original article

Photocatalytic removal of cadmium (II) and lead (II) from simulated wastewater at continuous and batch system

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ABSTRACT

Aims: The aim of this study was to evaluate the photocatalytic processes for cadmium (Cd^{2+}) and lead (Pb^{2+}) removal at continuous and batch system.
Materials and Methods: This study was performed at laboratory scale. The reactors used in this study consisted of three parts: Ultraviolet (UV) source, reaction cell, and mixing chamber. The experiments were carried out in a batch and continuous reactor for synthetic wastewater. The concentration of Cd^{2+} and Pb^{2+} was constant (25 mg/L) in all experiments and effect of titanium dioxide (TiO_2) dose, pH, and air dispersion was investigated on the removal efficiency.
Results: The results showed that with increasing TiO_2 dose and pH, the cadmium and lead removal increase. The maximum removal of cadmium and lead was obtained in TiO_2 dose 0.9 g/L and pH: 11 that were equal to 99.8 and 99.2% respectively. Furthermore, when air dispersion increased, the removal efficiency increased; while in the air dispersion 2 cm^3/L the removal efficiency was maximum (88 and 93.2% at the contact time 56 min for Cd^{2+} and Pb^{2+}, respectively).
Conclusion: According to these results the TiO_2 has been considered as photocatalyst is the separable and recyclable, so UV/TiO_2 process is an environment friendly process for toxic metal removal.

Key words: Advanced oxidation, batch and continuous system, heavy metals, titanium dioxide nanoparticle

INTRODUCTION

Recent technologies released many heavy metals to the environment and are caused serious problems.[1] Water pollution can lead to changing of physical, chemical and biological quality.[2] The presence of copper, zinc, lead, iron, nickel, and others metals has a potentially damaging effect on human physiology and other biological systems when the tolerance levels are exceeded.[1-3] Concentrations of heavy metals below these limits even have potential for long-term contamination, because heavy metals are known to be accumulative within the biological systems.[4] Many industrial and metallurgy process such as, plating, photography, aviation industry, nuclear energy, and petrochemical facilities had been discharged heavy metals to the environment and lead to contamination of water sources.[5-9] Heavy metals as lead and cadmium are a serious threat for live organisms, due to mutagenesis carcinogenesis and accumulation properties,

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even at concentrations too low. In addition, heavy metals are resistant and non-biodegradable.[3,5,10-12] The heavy metals of major concern to human health are lead, copper, mercury, cadmium, arsenic, chromium as well as zinc.[13] Chromium oxidation states are Cr (III) and Cr (VI) that the toxicity of hexavalent form is 500 times more than the trivalent form.[14]

Many methods of treatment for industrial wastewater have been reported in the literature are including chemical precipitation and ion exchange,[5-6] electrolysis and membrane filtration,[8] solvent extraction, coagulation-flocculation[1,2] absorption and electrochemical processes.[10,15] Application of these methods is not appeal due to high costs, continuous input of chemicals; incomplete removal of certain metals, producing toxic sludge, and these processes needs the high degree of operation skill.[3,16,17]

Advanced oxidation process (AOP) is an alternative way of treating undesirable pollutants including dye stuffs. [18] The AOP divided in to two categories (heterogeneous and homogenous catalysis), heterogeneous catalysis has been successfully employed for the degradation of various families of hazardous materials.[19] Semiconductors used as a catalyst in AOP, in which TiO2 has been extensively investigated as a heterogeneous photocatalyst for the remediation of contaminated environment.[20] Photocatalysis is one of the potential techniques to either oxidize or reduce hazardous pollutants.[14] Because, TiO_2 and ZnO are insoluble in water, photostable, non-toxic, less expensive and higher photocatalytic efficiency, they were selected as the photocatalyst for studies. TiO_2 have unique photocatalytic activity at an excellent choice of photo catalysis application.[21]

Basis of TiO_2/ultraviolet (UV) photocatalytic process is the semi-conduct optical stimulation of TiO_2 as a result of electromagnetic ray absorption. The TiO_2 particles can play roles of an electron donor or acceptor for molecules in the chemical reactions.[21] An advantage of photocatalytic method includes low temperature, low expenses and also radically low level of energy consumption in this method. These factors have caused the photocatalysts to be used in commercial scales.[22,23]

The aim of this study is to evaluate the Photocatalytic processes for Cd^{2+} and Pb^{2+} removal at continuous and batch system.

MATERIALS AND METHODS

Photocatalytic set up

This study was performed at laboratory scale and schematic of the photocatalytic reactor are shown in Figure 1. The reactors consisted of three parts: UV source, reaction cell and mixing chamber. The 15 W low-pressure Hg UV-lamps were used as the radiation source. Peristaltic pump (OEM Model) and Dolphin EP-30 air pump were used respectively for air circulation and injection. A glass reactor (1L) was the major photoreactor used in this study, except when otherwise specified. This reactor consisted of two compartments, the outer for containing wastewater and the inner for housing a UV lamp.

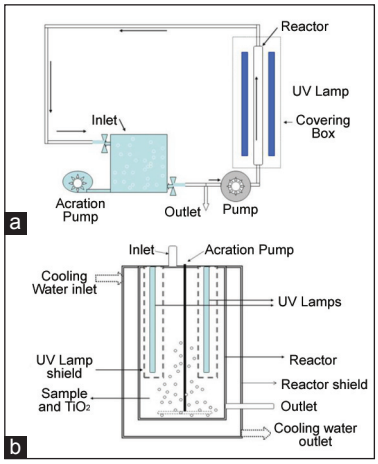

Figure 1: Schematic of the photoreactors employed in this study: (a) continuous, (b) batch

Chemical

A stock solution of Cd^{2+} and Pb^{2+} were prepared by dissolving $CdSO_4$. $8H_2O$ and Pb $(NO_3)_2$ in double distilled water. Before performing the experiment, the Cd^{2+} and Pb^{2+} concentration in the stock solution was measured. All the chemicals in this study were of extra pure or analytical grade. The titanium dioxide (TiO_2) used was Degussa P25, which is mostly anatase and has a BET (Brunauer-Emmett-Teller) surface area of 50 m^2/g and an average particle diameter of 21 nm. 0.1 N HCl or 0.1 N NaOH was used to adjust the pH solution.

Experiments

The experiments were carried out in a batch and continuous reactor for synthetic wastewater. The concentration of Cd^{2+} and Pb^{2+} was 25 mg/L in all experiments throughout the work. The synthetic solution was feed to reactor via peristaltic pimp at 0.125 L/min. In this study, the effect of pH solution, TiO_2 dose, numbers of sample recirculation and aeration level on metals removal efficiency were investigated. In order to achieve uniform TiO_2 suspension, the ultrasonic bath (Starsonic 18-35, Italy) was used. At the end of each experiment, cellulose nitrate membrane (0.2 μm) was used to separation of TiO_2 particles. all experiment was conducted at room temperature (23 ± 0.5°C). The Cd^{2+} and Pb^{2+} removal efficiency were calculated according to:

$$R=\frac{C_{in}-C_{out}}{C_{in}}\times 100$$

Where, $C_{in,}$ and C_{out} are initial and residual concentrations of the metal ion, respectively.

Analysis

The Cd^{2+} and Pb^{2+} concentrations in solution were determined using flame atomic absorption spectrophotometer (Varian

AA-20). The pH solution measurements were performed by using the WTW multi-parameter. All test methods were adopted from standard methods.[24]

RESULTS

Effect of TiO_2 dose

Tables 1 and 2 show the cadmium and lead removal onto TiO_2 in different doses at the contact time 120 min, cadmium and lead concentration 25 mg/L and different pH in the batch and continuous conditions, respectively. According to this table, with increasing TiO_2 dose and pH, the cadmium and lead removal increase. The maximum removal of cadmium and lead was obtained in 0.9 g/L TiO_2 dose and pH: 11 that were equal to 99.8 and 99.2% respectively.

Effect of pH

Effect of pH on the cadmium and lead removal onto TiO_2 in the batch and continuous conditions are shown in Figures 2 and 3 respectively. The removal efficiency of cadmium and lead removal increases with increasing pH solution. By increasing pH from 3 to 11, the removal efficiency increase of 2.8-77.3% for cadmium and 69.4-91.2% for lead at the continuous condition and 9.8-98.2% for cadmium and 90.2-99.6% for lead at the batch condition.

Effect of air dispersion

Figures 4 and 5 illustrate the effect of air dispersion on cadmium and lead removal, respectively. The results showed that as air dispersion increased, the removal efficiency increased while experiments is performed at the condition of without air, the removal efficiency was minimum (69 and 78.3% at the contact time 56 min for cadmium and lead, respectively) and in the air dispersion 2 cm^3/L (the maximum of air dispersion application), the removal efficiency was maximum (88 and 93.2% at the contact time 56 min for cadmium and lead, respectively).

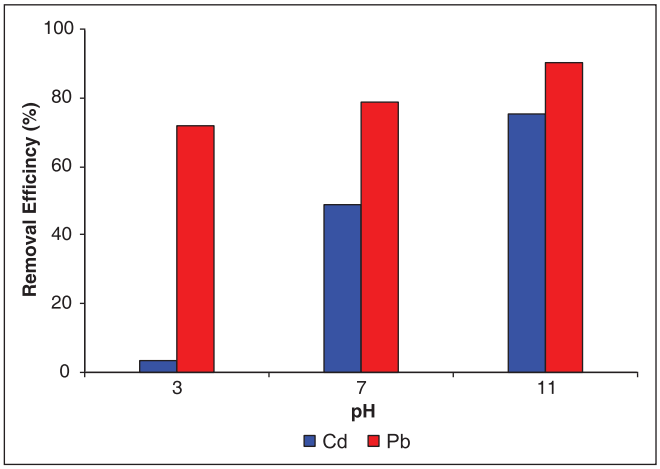

Figure 2: Effect of pH on Cd and Pb removal efficiencies in continuous experiments (titanium dioxide: 0.3 g/L, contact time: 120 min, Cd and Pb: 25 mg/l)

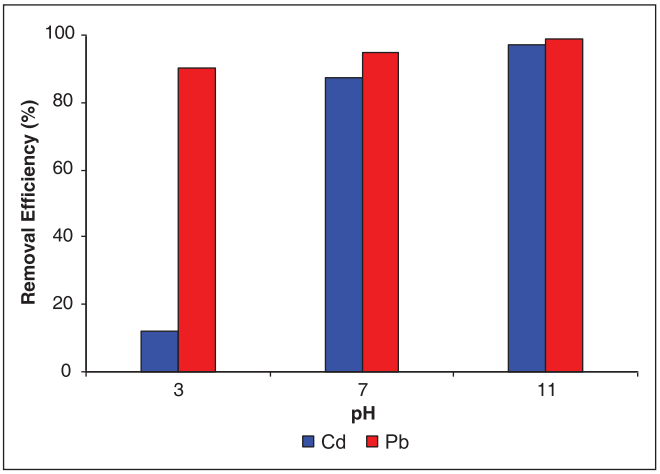

Figure 3: Effect of pH on Cd and Pb removal efficiencies in batch condition (titanium dioxide: 0.3 g/L, contact time: 120 min, Cd and Pb: 25 mg/l)

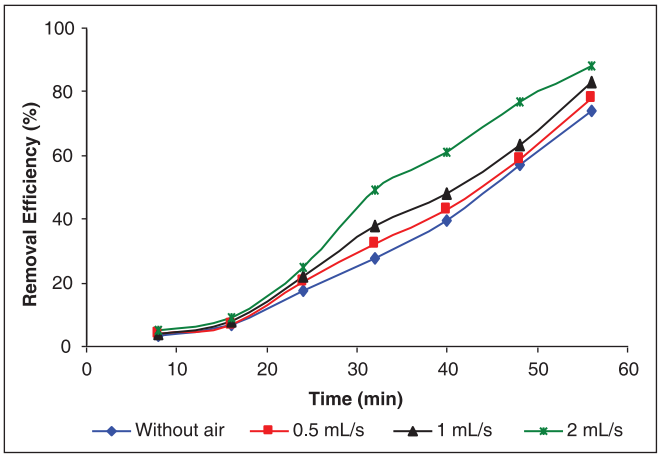

Figure 4: Effect of air injection on Cd^{2+} removal (continuous reactor, titanium dioxide: 0.9 g/L, Cd: 25 mg/L, pH: 11)

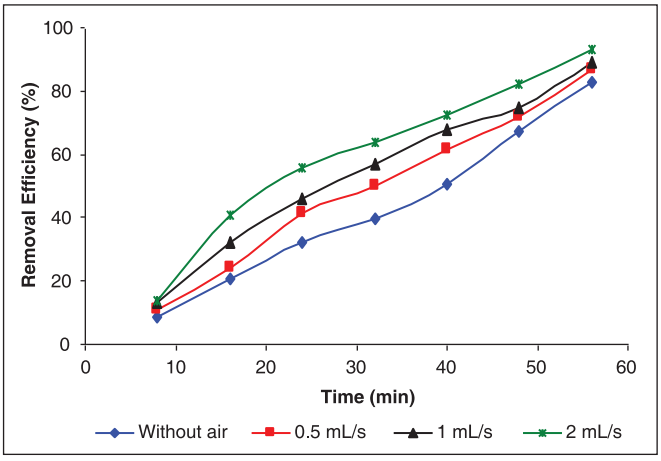

Figure 5: Effect of air injection on Pb^{2+} removal (continuous reactor, titanium dioxide: 0.9 g/L, Pb: 25 mg/L, pH: 11)

Table 1: Effect of TiO_2 dose on Cd^{2+} removal (contact time: 120 min, Cd: 25 mg/L)

TiO_2 dose (g/L)	pH: 3		pH: 7		pH: 11	
	Continuous	Batch	Continuous	Batch	Continuous	Batch
0.1	2.1	9.1	39.3	85.1	73.1	94.4
0.3	3.3	12.1	48.8	87.2	75.1	96.9
0.6	4.4	15.2	55.2	91.1	90.7	97.1
0.9	4.9	15.9	60.3	92.2	93.1	99.8

TiO_2: Titanium dioxide, Cd^{2+}: Cadmium

Table 2: Effect of TiO_2 dose on Pb^{2+} removal (contact time: 120 min, Pb: 25 mg/L)

TiO_2 dose (g/L)	pH: 3		pH: 7		pH: 11	
	Continuous	Batch	Continuous	Batch	Continuous	Batch
0.1	70.4	88.1	77.4	94.3	88.4	98.2
0.3	72.1	90.2	79.1	94.9	90.5	98.5
0.6	75.3	91.1	82.2	97.1	94.4	98.9
0.9	77.1	93.4	85.1	99.1	97.3	99.2

TiO_2: Titanium dioxide, Pb^{2+}: Lead

DISCUSSION

The photocatalytic process is AOP that has high importance due to low-cost to remove the organic pollutants. TiO_2 is a relatively inexpensive material, insoluble in water, nontoxic, and high activity.[25] In this study, according to the importance of removing toxic metals from industrial wastewaters, the photocatalytic process efficiency of TiO_2 were surveyed in the removal of lead (II) and cadmium (II) in tubular and batch reactors. The Pb II) and Cd (II) adsorption rate were strongly affected by pH solution. The results showed that with increasing the concentration of TiO_2 and pH values, the metal removal efficiency increases, so that at alkaline conditions (pH: 11), the metals removal from industrial wastewater increase which is consistent with results of similar studies.[11,26] The decrease in the efficiency of the adsorbate at the low pH could be due to protonation and the competition between protons and the metal ions for the adsorption sites on the sorbent.[27]

As Tables 1 and 2 indicate that the photocatalytic efficiency is increased with increasing the photocatalytic concentrations up to a certain rate. Thus, increasing the concentration from the optimum concentration has a negative impact on the photocatalytic efficiency because of the catalyst particles inhibit from the photons penetration.[28] These results are confirmed by Samarghandi *et al*. in the removal of phenol, lead, and cadmium by means of UV/TiO_2/H_2O_2 processes.[26]

According to Figures 3 and 4 in the photocatalytic process, the electron and hole produced in the photocatalyst surface by light photons. Oxygen gas is one of the most abundant and accessible and inexpensive that is capable of play the role of electron acceptor in the hydroxyl radical. So, the dissolved oxygen in the sample causes to significant increase of the removal efficiency.

The holes have high effect for the oxidation of heavy metals that may be adsorbed on TiO_2 and the oxidation efficiency depends strongly on an effective separation of holes and electrons.[29]

The main cause of hydroxyl radical's production is a production of free electron and holes in photocatalyst and the dissolved oxygen causes more production of hydroxyl radicals. With Increasing the amount of oxygen dissolved, produced Cd $(H_2)^+$, and Pb $(H_2)^+$ rate also increased. Mills indicated that low levels of dissolved oxygen have a negative effect on the removal efficiency. In other words, when oxygen levels are low, the metals are in oxidation state and tend to reeducation and conversion to X.[30]

CONCLUSION

In this study, cadmium and lead removal was investigated using TiO_2 and UV-C radiation in the pilot scale. If the TiO_2 concentration become more than optimum concentration, with increasing circulation number of sample volume in the tube reactor, the rate of toxic metal removal increases. As regard to in this method, used TiO_2 as photocatalyst is the separable and recyclable, so UV/TiO_2 process is an environment friendly process for toxic metal removal.

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