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Evaluation of removal efficiency of 2-chlorophenol in aquatic environments by modified fly ash

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Abstract
Background: Chlorophenols are classified as priority toxic pollutants. These acidic organic compounds present a serious potential hazard for human health and aquatic life. Chlorophenols accumulate in water, soil and air due to high stability, and impart an unpleasant taste and odor to drinking water and can exert negative effects on different biological processes. Among the different methods of removal, adsorption process by low price adsorbents, such as fly ash (FA) is common. Therefore, in this study, the effects of oxidation of FA as modified adsorbent were investigated when the adsorption of 2-chlorophenol (2-CP) was increased.
Methods: This experimental study was conducted from March to September of 2013. FA obtained from Zarand power plant (located in Kerman province) was oxidized with potassium permanganate. Effective factors on the oxidation of FA, such as temperature, oxidation time and concentrations of oxidizers were optimized. Raw sewage of Zarand coal washing plant was tested under optimal conditions. All tests were carried out according to the standard methods book for the examination of water and wastewater.
Results: Optimal condition for the preparation of oxidized FA was obtained at 70°C, 1 hour, and 1 mM of potassium permanganate concentration. The absorber obtained was able to remove 96.22% of 2-CP under optimized conditions (pH=3, 2 hours, adsorbent dose 0.8 g and room temperature). The removal efficiency of the real wastewater under optimal conditions was 82.1%.
Conclusion: Oxidized FA can be used for the removal of this pollutant from industry wastewater due to its high efficiency of removal in real wastewater, it is easy and inexpensive to prepare and could modify the sorbent.
Keywords: Chlorophenol, Adsorption process, Modified adsorbent.
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Introduction

The presence of chlorophenol in the environment is one major environmental concern due to its potential toxicity, carcinogenicity, mutagenicity, poor biodegradation, high stability and widespread pollution (1,2). Chlorophenol has 19 derivatives. The Environmental Protection Agency (EPA) classified 9 compositions of chlorophenol in priority categories. One of the most important is the 2-chlorophenol (2-CP) (3,4). Short-term exposure with high amount of 2-CP in laboratory animals leads to increasing respiratory rate, weakness, tremors, seizures, coma and finally death (5). The maximum allowable concentration of 2-CP in drinking water is 10 µg/L (6). This contaminant has high solubility in aquatic environment (7). This combination has been reported usually in petrochemical wastewater refineries, leather and textile industries, steel plants, manufacturing of pharmaceuticals, plastic, paint, paper industry, pesticides, herbicides and wood preservative (8-10). Commonly used techniques for the removal of phenol and its derivatives are catalytic and photocatalytic decompositions, electrochemical conversion, coagulation, flocculation, resins, microbial decomposition and adsorption (11-14). Recycling of waste materials as an economical solution to the purification of aquatic environment, in addition to environmental pollution control, is consistent with the policy of recycling waste materials management at its source . The application of low cost and the easy availability of materials in wastewater treatment have recently attracted great interest (15). Several studies have been performed using industrial waste materials, such as fly ash

(FA), to absorb NO_x, SO_x, organic compounds and mercury in air, heavy metals, color and organic compounds in water (14,16). FA, obtained from fossil fuels, can be considered as an alternative to activated carbon, due to the presence of high amount of unburned carbon particles (3,14,17). FA is a by-product of coal burning power plants, its characteristics are dependent on several factors, such as the method of burning coal, type of burn, fuel composition, combustion zone temperature, time of residence particle in the combustion zone, etc (18-22). Several studies have been carried out to enhance adsorption capacity, in which FA was modified and activated. Luo et al (23) in China, used absorbent oxidation with potassium permanganate to increase the efficiency of adsorption. In this study, the oxidation effect of FA on 2-CP adsorption efficiency in aquatic environments was investigated in order to increase the adsorption capacity of the absorbent.

Methods

This experimental study was conducted in the laboratory from March to September of 2013 at the Environmental Health Engineering Research Center of Kerman University of Medical Sciences. Raw FA of Zarand thermal power plant was obtained from cyclone dust collector. In total, 100 to 200 mesh particles were selected. Sieved FA was washed for 48 hours, using a distilled water to FA ratio equal to 10, in order to remove impurities and dissolution of metal oxides in water. Electro-conductivity (EC), pH and total dissolved solids (TDS) of the solution were measured before and after washing (24). The washed FA (WFA) was dried in an oven at 105°C to attain a constant weight (by trial and error method). Thereafter, FA was oxidized with potassium permanganate (PC) oxidizers to improve the efficiency of adsorption (23) and thus, oxidized FA (OFA) was obtained. So at first, the oxidizer solution was prepared with the desired concentration using potassium permanganate powder. The solution pH was adjusted in acidic range using sulfuric acid (Purity of acid: 98% and molarity =1) to increase the power of the oxidation.

Preparation of OFA

Optimal amounts of the effective factors (oxidizers concentration, time and temperature of oxidation) on absorbent oxidation were then determined:

1. Determination of PC concentration: To determine the optimal concentration of oxidizers, FA was oxidized at different concentrations (0, 0.5, 1, 5, 10, 30 mM) with potassium permanganate. This process was performed at room temperature for 30 minutes. Then, the adsorption efficiency of 2-CP (at concentration 50 mg/L) was determined at room temperature, contact time: 1.5 hours with 0.5 g of OFA obtained at different PC concentrations. The optimum PC concentration was selected by comparing the results.

2. Determination of temperatures of oxidation: In order to determine the optimal temperature of modification, FA was oxidized at different temperatures (room temperature (28 ± 2), 50, 60, 70 and 80°C). This process was performed for 30 minutes at the optimal concentration of oxidizers. The temperature was set at the desired range using paraffin bath. Thereafter, the optimum temperature was selected by comparing the 2-CP removal efficiency with OFA obtained at different temperatures.

3. Determination of time of oxidation: FA was oxidized at different times (0.5, 1, 2 and 3 hours). This experiment was set at the optimum temperature and concentration of oxidizers. The removal efficiency of 2-CP was then determined with OFA obtained at different times.

At all stages of this experiment, to separate the OFA from the oxidizers solution, the samples were centrifuged for 10 minutes at 3500 rpm. The OFA was then washed with distilled water on high speed stirrer for 4 hours and filtered using 0.45 micron filter. The samples were dried in an oven at 105°C to attain a constant weight. The scanning electron microscope (SEM) of the adsorbents was prepared before and after modification.

Sorption studies

The effective factors on adsorption process were optimized after optimization of all effective parameters on FA oxidation.

In order to investigate the effect of pH on absorption, 100 mL of 2-CP solution with different pH (2-1) at room temperature $(2 \pm 29°C)$ was added to 0.5 g of OFA. The pH was adjusted using 0.1 molar NaOH and HCl.

Different doses of OFA (from 0.3 to 1 g) with 100 mL of 2-CP solution (50 mg/L) were added at different times (for 30 to 180 minutes) in order to evaluate the effect of two factors (adsorbent dose and contact time) on the removal efficiency of 2-CP.

2-CP with different concentrations ranging from 20 to 250 mg/L were placed in contact with OFA at optimal conditions and pseudo-first order and pseudo-second order kinetic equations were tested, Freundlich and Langmuir isotherms were investigated also to adsorption of 2-CP on OFA (25, 26).

Wastewater from Zarand coal washing plant located adjacent to the power plant was sampled and transported to the laboratory under standard conditions. After determining the physico-chemical quality of real raw sewage, the 2-CP removal efficiency was determined by OFA under optimal conditions.

To determine the reusability of the adsorbent, the used FA in 2-CP removal was separated from the reaction solution and dried after washing with distilled water. Finally, the 2-CP removal efficiency was determined again.

The adsorption solution was exposed to the environment for 24 hours and then the concentration of 2-CP was measured to determine the desorption of contaminants from the surface of the absorber.

In order to obtain accurate results, all experiments were

repeated three times. The determination of 2-CP was done spectrophotometrically on a spectrophotometer UV-1800 SHIMADZU model at wavelength of 274 nm. All tests were conducted at the same time with distilled water and with a synthetic sample containing 2-CP in order to avoid interference of adsorption of residual permanganate on the adsorbent surface. Afterwards, the test solution with distilled water was placed in a spectrophotometer as a blank sample. Stirrer speed of 3001 Heidolph MR Model in adsorption process tests was set at 400 rpm. The required chemical substances were produced by Merck Company. Statistical analysis was done using SPSS version 19.

Results

The EC and TDS of FA solution increased after and before being washed for 48 hours. As EC and TDS increased from 2.3 to 4.07 (ms/cm) and 0.08 to 1.71 g/L, respectively. But, pH was fixed and equal to 6.2 after washing for 48 hours. The SEM images of the absorber before and after oxidation are shown in Figure 1.
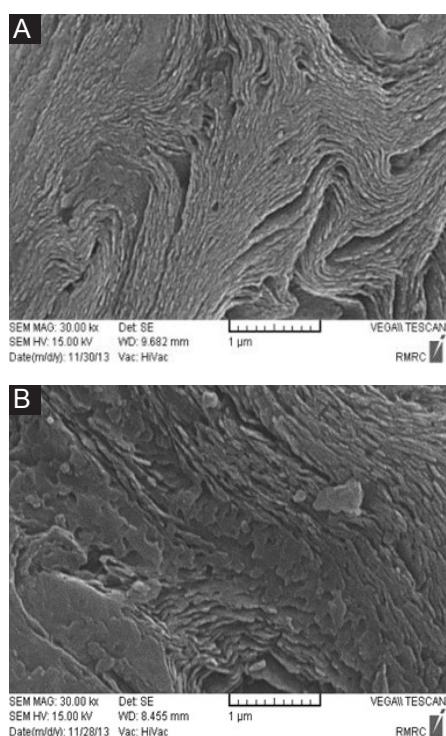
Figure 1 confirms an increase in porosity of the adsorbent surface after oxidation process. As shown in the figure, streaks surface was more open and the surface uniformity of the FA was reduced after oxidation. This effect was intensified by increasing the time. The weight percent of elements and compounds in WFA and OFA samples is shown in Table 1.

Oxidizers concentration

Figure 2 shows changes in 2-CP removal efficiency by changing the PC concentration in the absorber oxidation process.

When PC concentration is zero (WFA), 2-CP adsorption efficiency is less (67.3%) than the situation that absorber is oxide (OFA). But the removal efficiency decreased by increasing the concentration of the oxidizers. The highest adsorption efficiency obtained at lower PC concentration (1 mM) was 81.9%.

Effect of oxidation temperature

The effect of changes in oxidation temperature of FA on removal efficiency is shown in in Figure 3.

Increasing the temperature of FA oxidation (from 28 to 80°C) resulted in increased 2-CP removal efficiency (from 81.9 to 89.5%). Hence, 80°C was selected as optimum oxidation temperature of FA.

Oxidation time of FA

The effect of oxidation time on removal efficiency is shown in Figure 4.

As the time of absorber oxidation increases, the removal efficiency increased as well. But there was no significant difference in adsorption efficiency of OFA obtained at different times. Therefore, 1 hour was selected as the optimal time by considering the appropriate efficiency.
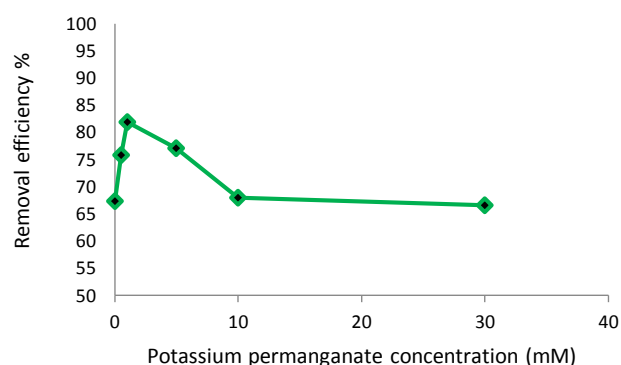

Figure 1. SEM image of a sample fly ash (FA) . (A) Raw FA, (B) oxidized FA.

Figure 2. Effect of potassium permanganate concentration in the removal of 2-chlorophenol (2-CP).

Table 1. Weight percent of elements and compounds in WFA samples and OFA

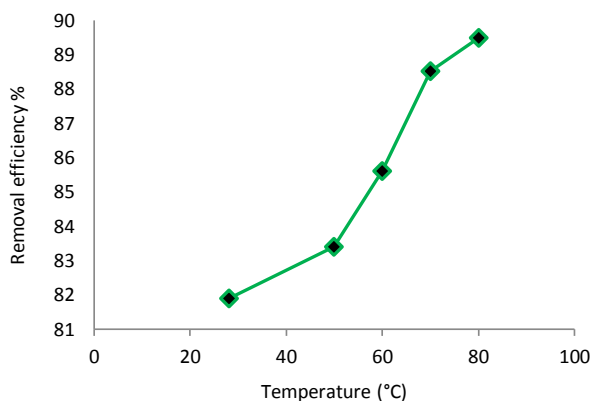| Present elements in samples (wt.-%)					Present compounds in samples (wt.-%)						
CO_2	SO_3	V_2O_5	Fe_2O_3	TiO_2	Carbon	Sulfur	Oxygen	Iron	Vanadium	Titanium	
91.97	6.22	1.2	0.61	0	77.94	7.73	10.91	1.32	2.09	0	WFA
94.92	5.08	0	0	0	86.52	6.8	6.68	0	0	0	AFA

Abbreviations: WFA, washed fly ash; OFA, oxidize fly ash.

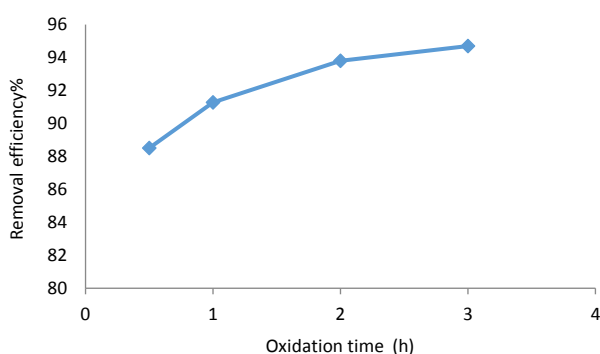**Figure 3.** Effect of oxidation temperature on the removal efficiency of 2-chlorophenol (2-CP).

Figure 5. Effect of pH on the removal efficiency of 2-chlorophenol (2-CP).

Figure 4. Effect of oxidation time on the removal efficiency of 2-chlorophenol (2-CP).
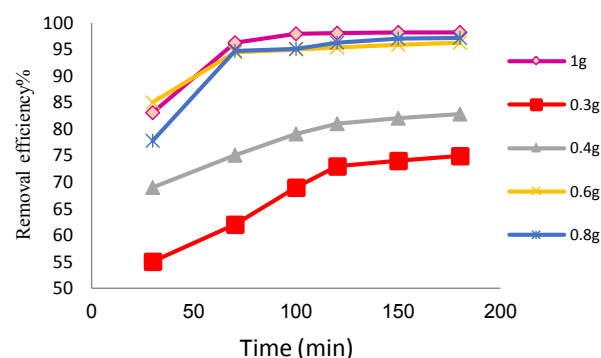
Figure 6. Effect of adsorbent dose and contact time on the removal efficiency of 2-chlorophenol (2-CP).

Effect of pH

In this study, the effect of pH is shown in Figure 5. pH reduction resulted in an increase in the removal efficiency, therefore, pH = 3 was obtained as the highest efficiency. The removal efficiency decreased greatly at neutral pH and increased again under alkaline conditions.

Effect of adsorbent dose and contact time

Changes in removal efficiency by the differing adsorbent dose and contact time are shown in Figure 6.
As the adsorbent dose and contact time increases, the removal efficiency and adsorption capacity increases as well. 0.8 g in 120 min was selected as optimum adsorbent dose.

Kinetics and isotherm of adsorption

An increase in the initial concentration of 2-CP resulted in an increase in the rate of adsorption and reduced the removal efficiency. Batch adsorption studies were conducted in varying concentration of 2-CP. The amount of sorption at time t, q_t (mg/g), was calculated using the following equation:

$$q_t = (C_0 - C_t) V/M \quad (1)$$

where C_0 is the initial concentration of 2-CP, C_t is the concentration at a given time t, V is the volume of the 2-CP solution in L and M is the weight of the activated carbon
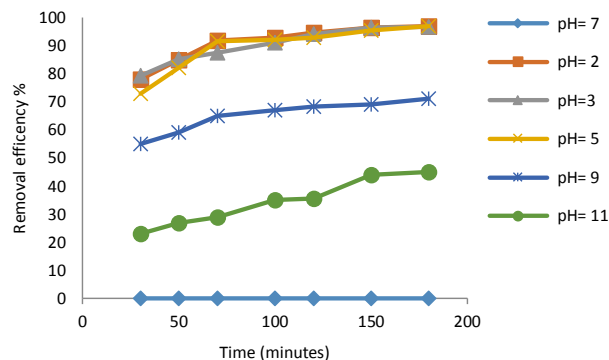
in g. For the prediction of isotherm parameter, the Freundlich and Langmuir isotherms were used. The Freundlich isotherm was used based on the assumption that the sorption process is involved in a heterogeneous layer. The non-linear form of the Freundlich equation is as follows:

$$q_e = K_F C_e^{1/nF} \quad (2)$$

The linearized form of the Freundlich equation:

$$\log q_e = \log(K_F) + 1/nF \log(Ce) \quad (3)$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg/ g), C_e represents an equilibrium concentration of the adsorbate (mg/L), K_F is the Freundlich adsorption constant related to the adsorption capacity of the adsorbent ((mg/g) (L/mg)1/n) and 1/n is the adsorption intensity. The Langmuir isotherm assumes that adsorption proceeds in the homogeneous sites, which are involved in the intramolecular binding on the adsorbent surface and attains a specific site occupation. Thus, no extension of adsorption was found on the occupied site of the adsorbent material. This states that the adsorption process is a monolayer process (26). Table 2 shows the parameters of isotherm and kinetic equations in 2-CP adsorption by oxidized FA.

The Freundlich isotherm was found to be the best expositor for equilibrium conditions of 2-CP absorption. Based on the determination coefficient (R^2) and the comparison

Table 2. Isotherm and kinetics parameters for the adsorption of 2-CP (adsorption values are in mg/L)

Adsorption isotherms						Adsorption kinetics							
Freundlich			Langmuir-type 1			Second degree- type 1					First degree		
$1/n$	K_f (m/g)	R^2	q_m(m/g	K_a	R^2	$q_{e(exp)}$	$q_{e(cal)}$	*k	h	R^2	R^2	k_1	q_e
0.362	4.07	0.906	0.042	0.074	0.8	6.91	7.57	0.011	0.635	0.996	0.81	0.023	3.24

between calculated equilibrium adsorption ($q_{e(cal)}$) and the obtained equilibrium adsorption amount through testing ($q_{e(exp)}$), the 2-CP adsorption of oxidized FA was followed by second degree kinetics.

Recyclability of adsorption and desorption rate

Studies have shown that reusability of the adsorbent (OFA) is possible. The removal efficiency of 2-CP under optimal conditions during the two times of adsorbent recycling were 78.4% and 63%, respectively. By evaluating the desorption rate, it was shown that after 24 hours, there was no desorption through the absorbent by contaminant. The removal efficiency of 2-CP in the actual wastewater of Zarand coal washing (82.1%) was less than the synthetic samples (96.2%) due to the presence of available interference in the actual samples.

Discussion

The effect of absorbent oxidation

The increased EC and TDS after washing the raw FAs for 48 hours, indicates that the soluble metal oxides, in the presence of water absorbent, are soluble. The risk of leakage of dangerous metals from the absorbent to the aqueous solution reduced when these compounds were removed from the absorbent during the pickling process (27,28). The increasing removal efficiency of oxidized FA is induced by the oxidation of carbon present in the FA with MnO_4^-. During the oxidation process, this carbon is converted to other forms of carbon (C=O, C-OH, OH-C=O, C-O-C). Thus, the ability of oxidized carbon is higher than raw carbon. Also, the observed increase in oxidized adsorption could be attributed to the presence of C=O double bonds in the oxidized FA, and absorbing interactions between the absorbent and pollutants is always the π-π type (29). Jeon et al in North Korea reported that the oxidation process of alginate acid to alginate carboxyl acid by potassium permanganate leads to an increase in carboxyl groups in the oxidized sample rather than the non-oxidized samples, indicating that the carbon type was changed (30). These results are in line with the results obtained in the present study. The observed reduction in adsorption efficiency with increasing concentration could be attributed to the deposition of potassium permanganate oxidizer on the surface of the absorbent. The empty spaces were filled with the oxidizing agent and the adsorption capability was reduced by reducing porosity on the adsorbent surface. The increasing removal efficiency of the oxidized absorbent at high temperatures was due to the effect of heat on absorbent oxidation.

Effect of pH

At acidic pH, chlorophenols are neutralized, whereas the absorbent surface is surrounded by hydronium ion. This results in an increase in surface tension between chlorophenols and binding sites on the adsorbent surface (31). At alkaline pH (greater than pH_{ZPC}), along with increase in the percentage of ionized species, the number of negative charged sites on the adsorbent surface increased. Thus, adsorption will decrease due to electrostatic desorption between the negative surface of the absorbent and Chlorophenol anions (2,8,12,32). The result of this study is in line with the result obtained by Baker and Ghanem in Japan on the removal of 2-CP using natural Zeolites (33). The reduction of adsorption efficiency could be attributed to the weakening of the interaction forces between Chlorophenol and the adsorbent surface (34).

Effect of adsorbent dose

Increasing removal efficiency and adsorption capacity by increasing the amount of adsorbent, could be attributed to the availability of empty binding sites. Nadavala et al (13) in America using calcium alginate and chitosan beads and Bayramoglu et al (35) in Turkey, using yeast bio-absorbent, reported that as time and adsorbent dose increased, the adsorption capacity of 2-CP increased as well. Their obtained results are consistent with the findings of the present study.

Effect of 2-CP original concentration

The number of adsorbed component molecules increased, when the concentration of 2-CP in a fixed number of adsorption sites increased. The generated competition resulted in reduced efficiency and increased q_t. The initial concentration provides a large driving force to overcome the mass transfer resistance of monochlorophenol between solid and aqueous phases. Kamble et al (10) in India, using FA-modified zeolite by detergent; and Mangrulkar et al (12) in India, using MCM-41 observed that initial concentration increases resulted to a decrease in efficiency and increasing q_t. The results of this study are consistent with the mentioned studies.

Conclusion

The oxidation process removes impurities, increases porosity and results in an increase in adsorption efficiency. During oxidation process, the carbon present in the absorber is oxidized and converted to carbon species containing greater affinity interaction with the contaminants. Finally, the adsorption rate improves. In this study, an

adsorbent with high adsorption capacity to wastewater treatment of coal washing plant adjacent to the power plant was obtained using a sample and inexpensive modified method, which requires no transportation cost and sophisticated technology. In addition to environmental pollution control, reuse of waste FA is consistent with the policy of recycling at source and waste management discussion.

Ethical issue
The authors certify that all data collected during the study period are presented in this manuscript, and no datum from this study has been or will be published separately.

Competing interests
The authors declare that they have no competing interests.

Authors' contributions
All authors participated in the design of the study, performed the literature search and wrote the manuscript, data acquisition, analysis, and interpretation. All authors critically reviewed, refined, and approved the manuscript.

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