Photocatalytic removal of o-chlorophenol by Using a Mixture of Modified Fly Ash and TiO2 Nanoparticles

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Abstract

Background: Photocatalytic process is used as a suitable method for o-chlorophenol removal. In this study, the efficiency of a mixture of modified fly ash and TiO2 nanoparticles in photocatalytic removal of o-chlorophenol was evaluated.

Methods: After acid washing of fly ash, the absorbent was oxidized with potassium permanganate. Then, the substrate mixture of modified fly ash and TiO2 nanoparticles was used for photocatalytic decomposition of o-chlorophenol.

Results: The percentage of carbon increased from 77.94% to 86.52% after acid washing of fly ash and absorption efficiency increased from 58.8% up to 83.3%. During the oxidation of acid washed fly ash, absorption efficiency reached to 93.27%. Photocatalytic removal efficiency of o-chlorophenol by mixture of modified fly ash and TiO2 increased to 98.9%. Photocatalytic removal efficiency of o-chlorophenol by TiO2/UV and without use of fly ash was 78.7%.

Conclusion: Industrial application of this method recommended because of the simple modification, high efficiency removal and prevention of environment pollution.

Introduction

Chlorinated phenol derivatives are the most common organic pollutants (1) accumulated in water and soil due to the stability of the carbon-halogen bond (2, 3).The major sources of phenolic compounds are waste water of petrochemical refinery, herbicides and pesticides production industries, coal conversion and textile, pharmaceutical, paint and steel mills industries(4). Conventional techniques for phenolic compounds removal are catalytic and photocatalytic degradation, biodegradation, coagulation and flocculation, solvent extraction, wet air oxidation, reverse osmosis, resins and absorption (5-8). Ortho-chlorophenol (o-CP) is one of the most important 19 chlorophenol derivatives (9). This pollutant has become a major environmental concern due to its high toxicity and low environmental degradation. The maximum permitted concentration of o-CP in drinking water is 10μg/L (10). o-CP is in the high priority pollutants category and is highly soluble in aquatic environment (11). Advanced

oxidation process, as a green technology, has the advantage of removing contaminants from the environment and converting them to other organic compounds and finally into harmless inorganic species such as CO_2 and H_2O (12). Some researchers have proposed to use a primary absorber, as Photocatalyst substrate, in order to improve the efficiency of Photocatalyst system (13).Wasu et al (2013) reported that increase in absorption capacity can improve Photocatalytic activity (14). So that, mixture of an adsorbent with high adsorption efficiency and a catalyst can improve the removal efficiency in the presence of UV light (15). Burning coal produces several wastes that fly ash comprises 70 to 75 % of that (16). Fly ash is classified in industrial waste category and due to the presence of high levels of unburned carbon particles, fly ash is a potential alternative to activated carbon (17, 18). In most cases, just a small amount of fly ash is being recycled (approximately 20% to 30%) and 70-80% of the residual is eliminated through Landfill (19). Fly ash properties depend on several factors such as how fuel is converted to ash, the burning method, fuel chemical composition, temperature and time in combustion zone, the volume and pressure of entering air to furnace during burning and deposition of it (20). Malakootian et al., conducted several researches on removal of phenol derivatives from aqueous solutions and used Fly ash to remove organic compounds such as colors, surfactants, phenols and heavy metals from aqueous(21-28). Fly ash has also been used for absorption of NOx, SOx, mercury and organic compounds in air (8, 29). In some studies, the absorption method of fly ash (17) and also photocatalytic decomposition of UV/TiO2 are used for o-chlorophenols removal (12). But, the efficiency of mixture of modified fly ash and TiO2 was not investigated in o-CP removal. Zarand dual fuel power plants (coal and mazut) located in the northwest of Kerman, produce large amounts of fly ash at sites around the power plants. In the present study, the fly ash was activated with sulfuric acid in order to provide an adequate absorptive capacity and then was oxidized with potassium permanganate. Then, the mixture substrate of modified fly ash

and TiO2 was used to enhance the efficiency of o-CP photocatalytic removal. Finally, the efficiency of this substrate was investigated in the removal of o-CP in real samples.

Materials and Methods

This experimental study was conducted in a laboratory-scale and simultaneous on synthetic and real samples from September 2013 to March 2014 at the Environmental Health Engineering Research Center, Kerman University of Medical Sciences, Kerman, Iran. Raw fly ash was collected from the dust collector cyclone of Zarand power plant located in the northwest of Kerman. Since, 70% of the particles were in the range of 100 to 200 mesh, the particles at this scale were selected. Then, fly ash was washed with deionized distilled water at a ratio of 1:10 in order to remove impurities and solving water-soluble compounds. Finally, the washed fly ash (WFA) was obtained.

1. Optimizing the effective parameters on acid washing of fly ash

Over several consecutive stages, the effective parameters on acid washing of fly ash were investigated. So that at each stage, just the effect of one variable, while keeping other factors constant, was investigated. Thus, all parameters were optimized. Fly ash was acid washed through 4 steps of different concentrations of sulfuric acid (0.01, 0.1, 1, 1.8M), different ratios of acid to RFA (3: 1, 7: 1, 9: 1, 10: 1, 11: 1 and13: 1), different times (1, 3, 5, 9 and 10h) and different temperatures (room temperature (29),70, 85, 100 and120 ° C) and converted to acidified fly ash (AFA). Samples were washed with distilled water and then ethanol until neutral pH and were dried in oven at 105C ° to achieve a constant weight (30). All samples were oxidized with potassium permanganate under stable conditions (30min, 28 °C, concentration; 10mM and ratio of fly ash to oxidizers: 5) (31). Thus the modified fly ash (MFA) was obtained. Then the MFA was mixed with TiO2 nanoparticles at constant ratio of 3:1(15). Photocatalytic removal efficiency of 100cc of o-CP solution (50mg/L) with

MFA/TiO2 substrates was determined in the presence of UV light. UV Lamp was used as light source (30W and 338 mw / m2) and the maximum wave length was 360nm. The light source was placed 20 cm higher than the sample surface. All parts of system were wrapped in aluminum foil to avoid light reflection. Chlorophenol absorption efficiency was also determined by acid washed fly ash, as absorbent, in order to assess the ability of fly ash which is activated by acid.

2. Optimization of the effective parameters on oxidation of acid washed fly ash

Effective factors on the oxidation process were optimized after determining the optimum values of effective factors on acid washed fly ash. AFA was oxidized in 4 steps:

1) Different concentrations of potassium permanganate as oxidizer (0.2, 0.5, 1, 5, 10, 50 and 70mM)

2) Different ratios of oxidizer to AFA (3: 1, 5: 1, 8: 1, 11: 1 and 13: 1)

3) Different oxidizing temperatures (room temperature (28± 2), 50, 70 and 80°C)

4) Different oxidizing times (0.5, 1, 2 and 3 hours).

To avoid precipitation of potassium permanganate on fly ash, after oxidation, it was separated from oxidizer solution by high-speed centrifuge (3500rpm). Then, it was washed by distilled water on stirrer at high speed (1500 rpm) for 4 hours. At the end, MFA and TiO2 nanoparticles with the ratio of 3:1were used for removing o-CP in the presence of UV light. o-CP absorption efficiency was also determined by final modified fly ash, as absorbent, to evaluate the adsorption efficiency of o-CP by oxidation process of fly ash.

3. Determining the optimum ratio of MFA to TiO2 nanoparticles

MFA was mixed at varying proportions with TiO2 (0: 4, 3: 1, 1.5: 2.5, 2: 2, 2.5:1.5, 1:3, 4: 0) and photocatalytic removal efficiency of o-CP was measured at the presence of UV light.

Photocatalytic tests

100 ml solution of o-CP was contacted with varied pHs (2, 3, 5, 7, 9 and11) and 0.5 g mixed substrate of MFA/TiO2 at room temperature ($2 \pm 29°C$) to evaluate the effect of pH on removal efficiency. The removal efficiency of o-CP in different doses of mixed substrate (from 0.2 to 1g) and different initial concentrations of o-CP (from 20 to 250 mg/L) was determined. Then absorption kinetics and removal efficiency of real waste water produced in Zarand coal washing plant (located in Kerman) was measured. TiO2, H2SO4, KMnO4, HCL, NaOH and o-CP were prepared from Merck Company. The remaining amount of o-CP was read by a spectrophotometer (model UV-1800 SHIMADZU) at wave length of 274nm. Data analysis was performed by using SPSS software version 20.

Result and Discussion

At the beginning, the EC of washing solution of fly ash was 0.0023 μs/ cm and after 48 hours washing, it increased to 0.00407 μs/ cm. At initiation of the experiment, TDS of washing solution was 0.08g/L and after 48 hours washing, it increased to 1.71g/L. This indicates the dissolution of water-soluble compounds in fly ash. The pH of washing solution at the beginning and end of washing for 48hours, showed no change and its value was equal to 2.6. SEM images of the WFA, AFA and MFA have been shown in Figures 1, 2 and 3, respectively.
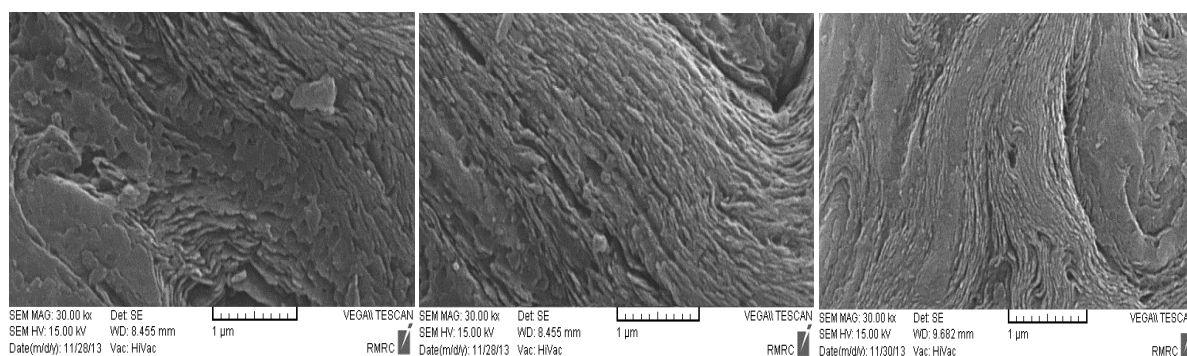
Figure 3. MFA SEM image   Figure 2. AFA SEM image   Figure 1. WFA SEM image

Comparison of Figures 1, 2 and 3 shows that the porosity of modified fly ash surface (MFA) has increased, in comparison with WFA and available veins are larger. Tahir et al in Pakistan reported improvement in color removal efficiency due to the formation of the new modified surface and surface area increase of absorption in fly ash after washing with sulfuric acid and formaldehyde (32). Zhang et al in China performed a study to confirm improvement of the physicochemical properties of AFA in comparison with RFA (30). The results of the present study are compatible with the results of the mentioned studies.

Weight percent of elements and compounds in WFA, AFA and mixture of MFA / TiO2 samples have been given in Table 1.

Table 1. Weight percent of elements and compounds in washed fly ash (WFA) samples, acidified fly ash (AFA) and mixture of modified fly ash with titanium dioxide (MFA / TiO2)

Adsorbent type	CO2	SO3	V2O5	Fe2O3	TiO2	Carbon	Sulfur	Oxygen	Iron	Vanadium	Titanium
MFA/TiO2	91.9	6.22	1.2	0.61	0	77.94	7.73	10.91	1.32	2.09	0
WFA	94.92	5.08	0	0	0	86.52	6.8	6.68	0	0	0
AFA	73.34	6.15	0	0	20.51	44.15	5.43	18.14	0	0	27.12

Weight percent of carbon increased after acid activation process and vanadium (V) was also removed from fly ash. Increase of the percentage of carbon after FA acid washing, confirmed the improvement of the absorption capacity of absorbent. The results of Vanadium removal, after FA acid washing, is compatible with the results of a study in Japan during 2010 and 2011 by Kashiwakura et al. that have reported successful removal of dangerous substances such as arsenic and selenium from FA during the acid washing process (33, 34).

The effect of acid washing of fly ash on o-CP absorption efficiency by MFA / TiO2

Changes of photocatalytic removal efficiency of o-CP by mixture substrate of MFA/TiO2 with changing effective factors on acid washing of fly ash (concentrations of acid, ratios of fly ash to acid, times and temperatures of acid washing) have been presented in Figures 4, 5, 6 and 7 respectively.
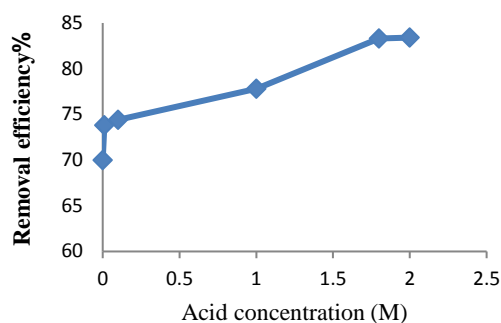
Figure 4. photocatalytic removal efficiency of o-CP by MFA/TiO2 based on acid concentration

While the fly ash was oxidized directly and without acid washing, the efficiency of photocatalytic decomposition of o-CP with MFA/TiO2 substrate was %70. On the other hand, the efficiency of the photocatalytic decomposition of o-CP by MFA / TiO2 substrate increased from 73.8% to respectively 83.29% and 83.4% by increasing the acid concentration from 0.01 to 1.8 and 2 molar. Therefore, 1.8M was chosen as optimum acid concentration in fly ash acid washing process. Statistically, o-CP removal efficiency had a significant relationship with acid concentration (P= 0.002).
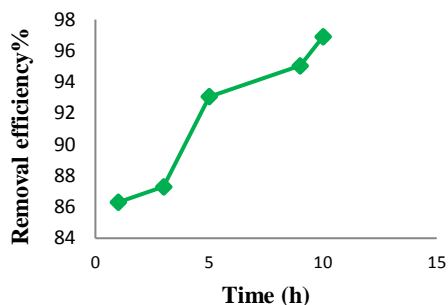

Figure 5. photocatalytic removal efficiency of o-CP by MFA / TiO2 based on the ratio of acid solution to RFA in acid washing process

At first, by increasing the ratio of acid to RFA up to 7, the photocatalytic decomposition efficiency of o-CP with MFA/TiO2 substrate increased and then remained stable. Therefore, the ratio = 7 were chosen as the optimum ratio. There was no significant relationship between o-CP removal efficiency and the ratio of acid to fly ash (P= 0.071).

Figure 7. Photocatalytic removal efficiency of o-CP by MFA/TiO2 based on different temperatures of fly ash acid washing

Figure 6. Photocatalytic removal efficiency of o-CP by MFA/TiO2 based on different acid washing times

Increasing the time and temperature of fly ash acid washing caused improvement of photocatalytic removal efficiency of o-CP by MFA/TiO2 substrate. But, there was no significant difference in removal efficiencies. Therefore, 5 hours and 28 °C (room temperature) were chosen as the optimal values (Figures 6 and 7).
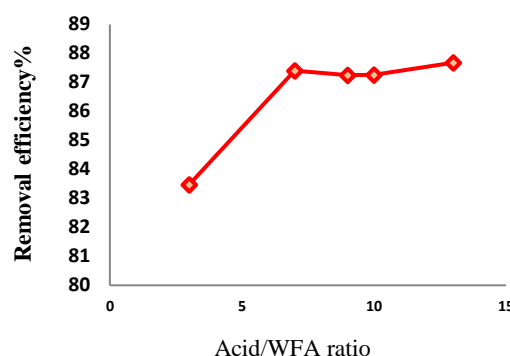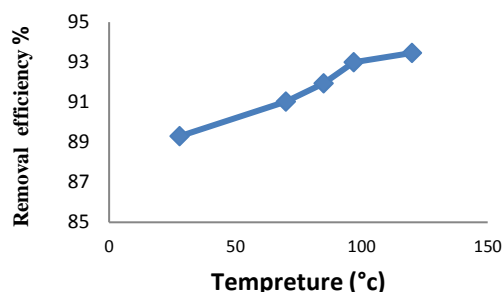
O-CP removal by adsorption process on acid activated fly ash

Activated fly ash by acid was used as an adsorbent for o-CP removal and the removal efficiency was equal to 83.3%.

Increase of acid concentration, temperature and time in the process of fly ash acid washing, due to increasing dissolution of fly ash impurities, porosity and surface area of the

absorbent, is resulted in the improvement of absorption efficiency (29, 35). The obtained results correspond with Wang et al report in Australia (36). Panitchakarn et al in Pakistan observed that the purity percentage of fly ash initially increased with increasing acid concentration, but finally acid concentration did not have any effect on purification of adsorbent. Also the ratio of acid to fly ash has no significant effect on fly ash purification. The researchers observed that with increasing time and temperature of fly ash acid washing, the percentage of absorbent impurities decreased and this situation eventually led to the increase of absorption capacity (37). As it is seen, the results of the mentioned study are compatible with the findings of the present study.

The role of Fly ash oxidation in photocatalytic removal efficiency of o-CP by MFA / TiO2

Changes of photocatalytic removal efficiency of o-CP by MFA/TiO2 with changing the effective factors on oxidation of fly ash (ratio of oxidant to fly ash, oxidant concentration, temperature and time of fly ash oxidation) have been presented in Figures 8, 9, 10 and 11 respectively.
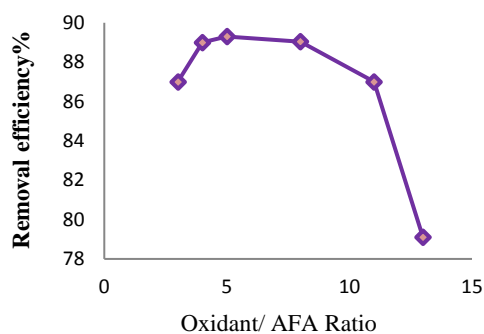

Figure 8. Photocatalytic removal efficiency of o-CP by MFA/TiO2 based on different ratios of oxidant to AFA in fly ash oxidation process

With increasing the ratio of oxidants to the AFA, the photocatalytic removal efficiency of o-CP by MFA/TiO2 decreased. Thus the ratio of 4:1 for oxidants to AFA was selected. Removal efficiency of o-CP by AFA/TiO2 was less (88.3%) than that of MFA/TiO2.
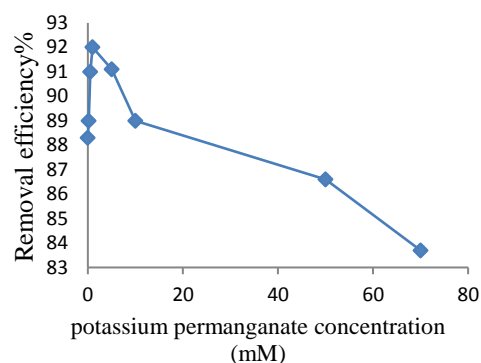

Figure 9. photocatalytic removal efficiency of o-CP by mixture of MFA/TiO2 based on different oxidant concentration in fly ash oxidation process

Increase of oxidants concentrations in modification of fly ash reduced o-CP removal efficiency and the best removal efficiency was achieved when potassium permanganate concentration was 0.5 mM. Statistically, there was a significant relationship between potassium permanganate concentration and removal efficiency (P =0.004).
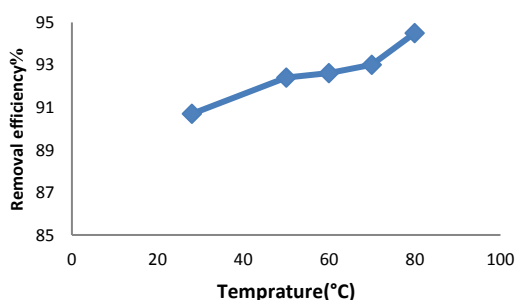
Figure 11. Photocatalytic removal efficiency of o-CP by MFA/TiO2 based on different temperatures of fly ash oxidation

Figure 10. Photocatalytic removal efficiency of o-CP by MFA / TiO2 based on different oxidation times

of UV light and the maximum removal efficiency was related to the substrate that was oxidized at 80° C for 1 hour.

O-CP adsorption by modified fly ash

The absorbent of final modified fly ash was used alone for o-CP removal and the removal efficiency was 93.27%.

Improvement of the absorption efficiency in oxidized absorbent is due to carbon oxidation of fly ash by MnO4-. So that adsorption ability of oxidized carbon is higher than that of the raw carbon. Also, the observed absorption increase in oxidized absorbent is due to the presence of C = O double bonds in oxidized fly ash and the π-π absorption interaction between absorbent and pollutants (38). Jeon et al, in North Ko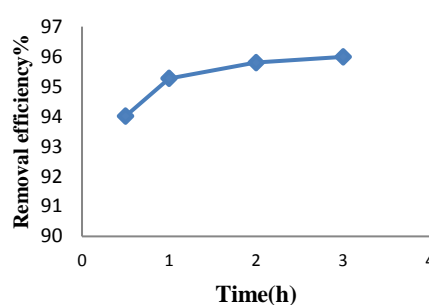rea, reported that the oxidation process of acid alginate to acid arginate carboxyl by potassium permanganate leads to the increase of Carboxyl groups in oxidized samples compared to non-oxides samples; it means the carbon type is changed (39) which is compatible with the present results. The observed reduction in absorption efficiency with increasing the oxidizer concentration is due to the deposition of potassium permanganate on surface of the adsorbent, so that the absorption capability decreased by filling empty spaces and porosity reduction on fly ash surface.

Optimum ratio of MFA to TiO2:

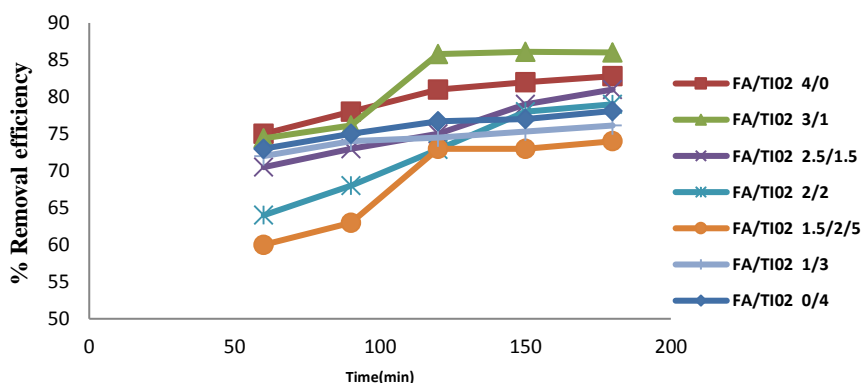O-CP removal efficiency at different ratios of MFA:TiO2 has been presented in Figure 12.

Figure 12. Photocatalytic removal efficiency of o-CP by changing the ratio of MFA to TiO2 (Room temperature, catalyst dose = 0.3g, o-CP concentration= 50mg / L)

MFA and TiO2, each in isolation, had a lower efficiency than MFA/TiO2 mixture and the best efficiency was in the ratio of 3:1 of MFA/TiO2.The Photocatalytic processes are chemical reactions that occur on the Photocatalyst surface. The reaction rate depends on the contact surface of catalyst and light. The rate of reaction will increase in the case of analyte distribution over a greater surface area (40,41). Obviously, in the first phase, when the absorption process occurs, the photocatalytic process is more efficient because pollutant is very close to Photocatalyst. This occurs when TiO2 is placed in fly ash (fly ash acts as an absorber). In other words, the efficiency changes depending on the type of fly ash and also the type of reform process (42). In the present study, reform process of fly ash led to the improvement of the absorption efficiency of fly ash. This action increased the efficiency of photocatalytic process. It is expected that TiO2 compounds located on fly ash surface have similar function to their hosts. During this process, both substrates are loaded with pollutant and adsorption process occurs before photocatalytic process (43). During o-CP photocatalytic removal, the adverse produced compounds are eliminated by photocatalytic decomposition (12). Visa et al have suggested

that TiO2/MFA mixed substrate can be used as a valid option to remove contaminants. Also, removal efficiency at the presence of UV light is more than absorption process in the absence of light (15). The mechanism of catalysis by mixture of TiO2/MFA consists three phases: pollutant absorption on surface of TiO2 /FA, optical dispersion of pollutant on the surface and the final product desorption from the surface of TiO2. The results showed that pollutant is absorbed on the fly ash, selectively when fly ash is loaded with TiO2 and leads to more pollution in TiO2 surrounding. Then the absorbed pollutant by diffusion process will transfer to catalyst and decomposition will happen (44). An analyte desorption from the substrate surface by methanol organic solvents and then measuring the concentration of o-CP confirmed that Photocatalytic reaction leads to loss o-CP completely and convert to an eco-friendly species.

Effect of pH and mixed substrate dose on o-CP removal efficiency:

The photocatalyst removal efficiency of o-CP by MFA/TiO2 based on pH and substrate dose is given in Figures 13 and 14.
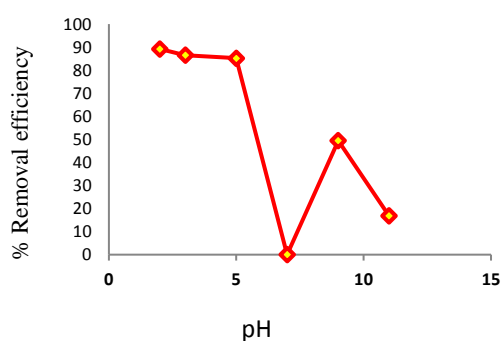

Figure 14. o-CP photocatalytic removal efficiency based on substrate doses

Figure 13. o-CP photocatalytic removal efficiency based on pHs

Removal efficiency increased by decreasing the PH, so that the maximum removal efficiency was observed at pH = 2. The presence of H+ ion at acidic pH leads to the formation of H0 radicals. Also, HO20 radicals that are formed from

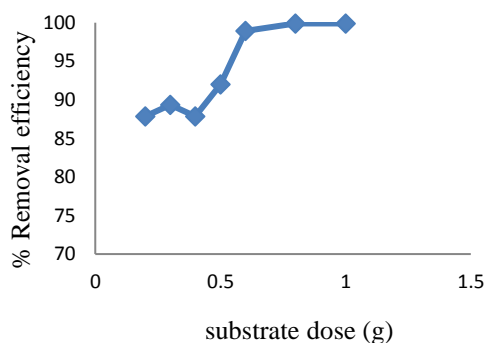dissolved oxygen are finally converted to OH0 radicals and the efficiency will increase consequently. At alkaline environment the available o-CP is as an anion that is more reactive and reacts with available radicals easily. For this

reason, o-CP degradation at alkaline environments is more than that in neutral environment. However, excessive increase of hydroxyl concentration could be a hindrance for light penetration to TiO2 surface. In addition, high pH creates a favorable context to form carbonate ions that are the effective absorbents of OH-ions and can reduce the decomposition speed. The results of this study are consistent with the results of the study conducted by(45).

Mixed substrate dose of 0.6g was selected as the optimal dose of mixed substrate. Statistically, there is a significant correlation between substrate dose and removal efficiency (P =0.0023). Efficiency reduction following substrate dose increase is due to the increase of the solution turbidity, reduction of light penetration rate and increase of the pass way by optical photons (46).

Effect of irradiation Time

Increase of the irradiation time motivated catalyst particles increase too. This led to the increase of the number of OH radicals and positive holes and consequently the efficiency of the Photocatalytic process increased. The obtained findings are consistent with the results that have been previously reported by Shirzad Siboni et al and Parasta et al (47, 48).

Comparison of R2 at first and second order kinetics of o-CP removal by MFA/TiO2 showed that removal process follows the second order kinetics and also the constant reaction rate was equal to 0.178. Decreasing the initial concentration of O-CP and increasing time leads to the increase of removal efficiency. With increasing initial

concentrations of pollutants, due to sticking to the surface of the solid catalyst, the overall surface of excitation was reduced. Also, production of intermediate products which are more reactive than the primary pollutants, generates a competition in reaction with the radicals and leads to the reduction of the removal efficiency (45, 46).

Conclusion

Cost-effective modification process carried out on the fly ash improves the adsorption efficiency. This increases the efficiency of photocatalytic process. So that, we can reach to a suitable substrate for waste water treatment in the industrial scale and MFA/TiO2 has a higher efficiency than MFA and TiO2/UV in isolation. This mixed substrate can be resulted in photocatalytic removal efficiency of 88.4% in the real waste water. Due to the cost-effectiveness and availability of fly ash and simple modification process, this method is recommended and can be applied extensively.

Acknowledgement

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