributed to adsorption. Increasing the PMS concentration to 150 mg/L increased the phenol removal efficiency due to the production of more free radicals (Truong et al. 2021). Probably at concentrations higher than 150 mg/L $\text{SO}_4^{\cdot-}$ radicals have a self-scavenger role. It also reacts with $\text{SO}_4^{\cdot-}$ radicals at concentrations of PMS above 150 mg/L excess HSO_5^- and leads to weak $\text{SO}_5^{\cdot-}$ radical production (Eqs. (5-8)) (Ghanbari et al. 2020, Hu et al. 2018, Liu et al. 2021).

3.6. Phenol removal kinetics

Phenol removal kinetics were evaluated at pH=3, catalyst dose 80 mg/L, PMS concentration 150 mg/L, phenol concentration (50-250 mg/L), and contact time (20-150 min) (Fig. 6). According to the results, the highest rate of phenol degradation was achieved at an initial concentration of 50 mg/L with the rate of 0.0144 min^{-1} . The correlation coefficient (R^2) for all concentrations was higher than 0.94, which indicates that in the studied system, the data suitably fit the first-order kinetics. Also, with increasing phenol concentration, the reaction proceeded at a slower rate (Saputra et al. 2020). The results of studies by other researchers for phenol degradation followed first-order kinetics (Li et al. 2020, Othman et al. 2020, Saputra et al. 2020, Vaiano et al. 2018).

3.7. Reuse of the studied catalyst

Reuse of pier waste sludge catalyst was evaluated in 5 cycles under optimal conditions of pH=3, catalyst dose 80 mg/L, phenol concentration 50 mg/L, PMS concentration 150 mg/L, and reaction time 150 min (Fig. 7). The fresh catalyst removed approximately 94% of the phenol. During the first, second, and third cycles, 83.5%, 71.9%, and 64.2% of the phenol were removed, respectively. However, in the fifth cycle, the catalytic activity of the pier waste sludge decreased and approximately 42% of phenol was removed. We

hypothesize that this decrease in efficiency is related to catalyst leaching and leakage of active catalyst components into the liquid phase, as well as changes in the structure and deposition of by-products at the catalyst sludge catalyst surface (Khan et al. 2017, Saputra et al. 2013). The catalytic activity of Mn_2O_3 in the second cycle was reduced to 27% for phenol decomposition (Saputra et al. 2013). Phenol removal efficiency by MnO_x/ACP catalyst in the first cycle decreased to 38% after 90 min (Saputra et al. 2020). Therefore, it can be concluded that the pier sludge is a suitable catalyst with optimal activity and stability.

3.8. Energy consumption by the system

To select advanced oxidation systems to remove pollutants, special attention is paid to the consumption of electrical energy (Moussavi & Rezaei 2017). Electrical energy consumption (EEC, kw.h/m^3) in the pier waste sludge catalyst/PMS system at $\text{pH}=3$, catalyst dose 80 mg/L , PMS concentration 150 mg/L , phenol concentration 50 mg/L , and reaction time 100 min was quantified according to the following formula (Bessegato et al. 2018, Dhaka et al. 2018, Tavasol et al. 2021).

$$\text{EEC} = \frac{P \times t \times 1000}{V \times 60 \times \log \left(\frac{\text{Inlet phenol}}{\text{Outlet phenol}} \right)} \quad (9)$$

In this formula, t denotes the time of reaction (min), P implies the input power (kW), V denotes the treated volume of petrochemical wastewater (L).

The amount of EEC for the investigated system was attained 77.69 kw.h/m^3 . In the UV/PMS oxidation system, the EEC level was 143.7 kw.h/m^3 (Dhaka et al. 2018). The quantity of EEC to remove phenol from aqueous solutions by UV process was obtained 400 kw.h/m^3 (Yazdanbakhsh et al. 2020). Therefore, due to less energy consumption in this study than published works, the pier waste sludge catalyst/PMS system can be considered as a suitable process for phenol remediation purposes.

4. Conclusion

This study reported the performance of a catalyst extracted from pier waste sludge in combination with PMS to remove phenol from petrochemical wastewater. In this study, the effects of parameters of pH (3-9), catalyst dose (0-100 mg/L), PMS concentration (0-250 mg/L), and initial phenol concentration (50-50 mg/L) on phenol decontamination were tested. According to the results in low phenol concentrations (50 mg/L), catalyst dose of 80 mg/L , and PMS concentration of 150 mg/L , the highest phenol removal efficiency from real wastewater (94%) was achieved after 150 min. The highest rate of phenol degradation was obtained in the initial concentration of 50 mg/L at the rate of 0.0144 min^{-1} . The correlation coefficient (R^2) for all concentrations was >0.94 , which indicates that in the studied system, the data obey the first-order kinetics. After the fifth cycle. The catalyst stability was reduced to less than 50%. According to the results, the energy consumption in the pier waste sludge catalyst/PMS system for

phenol removal was 77.69 kw.h/m³. Therefore, the pier waste sludge catalyst/PMS system is an excellent strategy to remove phenol from real wastewater.

Declarations

Author contribution

F. Khoshtinat: Formal analysis, Methodology, Writing- original draft. **T. Tabatabaie:** Supervision, Methodology. **B. Ramavandi:** Supervision, Conceptualization, Writing- review& editing. **S. Hashemi:** Conceptualization.

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Availability of data and materials

The datasets used in this study are available from the corresponding author on reasonable request.

Declarations

Ethical approval not applicable.

Ethics approval and consent to participate

Not applicable

Consent to publish

All authors declare they have given consent to publish this article.

Competing interests

The authors declare no competing interests.

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Figures

Figure 1

Figure 2

Effect of wastewater pH ([Phenol]: 100 mg/L; [PMS]: 100 mg/L; [Catalyst]: 30 mg/L).

Figure 3

Effect of catalyst mass (pH: 3; [PMS]: 100 mg/L; [Phenol]: 100 mg/L).

Figure 4

Effect of phenol concentration (pH: 3; [PMS]: 100 mg/L; [Catalyst]: 80 mg/L).

Figure 5

Effect of PMS dose (pH: 3; [Phenol]: 100 mg/L; [Catalyst]: 80 mg/L).

Figure 6

First-order kinetics for phenol degradation in the pier waste sludge catalyst/PMS system (pH: 3; [Catalyst]: 80 mg/L; [PMS]: 150 mg/L).

Figure 7

Reuse the catalyst to remove phenol from the petrochemical wastewater (pH: 3; [Catalyst]: 80 mg/L; [Phenol]: 50 mg/L; [PMS]: 150 mg/L; [Reaction time]: 150 min).

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