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Lead and Cadmium Ions Removal from Wastewater by Advanced Oxidation Process Using TiO_2 Nanoparticles

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Abstract
A variety of processes can be used in the treatment of industrial wastewaters. Advanced oxidation process (AOP) with TiO_2 nanoparticles (NPs) is one of them. In this study, UV/ TiO_2 / H_2O_2 process had been employed for the removal of lead and cadmium ions. Different operating conditions were used in batch experiments including initial heavy metals concentration ranging between (25, 50, 75 and 100) mg/l, H_2O_2 dosage (400, 600, 700, 900 and 1000) mg/l, TiO_2 (NPs) dosage (0.1, 0.3, 0.5, 0.7 and 0.9) g/l and pH (1, 3, 5, 7, 9, 11 and 13) using 1 Ultra violet (UV) lamp and the detention time was kept constant (210 min). For single and binary systems. The system at optimal conditions and dosage was found at pH= 9, TiO_2NPs = 0.3g/l, H_2O_2=700 mg/l and 25mg/l initial concentration for the ions of lead and cadmium. Results indicated that the optimum efficiencies of lead and cadmium ions removal were 96.69% and 93% for single system and 91.07% and 82.79% for binary system respectively. The pseudo-first order kinetics model fit the experimental data well.

Keywords: TiO_2 Nanoparticles, Cd (II), Pb (II), Advanced oxidation process

1. Introduction

The problem of water pollution has been increased by the discharge of heavy metal ions in industrial effluents (redo, et al. 2017).Heavy metals that are not biodegradable tend to accumulate in the bodies of living beings, making them more harmful than other water pollutants (Purkayastha et al., 2014). Lead and cadmium are highly toxic metals that can enter the aquatic system through agricultural practices and chemical industries such as electroplating, metallurgical alloying, metal-finishing, ceramics, photography, cadmium-containing pigments, textile printing, plastic production, cadmium-containing phosphate fertilizers, and refined petroleum products, among others (Hashem et al., 2017; Wan et al., 2018). As a result, suitable methods for removing lead and cadmium species from the aquatic environment as well as ecosystems are required (Ali et al., 2017). There are technologies for wastewater purification that can eliminate hazardous chemicals from the environment to a safe level while also doing it quickly, efficiently, and at a reasonable cost (Du et al., 2020). For the metal ions treatment process, Advanced oxidation is a low-cost purification method that is clean, quick, and environmentally friendly (Lau et al, 2018). For water treatment, a variety of AOPs are utilized, including H_2O_2/UV, TiO_2 /H_2O_2/UV, and TiO_2 /UV (Mohammed et al., 2020). The (•OH) radical can drive the oxidation process of even the least reactive contaminants to complete mineralization, and these radicals can eliminate biologically refractory pollutants with high chemical stability (Zhou et al., 2017). Reduction processes that generate elemental ions or metal ions at a lower oxidation state are being used to remove or recover heavy metals. There are numerous photocatalysts such as, GaP, WO_3, ZnO, ZnS, CdS and TiO_2 Nano sized, that are well known for their photo degradation and complete mineralization capability for water pollutants (Gao et al., 2016). Among them, TiO_2 Nano sized is the most active photocatalysts under photon energy of 300nm < λ <390 nm and also shows Titanium dioxide nanoparticles are considered extremely close to a perfect semiconductor for photocatalysis because of their excellent stability, low cost, and safety toward both humans and the environment when compared to other photocatalysts of comparable class (Wang et al., 2008). The benefits of using Nano sized photocatalysts are mainly associated with their large surface-volume ratio and high reactivity; itincreased light absorption rate and surface photo-induced carrier density, resulting in increased surface photo activity and

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photocatalytic activity of TiO_2 Nano catalysts. Heterogeneous photocatalytic oxidation/reduction processes have gained popularity among AOPs due to the fact that they may be carried out at room temperature and pressure (Nadeem et al. 2018).The objective of this study is to evaluate the efficiency of photo degradation forlead and cadmium ions by UV radiation within the presence of and TiO_2 nanoparticles during a laboratory reactor. Many parameters will be investigated like initial pH, initial H_2O_2 dosage, TiO_2 (NPs) amount and initial concentration for the pollutants to determine the optimum operational conditions.

2. Material and Experimental Work

2.1 Materials

Chemicals used in the experiments, as defined in table (1):

Table (1) chemicals

Compound	**Formula**	**Vender**
Hydrogen peroxide	H_2O_2	Thomas baker chemicals India 30% w/v
Titanium dioxide	TiO_2 (NPs)	Anatas, Changsha santech comp. 99.8% Size 30 ±5 nm
Lead nitrate	$Pb(NO_3)_2$	Thomas baker chemicals India
Cadmium nitrate	$Cd(NO_3)_2$	CDH Ltd India
Sodium hydroxide	NaOH	CDH Ltd India 98%
Sulfuric acid	H_2SO_4	Ridel-dehean 99%

2.2. Experimental procedure

Synthetic Pb (II) and Cd (II) solution was prepared at a concentration of 1000 ppm by dissolving 1.599 g, 23.7 g of lead nitrate and cadmium nitrate respectively in 1 liter of distilled water. All photocatalytic experiments were carried out in a batch mode laboratory-scale reactor. The reactor consisted of Pyrex glass cylinder 5L volume with a magnetic stirrer and UV lamp with diameter 1.25 (cm) and length 21 (cm) type (sp6-tv/5 18 w India), Which was fixed vertically at the top of the reactor, the lamp was immersed in the content of the cylindrical reactor as shown in Figure (1). The UV lamp was sheathed in a quartz sleeve for preservation. The distance between the UV lamp and the reactor wall was fixed at 5 cm to ensure maximum light irradiation. The initial pH of the solution was monitored using a pH meter (Hanna microprocessor, Padua, Italy).
The Advanced oxidation methods experiments were conducted in the mentioned reactor, which is contained 5000 mL of the simulated wastewater. Pb (II) and Cd (II) initial concentration was (25, 50, 75,100) mg/l. The equivalent stirring velocity of magnetic starrier was around 500 rpm at room temperature for 210 min.
The removal efficiency of metal ions under exposure of (UV-TiO_2 (NPs) -H_2O_2) was investigated. The concentrations were tested at a different times (10, 20, 30, 45, 60, 90, 120, 150,180 and 210) min. The pH was adjusted before adding the reagents by using NaOH or H_2SO_4. Different pH (1, 3, 5, 7, 9, 11 and 13), different dosage of H_2O_2 was used (400,600, 700,900 and 1000) mg/l at optimum pH, then the optimum concentration of H_2O_2 and optimum pH was used at different concentration of TiO_2 (NPs) photocatalyst (0.1, 0.3, 0.5, 0.7 and 0.9) g/l. After obtaining the optimal

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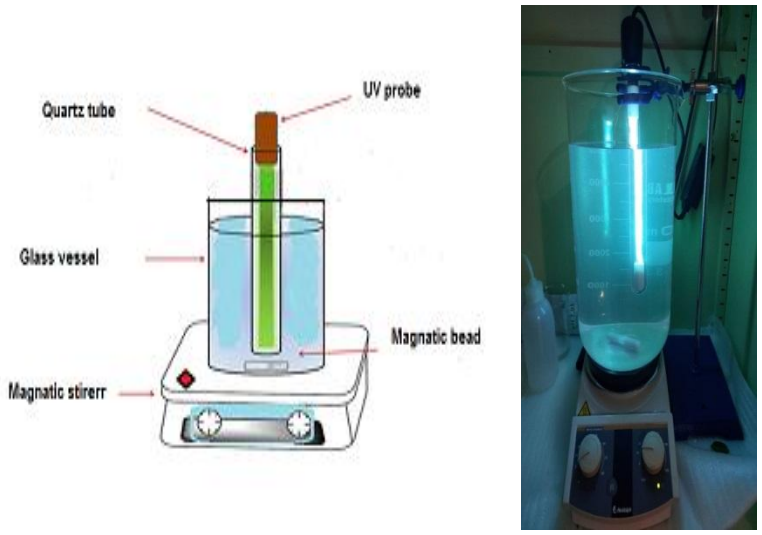
values from all experiments, they were used in the binary system.
The concentrations of Pb (II) and Cd (II) in the solution were measured by Atomic absorption spectroscopy (AAS). The removal efficiency (%) was calculated using equation 1:

$$(\%) = \frac{C_o - C_t}{C_o} * 100 \ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where C_o is the initial concentration of contaminants Pb (II) andCd (II)in the samples wastewater (mg/L).C_t is the concentration after photo irradiation (mg/l).



(a) **(b)**

Figure (1): Laboratory scale of batch reactor (a) Schematic –of batch reactor-with-suspended-UV-lamp (b) Photograph of batch reactor

2.3. ***Kinetic study***
To fit experimental data for heavy metal ion degradation, pseudo-first-order and pseudo-second-order models can be utilized. Eqns. below describe the linearized version of pseudo-first-order and second-order kinetic models:

$$\ln \frac{[C_o]}{[Ct]} = K_{1t}` \ldots\ldots\ldots\ldots\ldots 2$$

$$\frac{1}{[Ct]} - \frac{1}{[C_o]} = K_{2t} \ldots\ldots\ldots\ldots\ldots 3$$

Where : C_0 represents the starting concentration of metal ions and C_t represents the concentration at irradiation time t, K_{1t} and K_{2t} represent the pseudo-first and second-order rate constants in min-1 and l/mg.min, respectively, and t represents the irradiation duration (in min). For each experiment, plotting Eqns. above vs. time results in a straight line with slope (K_{1t} and K_{2t}, respectively), (Hassan et al., 2015).

3. Results and Discussion

3.1 Effect of pH Values

Figures(2)and(3) demonstrate the degree of reduction for Pb (II) and Cd (II) with relation to time at various pH values while keeping all other parameters constant (H_2O_2 = 900 mg/L, TiO_2 = 0.5 g/L,

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1UV lamp, and temperature=25°C). It can be seen that the rate of reduction of Pb (II) and Cd (II) steadily increased as pH increased, which could be due to ion adsorption on the catalyst's surface, and that as pH increases, the removal of Pb (II) and Cd (II) approaches very near values as showed in figure (4). The best Pb (II) and Cd (II) removal efficiency were found at pH=9, with percentages of removal of 96.87 percent and 93 percent, respectively, after 210 minutes (min). The heavy metal ions reduction increased as pH enhanced in accordance with metal ion properties and the surface of TiO_2 nanoparticles which changed to $TiOH^-$ to provide electrons and •OH radicals as well as to adsorb the cations. By Increasing the pH of the solution more than 9, the surface of TiO_2 changes to $TiOH_2^+$, in this case hydroxyl radicals (•OH) would not be easily to release, as well as cations is being difficult to adsorb and an increase in the removal efficiencies for both pollutants were observed due to formation of Pb $(OH)_2$ and Cd $(OH)_2$ precipitate (Ma, et al., 2012). The trend of the results agreed well with the findings of(Lau, et al., 2018).

Figure (2): Effect of pH on removalefficiencyof Pb (II) with time inUV/ H_2O_2/TiO_2 (NPs) process as a single system: [Con.] = 50 mg/l, TiO_2 dose =0.5gm/l, H_2O_2=900mg/l, 1 UV lamp, reaction time = 210 min, at room temperature.

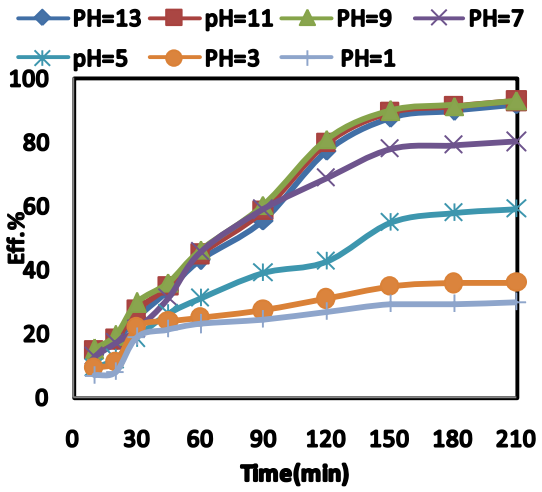

Figure (3):Effect of pH on removal efficiency of Cd (II) with time in UV/ H_2O_2/ TiO_2 (NPs) process as a single system: [Con.] = 50 mg/l, TiO_2 dose =0.3 gm/l, H_2O_2= 900 mg /l, 1 UV lamp, reaction time = 210 min, at room temperature

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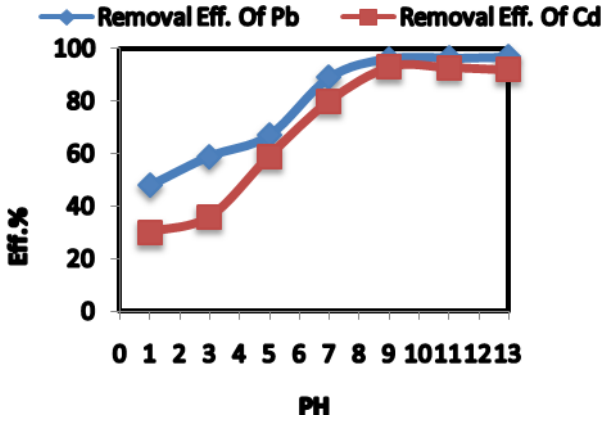

Fig. (4)The effect of PH on removal efficiency of Pb (II) &Cd (II)

3.2. Effect of H_2O_2 Dose

Figures (5) and (6) plot the reduction of Pb (II) and Cd (II) with different H2O2 dosage, (400,600, 700,900 and 1000) mg/l in solution keeping other parameters unchanged during the illumination time to investigate the influence the concentrations of hydrogen peroxide. As can be shown in these Figures, the ions reduction promoted with increasing the H_2O_2 loadings, further increased in H_2O_2 concentration to 1000 mg/l will reduced the removal efficiency because its act as radical scavenger (Malakootian et al., 2015, Hameed et al., 2019). Instead of metal ions, excess free radicals would react with excess H_2O_2 to generate complex hydroxyl ($\bullet HO_2$) (Wahyuni et al., 2015). A remarkable increase on the reduction of lead and cadmium ions was occurred at a loading H_2O_2 equal to (700 and 900 mg/L) after 210 min of irradiation. The reduction of Pb (II)and Cd (II) were (95.99%, 96.69%) and (93%, 95 %) respectively so it is considered an optimum values Because of the convergence in values of removal efficiencies,, but the reduction of Pb (II) and Cd (II) decreased to 92% and 90% as H_2O_2 loading increased to 1000 mg/l as shown in Figure (7). The current findings were in accordance with the findings of (Fu et al., 2017; Grzechulska-Damszel et al., 2009; Sarika et al., 2013).

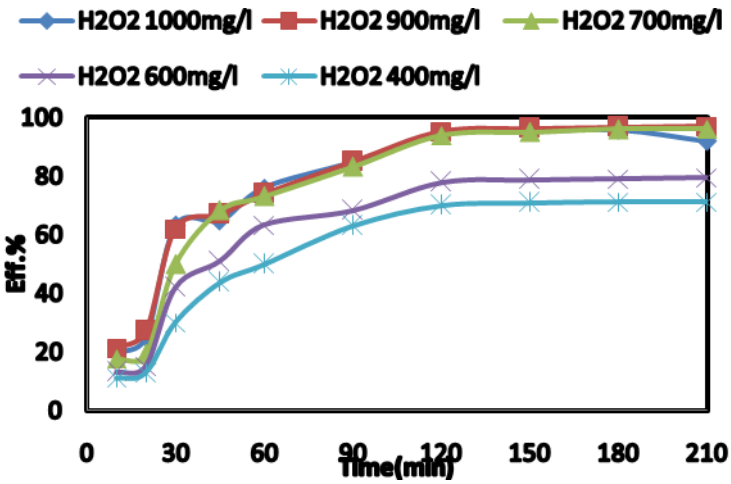

Figure (5): Effect of different H_2O_2 dose on removal efficiency of Pb (II) with the time in UV/ H_2O_2/ TiO_2 (NPs) process as a single system: [Con.] = 50 mg/l, TiO_2 (NPs) = 0.5g /l, 1 UV lamp, reaction time = 210 min, at room temperature

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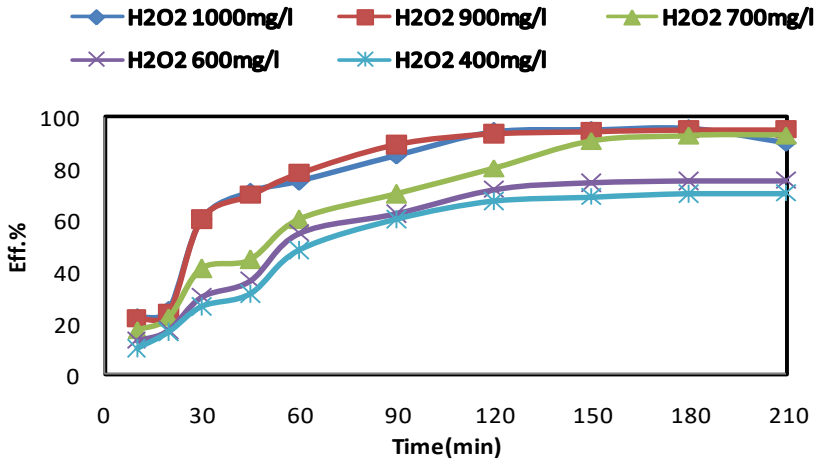

Figure (6): Effect of different H_2O_2 dose on removal efficiency of Cd (II) with the time in UV/ H_2O_2/ TiO_2 (NPs) process as a single system: [Con.] = 50 mg/l, TiO_2 (NPs) =0.5 g/l, 1 UV lamp, reaction time = 210 min, at room temperature

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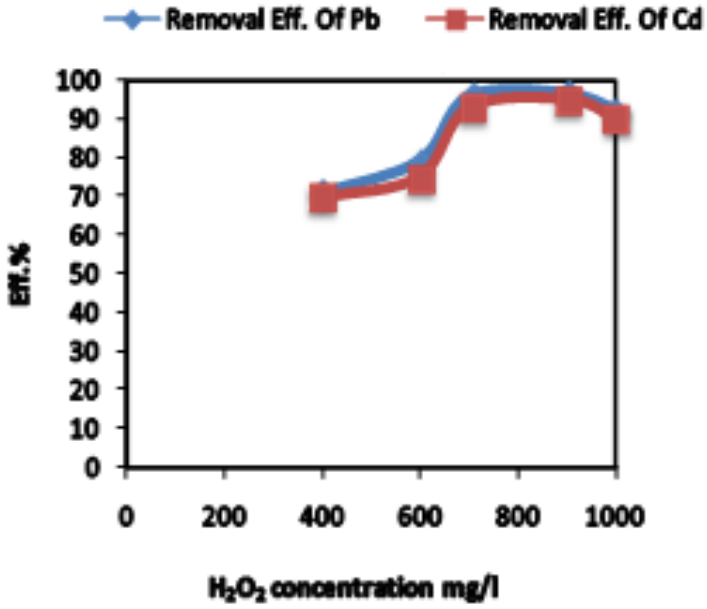

Figure (7): Effect of H_2O_2 on removal efficiency of Pb (II) &Cd (II) [Con.] = 50 mg/l

3.3. Effect of TiO_2 NPs Dose

Figure s (8) and (9) show that the experiments carried out at various applied loading of TiO_2 (NPs) (0.1, 0.3, 0.5, 0.7 and 0.9) g/l and keeping other parameters unchanged (H_2O_2 = 700 gm//L, pH= 9, 1 UV lamp) during 210 minutes of illumination. The best Pb (II) and Cd (II) removal efficiencies occurred at (0.5, 0.7) g/l concentration of TiO_2 (NPs) as shown in Figures (10). However, increasing of catalyst amount lead to increase the rate of Pb (II) and Cd (II) reduction but also it causes increasing in turbidity of the solution, As a result of the UV light being blocked or scattered, light penetration is reduced, and mass clumping or aggregation of the catalyst occurs, resulting in less availability of catalytic active sites (Hameed and Al-zobai, 2019). The results trended in the same direction as the findings of (Seung et al., 2019).

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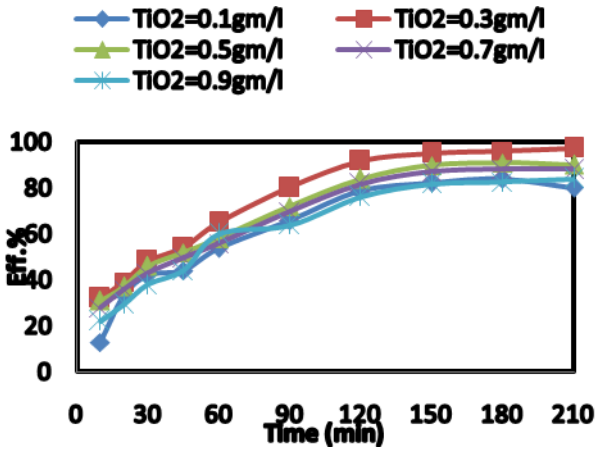

Figure (8): Effect of different TiO_2 (NPs) dose on removal efficiency of Pb (II) with the time in UV/ H_2O_2/ TiO_2 (NPs) process as a single system: [Con.] = 50 mg/l, H_2O_2=700 mg/l, 1 UV lamp, reaction time = 210 min, at room temperature

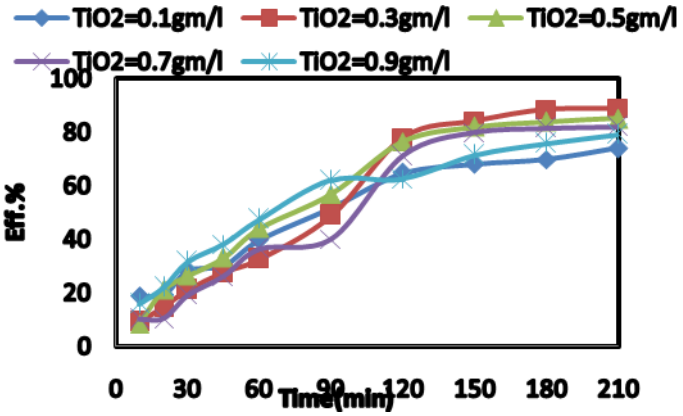

Figure (9): Effect of different TiO_2 (NPs) dose on removal efficiency of Cd (II) with the time in UV/ H_2O_2/ TiO_2 (NPs) process as a single system: [Con.] = 50 mg/l, H_2O_2=700 mg/l, 1 UV lamp, reaction time = 210 min, at room temperature

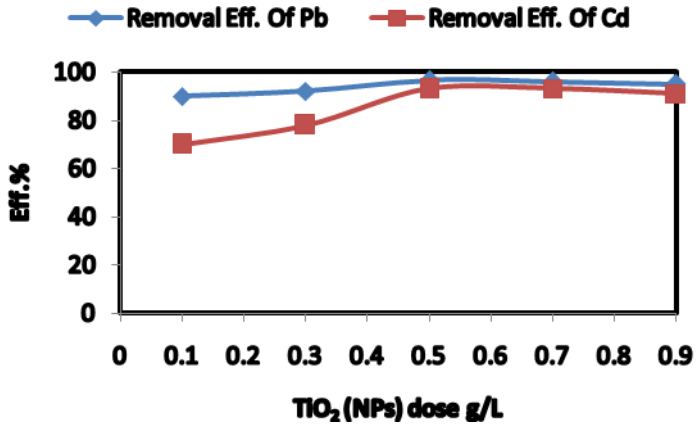

Figure (10): Effect of different TiO_2 (NPs) dose on removal efficiency of Pb (II) and Cd (II

3.4 Effect of Lead and Cadmium Initial Concentrations

As shown in Figures (11) and (12), four concentrations were tested at constant optimum conditions (H_2O_2 = 700 gm//L, pH= 9, 1 UV lamp) during 210 minutes of illumination.The Increasingin the concentrations ofPb (II) and Cd (II) decreased the removal efficiencies,the highest percentage ofPb

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(II) and Cd (II) removal efficiencies were (96.69%, 93%) respectively occurs in the concentrations of 25 mg/las shown in Figure (13). Further increase in the concentrations of the pollutants lead to decrease the removal efficiencies. Many studies have looked into the effect of increasing the initial concentration of pollutants on removal efficiency. They reported that higher concentrations of pollutants react with hydrogen peroxide and limit its action in a solution, as well as obstructing light penetration into the solution, resulting in fewer photons reaching the surface of the photocatalyst. As a result, the production of charge carriers and reactive radicals is reduced at the same time, lowering photo degradation efficiency (Barhon et al., 2012; Gao et al., 2016; Ali and Khan, 2017). As shown in Figures (13), Pb (II) and Cd (II) removal efficiencies were increased with initial concentrations equal to (25, 50) mg/l, Therefore, the concentration of 25 mg/l was selected as the optimum concentration at this stage.

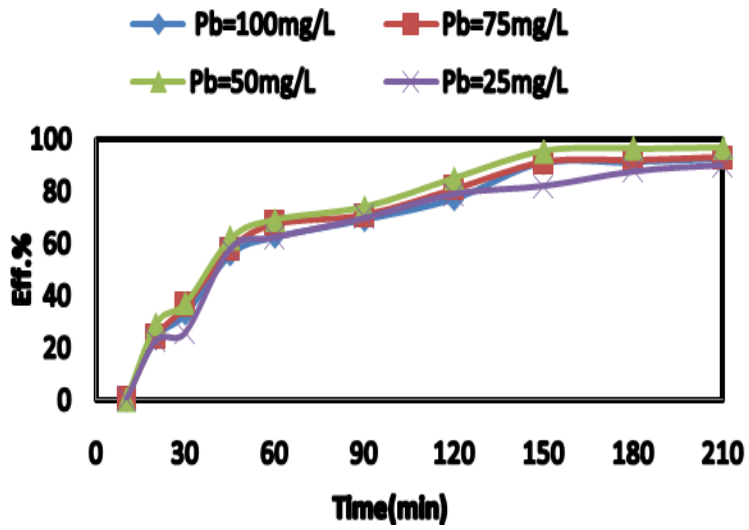

Figure (11): Effect of initial Pb (II) concentration on removal efficiency of with the time in UV/ H_2O_2/ TiO_2 (NPs) process as a single system, 1 UV lamp, H_2O_2=700 mg/l, TiO_2 (NPs) dose =0.5 g/l, reaction time = 210 min, at room temperature

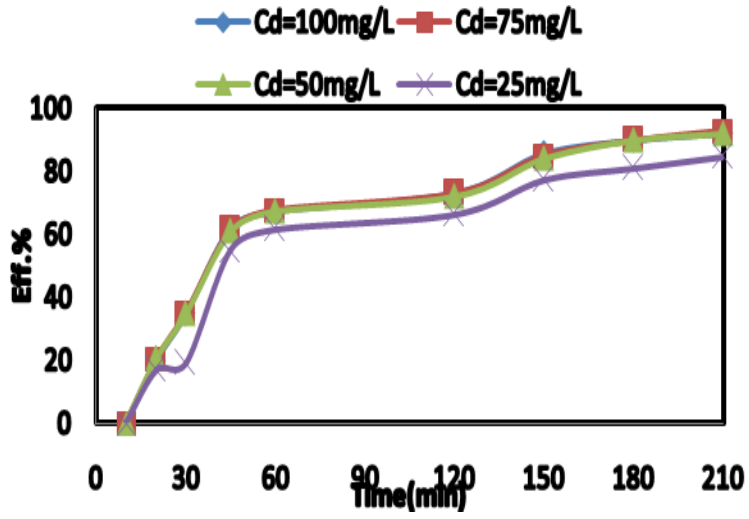

Figure (12): Effect of initial Cd (II) concentration on removal efficiency of with the time in UV/ H_2O_2/ TiO_2 (NPs) process as a single system, 1 UV lamp, H_2O_2=700 mg/l, TiO_2 dose =0.3 g/l, reaction time = 210 min, at room temperature

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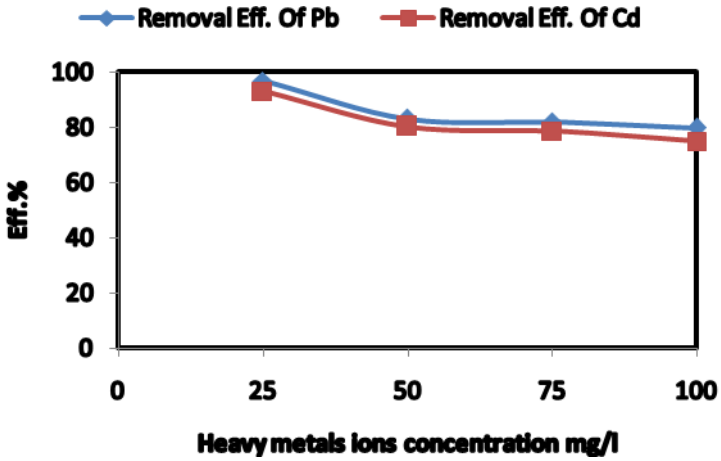

Figure (13): Effect of initial concentration on removal efficiency of Pb (II) and Cd (II)

3.5 Binary system with optimum conditions

Removal efficiency of binary system of Pb (II) and Cd (II) at optimum conditions with concentrations of 25 mg/l for Pb (II) and Cd (II), 700 mg/l H_2O_2, 0.3 gm/l TiO_2 (NPs), and 1UV lamp during 210 minutes of illumination, as shown in Figure (14). Because of the polarizing power, ionic radii, and dehydration energy of lead ions, the removal efficiency. The results trended in the same direction as the findings of (Kavand et al., 2020; Mohammed et al., 2020).

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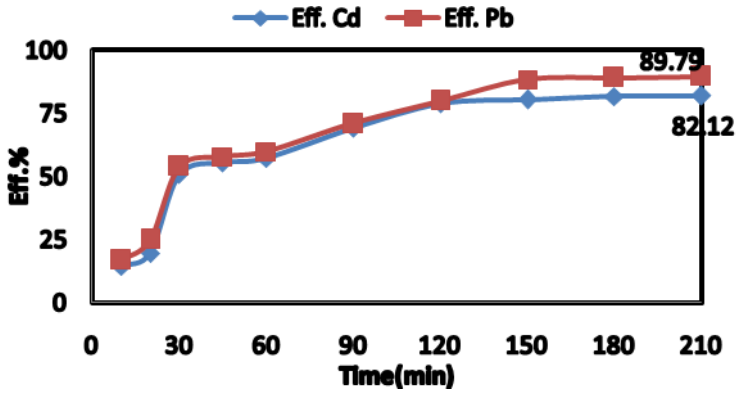

Figure (14): Effect of optimum conditions on removal of Pb (II) and Cd (II)

3.6. Kinetic study

The regression analysis of the concentration curves versus retention time show that the decomposition rate of lead and cadmium ions could be described by pseudo-first-order and pseudo-second-order models. Eqs. (2 and 3) were applied for all of the experimental results to find the rate of reaction degradation of Pb (II) and Cd (II) by UV/ H_2O_2/ TiO_2 (NPs). A plot of $\ln \frac{[C_o]}{[Ct]}$ and $\frac{1}{[Ct]} - \frac{1}{[C_o]}$ vs. time was illustrated in Figure (15) and Figure (16) respectively. It can be seen that the correlation coefficient of the second-order model was not good enough due to the low correlation coefficients, while the first-order reaction was obviously much better as shown in Table (2).

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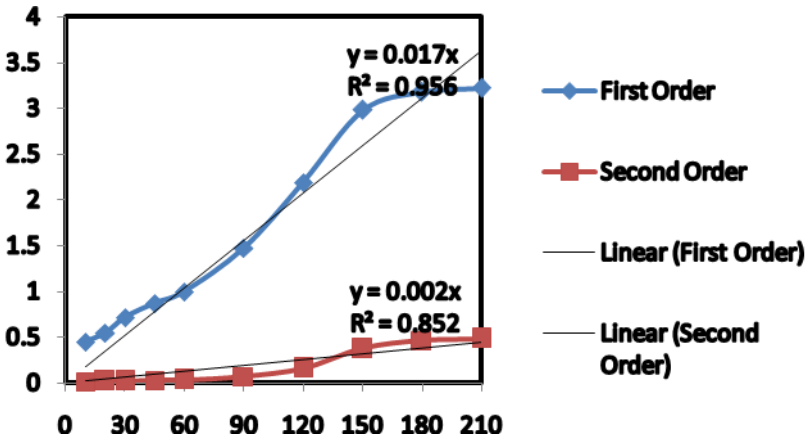

Figure (15): Pseudo first order &second order rate constants with different concentrations of lead ions

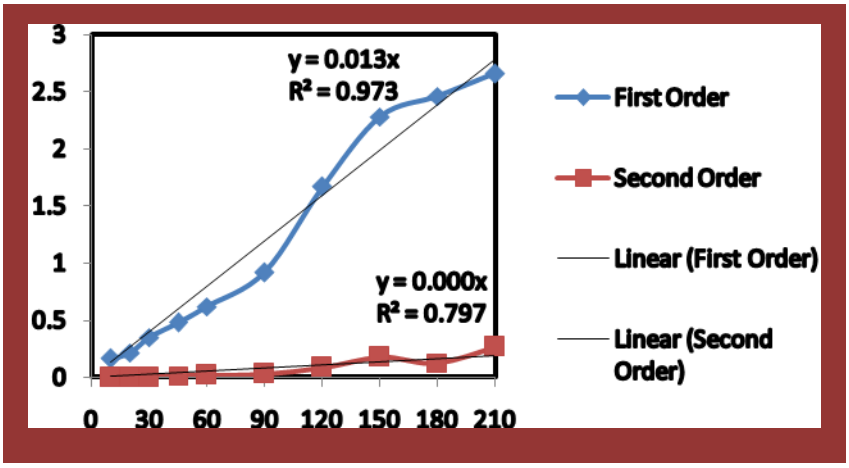

Figure (16): Pseudofirst order and second order rate constants with different concentrations of Cadmium ions

Table (2): PseudoFirst Order Rate Constant k min-1 at Optimum Operation Conditions

Pb (II) &Cd (II) [cons.] =25mg/l, H2O2=700mg/l, TiO2 (NPs) =0.3 gm/l, 1 UV lamp and 210 (min) reaction time.									
Removal Efficiency		***Pseudo First order***		***R2***		***Pseudo Second order***		***R2***	
Pb(II)	***Cd(II)***	$K_{1t}x10^{3}min^{-1}$		***Pb(II)***	***Cd(II)***	$K_{1t}x10^{6}$ L.mg^{-1} .min^{-1}		***Pb(II)***	***Cd(II)***
		Pb(II)	**Cd(II)**			**Pb(II)**	**Cd(II)**		
96.69%	93%	0.0173	0.0132	0.956	0.9731	0.0021	0.0009	0.8521	0.7974

Conclusion

UV/ H_2O_2/TiO_2 (NPs)process were used to examine the performance of AOPs for the degradation of Pb (II) and Cd (II)in wastewater. The reaction was influenced by different concentrations of H_2O_2, pH, the amount of TiO_2 (NPs) and the initial concentration of Pb (II) and Cd (II). The

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findings of this study indicate that TiO_2 (NPs) plays an important role in photo degradation by increasing the contact surface between the photo catalyst and the pollutants, making it a good choice for the purification of toxic lead-cadmium-containing hazardous wastes that might cause cancer. Furthermore, due of its strong potential in photo reduction of high-concentration toxins, TiO_2 (NPs) is particularly suited and efficient for industrial wastewater. The addition of the proper amount of hydrogen peroxide could improve the photo degradation rate. However, at high concentrations, H_2O_2 would quench hydroxyl radicals. The removal efficiencies for the system at best H_2O_2 /TiO_2 (NPs)/ UV conditions and dosage (H_2O_2 = 700 mg/L, pH=9, TiO_2 NPs= 0.5 g/L) for 25 mg/L load was found to be 96.69% for Pb (II), 93% for Cd (II) and 89.79% for Pb, 82.12% for Cd for single and binary systems respectively. The kinetic study shows that the pseudo-first-order model can predict the model well.

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