

Coupling adsorption by NiO nanopowder with UV/H₂O₂ process for Cr(VI) removal

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ABSTRACT

Chromium enters surface and ground waters through the wastewater of electroplating, textile, metallurgical, dye production, and other industries, leading to numerous adverse health effects. The potential property of nanoparticle adsorption of nickel oxide (NiO) and the economic nature of ultraviolet/hydrogen peroxide (UV/H₂O₂) process have eased the usage of these two processes for chromium removal. In this study, the parameters including chromium concentration, pH, and NiO dosage were examined by the adsorption process. Furthermore, following the separation of NiO nanoparticles by magnet and filtration, in UV/H₂O₂ reactor, the effects of H₂O₂ concentration, radiation time, and pH were studied on the removal efficiency. In the reactor containing NiO, with an increased dose of NiO from 0.2 to 1 g, the removal efficiency increased from 26 to 76%. Moreover, at different pHs (3, 5, 7, and 11) and reaction times (10, 20, 30, and 40 min), the maximum efficiency of 79% was obtained at pH = 3 and reaction time of 40 min. The isotherm of the adsorption followed the Langmuir model. In the UV/H₂O₂ reactor, elevation of H₂O₂ concentration from 20 to 100 μmol resulted in an elevated chromium removal efficiency at pH = 3 from 35 to 95%. In this process, pH = 3 was chosen as the optimum pH. The results indicated that the removal efficiency is highly influenced by pH, reaction time, dose of NiO nanoparticles, and H₂O₂. By optimizing the effective parameters, this process can be used to remove chromium in aqueous solutions. **Keywords:** Chromium, Hydrogen peroxide, Industrial wastewater, Nickel oxide nanopowder, Ultraviolet

Introduction

In comparison with the household and urban wastewaters, industrial wastewater reveals certain characteristics, whose improper discharge may cause irrecoverable damages to the environment. The presence of over-acidic and alkaline properties, toxic and hazardous contaminants, heavy metals, etc. are factors, which have differentiated the quality of industrial wastewaters from other wastewaters.¹

Heavy metals belong to the group of first-degree toxic contaminants, which cause environmental hazards and deteriorate human health. A majority of the heavy metals interfere with the biological reactions of living cells and disrupt the metabolic activities. Chromium is an important industrial metal, which is used in different processes and products. It enters the surface and groundwater through the wastewater produced by electroplating, textile, metallurgy, dye and pigment production, print and graphic, explosives, leather making, and fertilizer producing industries, thus contaminating the environment. In two typical oxidation states, chromium reveals its trivalent and hexavalent nature. Hexavalent chromium is toxic, carcinogenic, and mutagenic; whereas,

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trivalent chromium is less toxic. Accumulation of chromium in the animal and plant tissues can cause serious health hazards. Chromium disrupts the function of the liver, kidneys, and lungs. WHO has confirmed the carcinogenicity of hexavalent chromium in humans, and has determined the maximum allowable limit of chromium in drinking water as 0.1 mg/L.^{2, 3} Based on the Iranian drinking water standards, these values have been determined as 0.05 mg/L. Considering the health risks of chromium on the humans and environment, removal of chromium from the industrial wastewater and minimizing it to the standard limits specified by the environmental protection agency, is essential.⁴ Conventional methods for treating chromium-containing wastewaters include adsorption, ion exchange, and reduction of chemical methods including those involving iron or iron salt, followed by coagulation and sedimentation. Reduction by sodium sulfate or meta-bisulfate is a common method for hexavalent chromium removal. The disadvantages of the aforementioned methods include the need for addition of chemicals, formation of sludge, and release of sulfur dioxide.^{2,3} One of the fundamental solutions for resolving these issues includes the use of highly efficient and economical technologies. Nanotechnology and advanced oxidation processes (AOPs) are processes that play a crucial role either in isolation or combination for identification, measurement, and removal of contaminants from the environment. Nanoparticles (due to their small size, large cross-section area, crystal form, and unique network order, very high reactivity and adsorptivity) and advanced oxidation (due to production of free radicals) can be used to treat and convert the contaminants into harmless or low-risk compounds.^{4, 5}

Among the several advanced oxidation methods based on radiation, including ultrasonic and microwave oxidation, the UV-based oxidation has claimed a special position. UV effectively removes and reduces the contaminants from the aqueous environments by breaking down strong oxidant molecules, increasing production of free radicals, and increasing the adsorption area of nanoparticles.^{4, 6}

A review of several studies indicates that

the hybrid oxidant/ultraviolet, nanoparticles/ultraviolet, and nanoparticles alone processes revealed significant results in the reduction of environmental contaminants.⁷ Reduction of chromium in the presence of UV/zinc oxide (UV/ZnO) processes by Sampa Chakrabarti et al.,² and UV/ titanium dioxide (UV/TiO₂) by Wang et al.⁸ are two samples of hybrid processes of nanoparticles apart from UV. Furthermore, Joshi et al. employed titanium dioxide, zinc oxide, and cadmium sulfide nanoparticles individually for removal of hexavalent chromium.⁹ Asadi et al. also studied the efficiency of aluminum oxide nanoparticles in the removal of hexavalent chromium from aqueous solutions.¹⁰ Based on the results obtained from previous studies, it has been found that nickel oxide (NiO) has unique chemical, magnetic, and catalytic properties among the metal oxide nanoparticles, indicating it to be an effective candidate in the wastewater treatment studies.^{11, 12}

Moreover, the results of other studies have confirmed that the hybrid UV/H₂O₂ process is considered an economic and efficient AOP method for removal of wastewater contaminants. In comparison with other AOPs, this process creates hydroxyl free radicals to reduce the level of contaminants in the aqueous systems, which can cause direct degradation of the target contaminant or its conversion to intermediate products.¹³⁻¹⁵ The NiO adsorbent may be used to control the mobility of metal ions in the environment. NiO nanoparticles, due to their high surface area, low production cost, and natural porosity have a suitable adsorption capacity for the removal of heavy metals from the aqueous solutions. Therefore, in this study, the efficiency of chromium removal through adsorption by NiO nanoparticles followed by oxidation by UV/H₂O₂ process from aqueous solutions, was investigated.

Materials and Methods

Materials

This research was an applied study performed as a batch study at the laboratory scale. UV bubble lamp of 125 W, used in this study, was purchased from Arda Co., France; NiO nanoparticles used as an adsorbent were purchased from Sigma Aldrich Co.; and other

chemicals were bought from Merck Co., Germany.

Experimental Procedure

The properties of the studied NiO have been listed in Table 1 and Fig. 1 (XRD and TEM analysis). Since the NiO nanoparticles have a magnetic effect, we initially used the adsorption process, as this adsorbent is regenerable. Alternatively, the oxidation with hydrogen peroxide (H_2O_2) is expensive; hence, we used

two sequential processes, including adsorption and oxidation.

Table 1. Nickel oxide nanoparticle characteristics

Nickel (II) oxide	
Appearance Form	Dark grey powder
Relative density	6.67 g/cm ³ at 25 °C (77 °F)
Linear Formula	NiO
Molecular Weight	74.69 g/mol
Nanopowder particle size	<50 nm
Purity	>99.8%

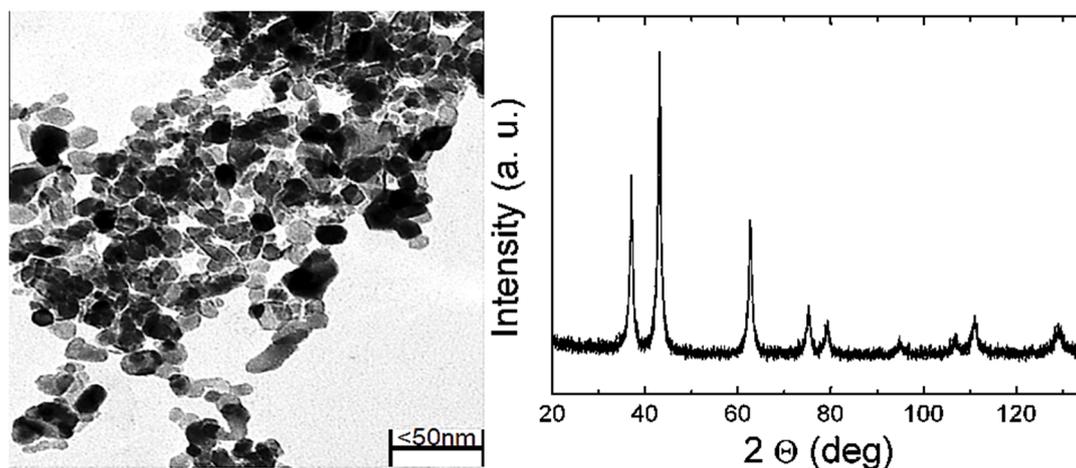


Fig. 1. Analysis of XRD and TEM of nickel oxide (NiO) nanoparticles

To prepare synthetic wastewater, a stock solution of hexavalent chromium (1000 mg/L) was prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in distilled water, and then the concentrations of 10, 20, 30, 40, and 50 mg/L were prepared from it. To adjust the pH, sulfuric acid and sodium hydroxide of 1 N were used. In this study, the effect of the adsorbent's dosage (0.2, 0.4, 0.6, 0.8, and 1 g), pH (3, 5, 7, 9, and 11), initial concentration of chromium (10, 20, 30, 40, and 50 mg/L), and contact time (10, 20, 30, and 40 min) was examined during

the removal of hexavalent chromium using the adsorption method. For suitable mixing and contact between the adsorbent and chromium, a mechanical shaker was used at 250 rpm. After the reaction, the NiO nanoparticles and the chromium adsorbed on them were separated from each other by a magnet (Fig. 2). The remaining nanoparticles saturated with chromium were also separated by a 0.45 μ filter. The concentration of chromium in the solution was determined, according to the method 3500-Cr based on Standard Methods for the

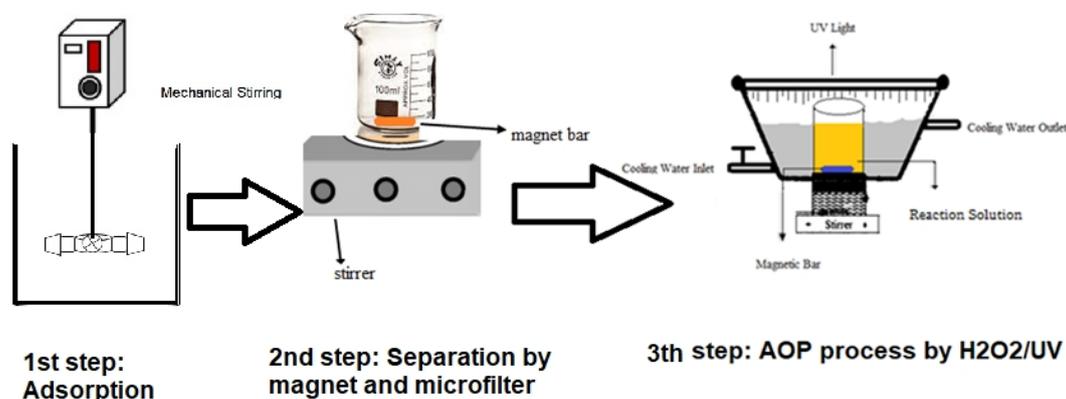


Fig. 2. Schematics of adsorption processes and AOP in removing chromium

Examination of Water and Wastewater, using photometer 1.5 diphenyl carbazide method at $\lambda_{\max} = 540 \text{ nm}$ after 10 min inactivity by UV/visible spectrophotometer device.¹⁶ In the next stage, the solution resulting from the adsorption process output (under optimal conditions) was fed into an advanced oxidation process (UV/H₂O₂). Several parameters including H₂O₂ concentration (20, 50, 100, and 200 μmol), radiation time (5, 10, 20, 30, and 40 min), and pH (3, 5, 7, 9, and 11) were investigated. To perform this stage of the experiment, the output chromium solution of the adsorption process was transferred in the reactor to ensure mixing of the solution with UV radiation. Overall, to expose the chromium-containing solution to UV, a photoreactor was used (Fig. 2). Measurement of the chromium level in the solution at this stage was reperformed after 10 min of inactivity of the samples, as with the previous stage using an UV/visible spectrophotometer device.^{8, 9}

Calculations

The amount of chromium adsorbed during equilibrium ($q_e(\text{mg/g})$) and the chromium removal efficiency (E) was calculated by Eqs. (1) and (2), respectively.

$$q_e = \frac{V}{M} \times (C_0 - C_e) \quad (1)$$

$$E = \frac{C_0 - C}{C_0} \times 100 \quad (2)$$

where, in these relations, C_0 and C_e are the initial and final concentrations of chromium (mg/L), V represents the solution volume (L), M is the adsorbent's mass (g), q_e denotes the adsorption capacity at the time of equilibrium (mg/g), and E is the contaminant removal efficiency (%). In this study, Langmuir and Freundlich isotherm models were examined to inspect the relationship between the extent of adsorption of the chromium-containing solution and the utilized adsorbent. Langmuir and Freundlich isotherm models are expressed by Eqs. (3) and (4), respectively:

$$\frac{C_e}{q_e} = \frac{1}{q_m^b} + \frac{1}{q_m} C_e \quad (3)$$

$$\log q_e = \log k_f + \frac{1}{n} \ln C_e \quad (4)$$

where q_m and b are the Langmuir constants, which are associated with the maximum adsorption capacity (mg/g) and adsorption energy (L/mg). K_f and n are the Freundlich constants, representing the adsorbent capacity and adsorption intensity.^{17, 18} After performing the experiments and obtaining the results, Excel software was used to plot the diagrams and analyze the data.

Results and Disruption

Optimization of the parameters of the chromium adsorption process by NiO nanoparticles Investigating the effect of NiO value in the chromium removal process

Investigating the effect of adsorbent mass and determining the optimal mass are two important issues that should be considered during the adsorption process. The results obtained from the investigation of the adsorbent dose effect in the removal of hexavalent chromium are presented in Figure 3. Based on the findings of the study, at $\text{pH} = 3$, with an elevation of the adsorbent mass from 0.2 to 0.1 g, chromium removal efficiency increased from 26 to 76%, which can be attributed to the increased surface of the adsorbent and the increased number of available active sites for adsorption.¹¹ As the extent of growth in the chromium removal efficiency did not significantly increase from 0.8 to 1 g of the adsorbent (from 72 to 76%), thus considering the economic issues, the optimal concentration for the nanoadsorbent was considered as 0.8 g. In a study on the effect of adsorption of NiO nanoadsorbent in the removal of hexavalent chromium, it was found that with an elevation of the adsorbent mass from 0.1 to 0.6 g, increased efficiency was observed from 45 to 86%.¹⁷ In another study, NiO nanoadsorbents were used from the removal of Cr^{3+} from aqueous solutions. Elevation of the adsorbent concentration from 0.02 to 0.3 g caused the increased removal of trivalent chromium, whereas further consumption of the adsorbent had no effect on the efficiency of adsorbent and removal.⁷ In a study on the adsorption of DR80

dye by NiO nanoparticles, the results revealed that with the elevation of the adsorbent concentration, the extent of dye adsorption also increased, and the optimal concentration of the adsorbent was reported as 1 g/L.^{19,20}

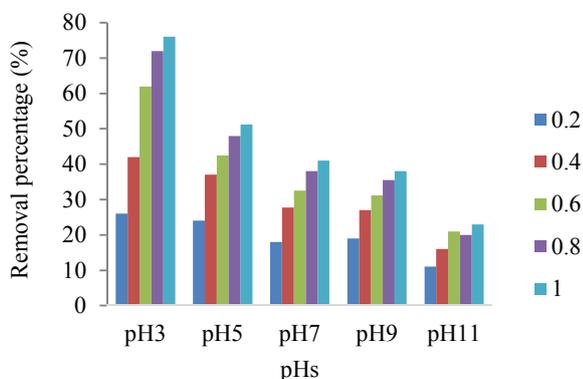


Fig. 3. The chromium removal efficiency by different concentrations of NiO nanoparticles

Determining the effect of pH and contact time on the removal of hexavalent chromium

pH is an important qualitative parameter of wastewater, which can affect the adsorption capacity by influencing the degree of ionization and the adsorbent surface characteristics along the reaction.²¹ Therefore, in this study, the effect of soluble pH on removal of hexavalent chromium in the presence of adsorbent dose (0.2, 0.4, 0.6, 0.8, and 1 g) per 100 ml of chromium solution with concentrations of 10, 20, 30, 40, and 50 mg/L was examined, with the results presented in Figure 4. The maximum chromium removal efficiency was observed at pH = 3. Overall, it can be concluded that the adsorption efficiency increased at low pHs because several functional groups including amine groups presented across the adsorbent surface become protonated at acidic pHs and adsorb the negatively-charged chromate ions through electrostatic interaction.²²

Khoshravesh et al. studied the hexavalent chromium removal by sodium nanoclay. In this study, the chromium adsorption was higher at low pH, and the optimal pH was 3.²³ Furthermore, in a study by Asadi et al. on hexavalent chromium removal by ZnO nanoparticles, an acidic pH was considered effective for removal.²⁴ In another study, NiO

nanoparticles were used for removal of orange mono azo dye. It was found that the effect of dye removal on the Azo dye was efficient at low pH.¹² In a study conducted on the use of different magnetic nanoparticles for removal of hexavalent chromium, the results considering the effect of independent variables in hexavalent chromium removal, reported that the chromium removal percentage decreased with a change in pH from 2 to 9.3. The results of our study are in accordance with these aforementioned findings, and with an elevation of the solution pH, hexavalent chromium adsorption diminishes significantly.

In this research, the range of the effect of reaction times of 10, 20, 30, and 40 min, as one of the independent variables, was tested at the optimal pH. Adsorption increased with prolongation in the contact time until it reached the reaction equilibrium time. Based on the figure, at an optimal pH (pH = 3), with prolongation of reaction time from 20 to 40 min, chromium removal efficiency increased from 72 to 79%. As this increase is not considered economical in relation to the time, the optimal reaction time was considered to be 20 min. Indeed, at the beginning of the reaction, the empty sites present in the nanoadsorbent cause effective chromium removal; however, after attaining equilibrium, the remaining void spaces are laboriously occupied by chromium due to the repulsive forces between the adsorbent molecules, thereby decreasing the removal efficiency.^{7,25} In a study measuring the effect of adsorption of different magnetic nanoparticles on the removal of hexavalent chromium, the results indicated that the removal percentage increased by prolonging the contact time from 10 to 60 min.²¹ In another study where NiO was used as the adsorbent in the removal of trivalent chromium, the results suggested that with the prolongation of contact time, the trivalent chromium removal efficiency increased, and the contact time of 30 min was reported as the optimal retention time, after which no significant change was observed in the removal efficiency. Collectively, with prolongation of the contact time, the extent of adsorption of hexavalent chromium increases until it attains

equilibrium time, after which it remains almost constant.⁷

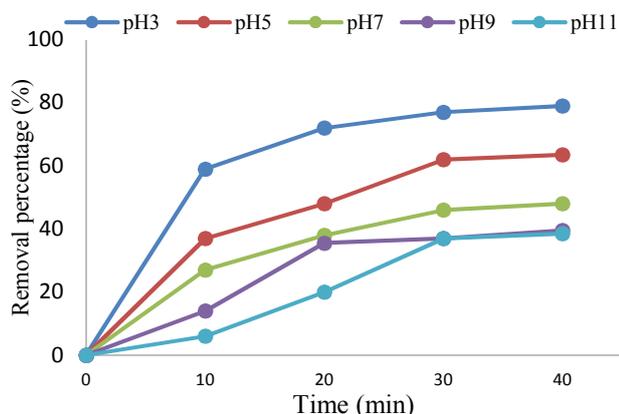


Fig. 4. The chromium removal efficiency by the NiO adsorption process at different pHs and times

The effect of the concentration of chromium on the removal efficiency

The changes in the initial concentration of the adsorbate are another factor affecting the extent of adsorption. To examine the chromium removal efficiency, the effect of the concentrations of 10, 20, 30, 40, and 50 mg/L of potassium dichromate, was examined. At this stage, considering the optimal adsorbent mass of 0.8 g obtained from the previous stage, the rest of the experiment was investigated at the optimal pH. The obtained results are presented in Figure 5. Based on the figure, the results suggested that with an elevation of the concentration of hexavalent chromium from 10 to 50 mg/L, a significant decrease was observed in the extent of chromium removal (72–48%). Indeed, due to the saturation of the active sites of adsorption by the hexavalent chromium molecules, elevation of chromium concentration can lead to diminished adsorption capacity or the active sites of the adsorbent services. In a study where NiO nanoparticles were used for removal of HDR80 dye, the results revealed that at lower dye concentrations, dye removal occurs more effectively.¹² In a study, in which different nanoparticles were used as the adsorbent under optimal values of the process parameters in the removal of hexavalent chromium, the chromium removal efficiency decreased from 97.3 to 58.9% with an elevation of concentration from 50 to 150 mg/L.²⁶ In a study, where zerovalent

iron nanoparticles were used as an adsorbent in the removal of hexavalent chromium, the removal efficiency increased at low concentrations of chromium.²⁵

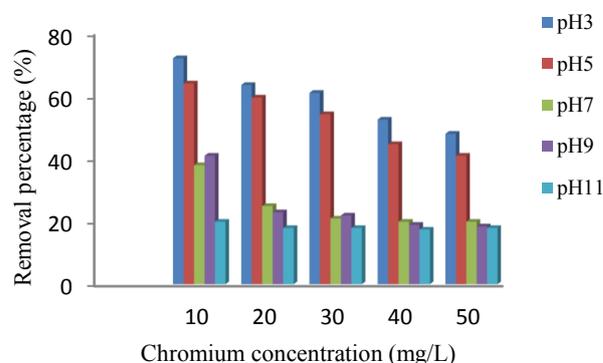


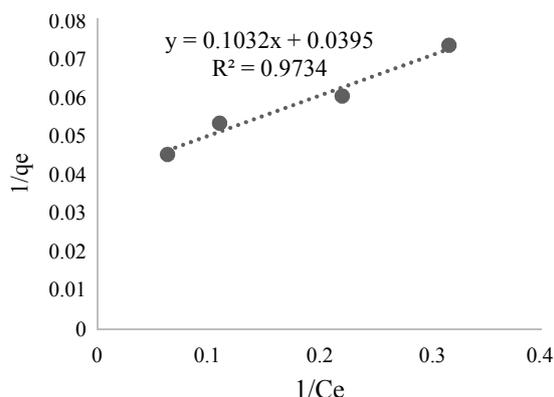
Fig. 5. The chromium removal efficiency by NiO nanoparticles at different concentrations of chromium

Investigating the adsorption isotherm of hexavalent chromium by NiO nanoparticles

By studying the equilibrium adsorption, one can interpret the equilibrium process between the adsorbent and adsorbate. Investigation of the experimental data with the two models of Langmuir and Freundlich and comparison of their correlation coefficients indicated that in the chromium adsorption process by NiO nanoparticles, a considerable correspondence was observed through Langmuir isotherm. Considering the high correlation coefficient ($R^2 = 0.97$) and good correspondence of the results with Langmuir equation, it can be concluded that single-layered and chemical adsorption of hexavalent chromium ions is observed on the NiO nanoparticles. An excellent correspondence of the results confirms the adsorption of hexavalent chromium on NiO nanoparticles following the isotherm (Fig. 6).

The results of the study by Khoshhesab, in the removal of trivalent chromium by NiO nanoparticles, reported that the adsorption isotherm followed the Langmuir model and the maximum chromium adsorption capacity was obtained as 17.5 mg/g.⁷ In another study, where oxide nanoparticles were used in the removal of lead from aqueous solutions, it was observed that the adsorption followed the Langmuir rule, and with an elevation in the pH, the extent of adsorption declined.²⁷ In the study by Shirzad

Siboni et al., the adsorption of hexavalent chromium by an anionic resin also followed the



Langmuir isotherm.¹⁶

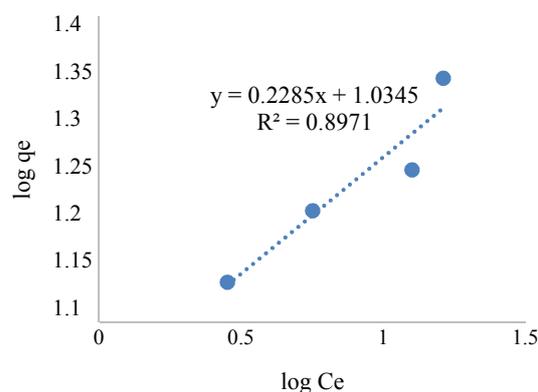
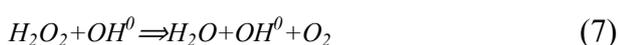


Fig. 6. Freundlich (a) and Langmuir (b) adsorption isotherms for chromium adsorption by NiO nanoparticles

Optimization of the parameters of advanced oxidation UV/H₂O₂ process

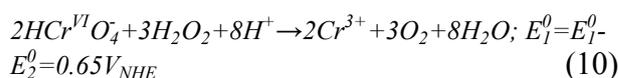
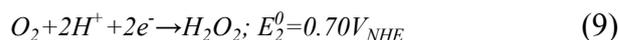
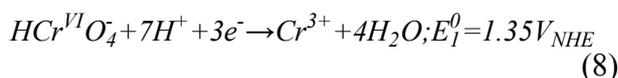
The effect of concentration of hydrogen peroxide in UV/H₂O₂ process

H₂O₂ produces hydroxyl free radicals, which are used along with UV optical degradation in this study.²⁸ In this process, the UV radiation increases the production of the hydroxyl radical from H₂O₂. H₂O₂ is converted to two OH radicals according to the following processes:



To determine the optimal concentration of H₂O₂ in the chromium removal process, different concentrations of H₂O₂ (ranging from 20 to 200 μmoles) were examined on the output solutions of the adsorption process, with the results demonstrated in Fig. 7. As can be seen in the figure, with an elevation in the amount of input H₂O₂ from 20 to 100 μmoles, chromium removal efficiency increased from 35 to 95%, at pH = 3. This behavior is expected because the reduction of Cr(VI) to Cr(III) through proton-coupled electron transfer (PCET) reaction is favored under acidic conditions. The removal efficiency of chromium was reduced (from 95 to 93%) by increasing the H₂O₂ concentration from

100 to 200 μmoles, which can be due to the function of H₂O₂ as a radical scavenger or due to production of radicals with an activity less than that of hydroxyl (such as hydroperoxyl).¹³ Therefore, 100 μmoles was chosen as the optimal dose of H₂O₂. In a study where UV/H₂O₂/TiO₂ was used in the removal of phenol from wastewater, with elevated concentration of H₂O₂, the extent of phenol removal increased, and the optimal H₂O₂ value was reported to be 0.3 g/L.²⁸ The results of this study are in accordance with the findings obtained by Kim et al. in 2015 for removal of hexavalent chromium in the presence of H₂O₂ in frozen aqueous solutions.²⁹ Cr(VI) can be reduced to Cr(III) by H₂O₂ through PCET (reaction 10), which is obtained from the half-reduction reactions of Cr(VI) (reaction 8) and dioxygen (reaction 9). According to reaction 10, the reduction of Cr(VI) by H₂O₂ should be favored at high concentrations of H₂O₂ and protons.²⁹



As can be observed in Figure 8, the removal percentage of hexavalent chromium has been

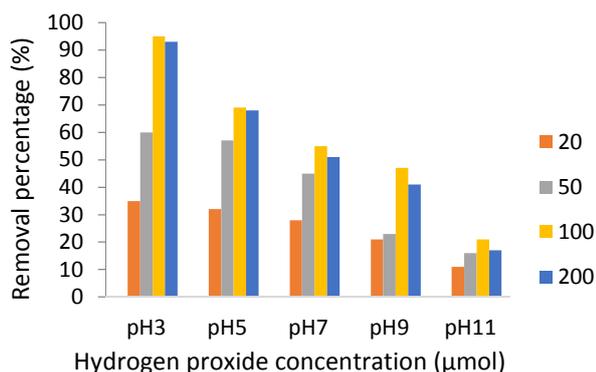
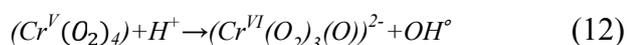
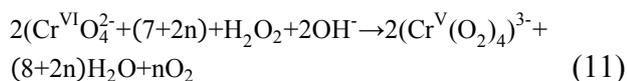


Fig. 7. The hexavalent chromium removal efficiency by H₂O₂/UV process for different concentrations of hydrogen peroxide

maximum at pH = 3, and the results of this study revealed that the optimal pH in the advanced oxidation process was again pH = 3, as with the adsorption process. The reaction mechanism between Cr(VI) and H₂O₂ is critically dependent on the solution pH. Under acidic conditions, the complete reduction of Cr(VI) to Cr(III) by H₂O₂ is favored through PCET reaction (reaction 6). Alternatively, under neutral and basic conditions, the tetraperoxo chromate(V) anion ([Cr^V(O₂)₄]³⁻) is preferentially formed by the simultaneous single-electron transfer from H₂O₂ to Cr(VI) and sequential substitution of oxo ligands by peroxy groups (reaction 11); however, [Cr^V(O₂)₄]³⁻ is easily decomposed into [Cr^{VI}(O₂)₃(O)]²⁻ with the generation of •OH (reaction 12), which creates a null cycle combining with reaction 11.²⁹



The results of this study revealed that the radiation time affects the chromium removal percentage. At the optimal pH, with prolongation of the time from 5 to 40 min, the removal efficiency increased from 71 to 97%. This is due to the fact that in the AOPs, with production of hydroxyl active radical, contaminants are removed and over time it causes increased production of OH radicals.²⁹

Alternatively, as the removal efficiency is 95% within 10 min or as further prolongation caused no significant change in the removal efficiency, thus 10 min was chosen as the optimal reaction time. In the study by Ahmadi et al., who also used UV/H₂O₂ process for the removal of sodium dodecyl sulphate anionic surfactant, the results suggested that with the prolongation of radiation from 2 to 30 min, the extent of removal increases; however, notably, the dye removal growth has not been significant.³⁰ In another study, where UV/NiO was also used in the removal of polyazo dye, the extent of removal did not have any significant change with the further prolongation of radiation after the optimal time, and the optimal retention time and removal efficiency were reported to be 40 min and 68%, respectively.²⁰ The results of this study are in accordance with the findings obtained by Cheng et al.³¹

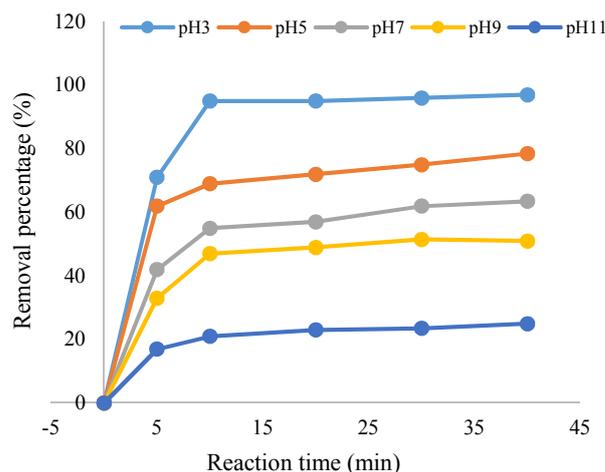


Fig. 8. The hexavalent chromium removal efficiency by H₂O₂/UV process at different pHs and times

Conclusion

This study was performed with the aim to remove chromium by adsorption-advanced oxidation hybrid method. The results revealed that with an elevation in the pH, the removal efficiency of hexavalent chromium by the two-step process of adsorption and advanced oxidation declines, and the maximum removal efficiency was observed at pH = 3. The mechanism for adsorption of hexavalent chromium on NiO nanoparticles had a better correspondence with Langmuir isotherm model.

Collectively, investigation of the efficiency of the advanced oxidation UV/H₂O₂ process after the adsorption process, in the removal of hexavalent chromium, indicated that this method is largely dependent on radiation time, pH of the sample, and H₂O₂ concentration. Collatively, it can be concluded that the use of adsorption process by NiO nanoparticles followed by application of UV/H₂O₂ can be an effective method for the removal of hexavalent chromium.

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