

# Studies on Cr(VI) removal from aqueous solutions by nanotitania under visible light and dark conditions

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**Abstract.** The current study deals with Cr(VI) removal by nanotitania under fluorescent light and dark conditions. The equilibrium removal capacities, 85.85 and 59.4 mg of Cr(VI) g<sup>-1</sup> of nanoparticle were noted for nanotitania interacted under light and dark conditions, respectively, at optimized conditions (pH: 7.0, contact time: 30 min, initial Cr(VI) concentration: 20 mg l<sup>-1</sup>, nanoparticle dosage: 0.1 g l<sup>-1</sup>). Under both the conditions, the equilibrium removal data fitted well with the Langmuir isotherm model. The nanotitania followed a second-order kinetics under light condition whereas a pseudo-second-order kinetics was observed under dark condition. The surface characterization of nanotitania was carried out by zeta potential measurement and transmission electron microscope (TEM). Fourier transform infrared (FT-IR) studies carried out under light and dark conditions indicate the interaction of surface functional groups to Cr(VI). Cr(VI) removal study carried out in the Cr(VI)–Cr(III) mixture showed a decrease in Cr(VI) removal capacity with increase in Cr(III) concentration. A 92% regeneration of nanoparticle was observed indicating efficient reusability of the system. The applicability of the nanotitania in Cr(VI) contaminated water was studied by spiking Cr(VI) in natural water matrices like ground water and lake water.

**Keywords.** Removal capacity; Cr(VI) removal; titania nanoparticle.

## 1. Introduction

The release of toxic heavy metal ions into the environment has increased since the industrial revolution.<sup>1</sup> Hexavalent chromium is one of these metals that accumulated at a rapid state posing serious threats to the human being. Hexavalent chromium has proved to be carcinogenic and its effects more detrimental in comparison with the other valence states like trivalent chromium due to its greater mobility.<sup>2</sup> Therefore, the permissible level in drinking water is set to 0.05 mg l<sup>-1</sup> by US EPA. Therefore, limiting the environmental concentration to the permissible level is essential for the safety of human health and environment.<sup>3</sup>

Ion exchange mechanisms or electrokinetic separation techniques are the conventional physical methods used for Cr(VI) removal.<sup>4–6</sup> Chemical treatments of contaminated waters are not effective due to the secondary pollutions. Therefore, removal by adsorption and catalytic reduction has emerged as a better alternative in recent years.<sup>7,8</sup>

Currently nano-sized materials like nano-membranes, nano-fibres, carbon nanotubes and nanoparticles are being widely used for the treatment of wastewater<sup>9–11</sup> owing to their large surface areas and activity. Nano-sized metal oxides are the major class of nanomaterials that are widely applied for waste water treatment like zinc oxide and iron oxide to name a few.<sup>12,13</sup> Mesoporous titanium oxides are proved to be good substrates for removal of heavy metal

ions like Cd(II), Cr(VI), Cr(III), Cu(II) and Co(II) ions.<sup>14</sup> Nanotitania has been widely employed in removal of dyes like rhodamine B<sup>15</sup> and improve the removal efficiencies by providing high surface to volume ratio. Nanotitania has thus been proved to be a faster adsorbent system than the bulk for the removal of different heavy metals like Zn, Cd, Pb, Ni, Cu.<sup>16</sup> Moreover, photocatalytic property of titania has also been exploited for the reduction of Fe(VI) and Cr(VI) under UV irradiated condition.<sup>17–19</sup> The experiments carried out under dark condition were provided as control.

The present work reports the application of nanotitania without any surface modifications for the removal of Cr(VI) by means of process optimization. The study also aims at quantifying the effect of visible light on Cr(VI) removal compared through the measurement of removal capacities. The specificity of nanotitania towards the solutes by studying the Cr(VI) removal in a mixture of Cr(III) and Cr(VI). Fourier transform infrared (FT-IR) studies are carried out to determine the involvement of surface functional groups in Cr(VI) removal. The application potential of nanotitania in real water matrices and its reusability are also explored.

## 2. Materials and methods

### 2.1 Materials and reagents

Dry titanium (IV) oxide nanopowder (TiO<sub>2</sub>, 99.7% anatase, particle size: <25 nm) Sigma-Aldrich, India, were used

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for metal removal. The stable suspension of nanoparticles was achieved by ultrasonating the samples at 130 W for 5 min by Vibra Cell VCX 130, Sonics, USA. The solutions of hexavalent chromium and trivalent chromium for batch removal study were prepared by dissolving  $K_2Cr_2O_7$  and  $Cr(NO_3)_3 \cdot 9H_2O$  in deionized (MilliQ) water. The pH was adjusted using NaOH (1 N)/ $H_2SO_4$  (1 N). The hexavalent chromium content in solution was analysed using the 1,5-diphenylcarbazide (DPC) method. Reagent was prepared by mixing 0.25% w/v in 50% acetone. Desorption of Cr(VI) bound to nanotitania was carried out using 0.01 N NaOH. All the reagents were of analytical grade and were procured from Sigma-Aldrich, India. The real water samples for removal study were collected from three different sources namely (1) lake water, VIT University, Vellore, India, (2) ground water, Suthipet, India and (3) ground water, Solur, India.

## 2.2 Characterization of nanotitania

The characterization of the above-said nanotitania was carried out previously in our lab and is reported.<sup>20</sup> The hydrodynamic size distribution of nanoparticles was measured in distilled deionized water (Milli Q) by the particle size analyser (90 Plus Particle Size Analyzer, Brookhaven Instruments Corporation, NY, USA). The particle size was represented as the mean hydrodynamic diameter ( $z$ -average mean). The particle size and shape of nanotitania was observed through transmission electron microscopy (TEM, Philips CM12, Netherlands). The crystal structure of nanotitania was characterized using powdered XRD for the confirmation of the anatase phase.

## 2.3 Elemental analysis of chromium

The concentration of Cr(VI) remaining in the solution was measured using a colorimetric method using 1,5-diphenylcarbazide. Samples were mixed with this complexing agent at pH 2.8 to obtain a purple colour. The colour change indicated the presence of Cr(VI). The colorimetric measurements were carried out at a wavelength of 540 nm. Total Cr analysis was carried out at a wavelength of 357.9 nm using a Flame Atomic Absorption Spectrophotometer (Analyst400/HGA 900, Perkin Elmer, USA).

## 2.4 Removal capacity and percentage of removal

Removal capacity and the percentage of removal by nanotitania were measured by the following equations:

$$q = \frac{V(C_0 - C_e)}{m}, \quad (1)$$

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100, \quad (2)$$

where  $q$  is the removal capacity in  $mg\ g^{-1}$ ,  $V$  the volume of chromium in solution (l),  $C_0$  the initial Cr(VI) concentration

in  $mg\ l^{-1}$ ,  $C_e$  the Cr(VI) concentration at the equilibrium and  $m$  the weight of the adsorbent (g). Each experiment was repeated in triplicates. The results are provided as the mean value  $\pm$  S.D.

## 2.5 Optimization of removal conditions under visible light conditions

The optimization studies for Cr(VI) removal were carried in batch experiments under visible light conditions. Visible light irradiation was provided by white fluorescent lamps (3000 lux, 15 W, Philips, India). Removal tests were carried out with  $0.1\ g\ l^{-1}$  of titanium dioxide nanoparticles and  $20\ mg\ l^{-1}$  initial Cr(VI) concentration in 50 ml solution at  $28^\circ C$  for 150 min with varying pH (2.0–12.0). Optimum contact time was determined by carrying out removal study at optimized pH value (initial Cr(VI) concentration:  $20\ mg\ l^{-1}$  and  $0.1\ g\ l^{-1}$  adsorbent dose in 50 ml solution at  $28^\circ C$ ). Removal studies were carried out at different time intervals (15, 30, 60, 90, 120, 150 min) to determine the optimum contact. Different adsorbent dosage ( $0.01$ – $0.5\ g\ l^{-1}$ ) was used in study for determining the amount of sorbent that gives maximum removal. Removal studies were carried out for different initial Cr(VI) concentrations in the range  $5$ – $100\ mg\ l^{-1}$  at optimized parameters to determine the changes in removal capacity.

## 2.6 Cr(VI) removal under dark condition

Cr(VI) removal study was carried out under dark condition in batch experiments in order to determine the impact of the irradiation condition. This was done at the parameters optimized through the above study.

## 2.7 Equilibrium modelling

The mode of interaction of Cr(VI) ions with the nanotitania at equilibrium under visible light and dark conditions were modeled using Langmuir, Dubinin–Radushkevich and Freundlich isotherms at  $28 \pm 1^\circ C$ . The following equations were employed for modeling:

*The Langmuir isotherm:*

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \left( \frac{1}{q_{\max} b} \right). \quad (3)$$

Here,  $q_e$  is the metal concentration present on solid nanotitania,  $C_e$  the metal residual concentration in solution,  $q_{\max}$  the maximum uptake corresponding to sites saturation and  $b$  the Langmuir isotherm constant. The graph was plotted between  $C_e/q_e$  vs.  $C_e$ , to obtain the values of  $q_{\max}$  and  $b$ .

*The Freundlich isotherm:*

$$\log q_e = \log K_f + \left( \frac{1}{n} \right) \log C_e. \quad (4)$$

Here,  $K_f$  is the Freundlich constant and  $n$  stands for removal intensity,  $q_e$  the amount of chromium on the nanoparticle at equilibrium and  $C_e$  the residual concentration of Cr(VI) in the solution. The graph was plotted between  $\log q_e$  vs.  $\log C_e$ , to obtain values of  $K_f$  and  $n$ .

The Dubinin–Radushkevich isotherm:

$$\log q_e = \log q_D - B_D RT \left( \ln 1 + \frac{1}{C_e} \right), \quad (5)$$

$$E_D = \frac{1}{(2B_D)^{1/2}}. \quad (6)$$

Here,  $q_e$  is the amount of chromium on the nanoparticle at equilibrium,  $q_D$  the theoretical removal capacity,  $C_e$  the residual concentration of Cr(VI) in the solution,  $B_D$  the D–R constant and  $E_D$  the energy of the system. The  $\log q_e$  vs.  $\ln(1+1/C_e)$  graph provide  $B_D$  and  $E_D$  values.<sup>21</sup>

## 2.8 Removal kinetics

The removal kinetics was modeled for pseudo-first order and pseudo-second order. The models for Cr(VI) removal under both visible light and dark conditions were checked to determine the kinetics of removal. The best fit was considered for the model with the highest correlation coefficient value ( $r^2$ ).

Pseudo-first-order kinetics is based on the removal capacity and is represented by the following equation:

$$\log(q_e - q_t) = \log_{10} q_e - \left( \frac{k_1}{2.303} \right) t, \quad (7)$$

where  $q_e$  and  $q_t$  are the removal capacities ( $\text{mg g}^{-1}$ ) at equilibrium and at time  $t$ , respectively,  $k_1$  is the pseudo-first-order rate constant ( $1 \text{ min}^{-1}$ ).

The plot of  $\log(q_e - q_t)$  vs.  $t$  gives a linear relationship from which the slope  $k_1$  is determined.

The pseudo-second-order kinetic model equation is represented by the following equation:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2 t. \quad (8)$$

The plot of  $1/(q_e - q_t)$  vs.  $t$  gives a linear relationship if the pseudo-second order is applicable.

## 2.9 Zeta potential study

Deionized water media having different pH values (5, 7 and 9) were prepared. The conductivity of each medium was changed to a constant value, 10 mS using 0.1 M KCl. Nanotitania were added to each preparations at a concentration of  $10 \text{ mg l}^{-1}$ . The zeta potentials were measured by 90Plus particle size analyzer, Brookhaven Instruments Corp., USA, after the preparations were equilibrated for 1 h.

## 2.10 FT-IR analysis

The surface chemical characteristics of the nanotitania were characterized by Nicolet 6700 Fourier Transform-Infra Red Spectrometer (IR solution, Shimadzu, Japan). Un-interacted and Cr(VI) interacted nanotitania under both visible light and dark conditions were mixed with 100 mg KBr and using attenuated total reflectance mode.

## 2.11 Effect of Cr(III) on Cr(VI) removal

Cr(VI) and Cr(III) were mixed in various ratios (5:95, 10:90, 20:80, 50:50) for determining the effect of Cr(III) on Cr(VI) removal. The experiments were carried out under visible light condition. The initial total chromium concentration was maintained at  $20 \text{ mg l}^{-1}$ . The initial and final total Cr in the solution was measured by atomic absorption spectrometry.

## 2.12 Application and reusability of nanotitania

Cr(VI) removal capability of nanotitania in real water matrices was measured by batch studies in (1) lake water, VIT University, Vellore, India, (2) ground water, Suthipet, India, and (3) ground water, Solur, India. The environmental samples were spiked with  $20 \text{ mg l}^{-1}$  Cr(VI) solution and experiments were carried out under visible light condition. The reusability of the adsorbent was analysed by desorption of nanotitania under visible light condition using 0.1 N NaOH.

## 2.13 Statistical analysis

Each set of experiments were conducted in triplicates. Experimentally obtained results were checked for statistical significance by one-way ANOVA coupled with Tukey's multiple comparison test using GraphPad Prism 5.0 software.

# 3. Results and discussion

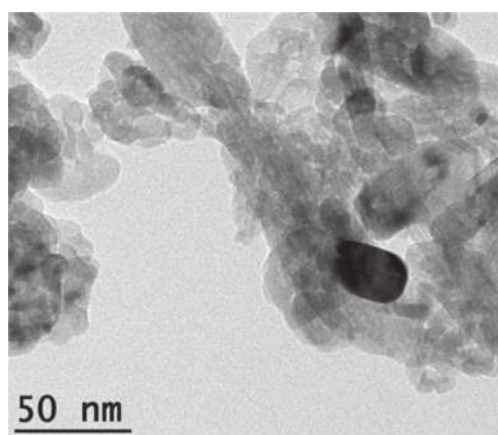
## 3.1 Characterization of nanotitania

The hydrodynamic mean diameter of nanotitania used here was measured to be between 0–50 and 200–300 nm at zero hour ( $t_0$ ) in a previous study carried out by another group in our laboratory.<sup>22</sup> The powdered XRD analysis of uninteracted sample showed the presence of predominantly anatase phase nanotitania. The size range observed by TEM corroborated with the hydrodynamic mean diameter values (figure 1).

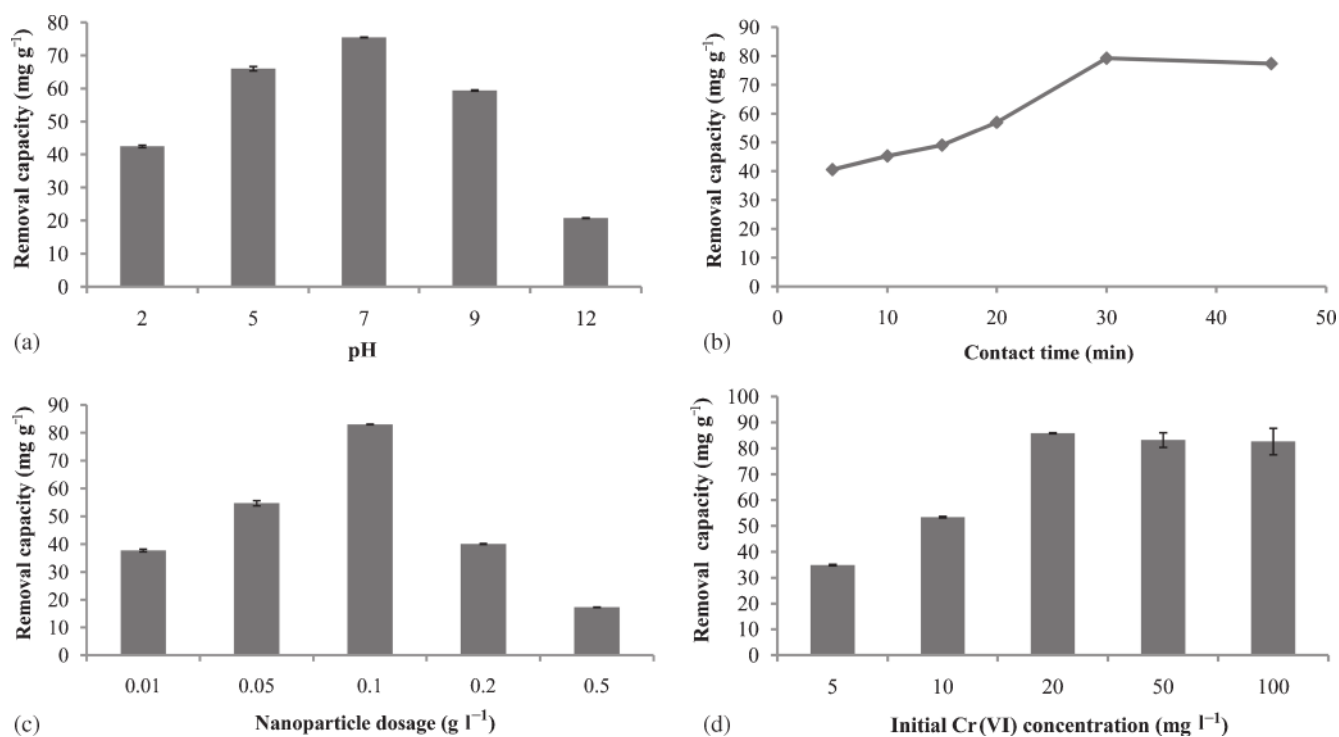
## 3.2 Optimization of removal parameters

Experiments were conducted for the nanotitania under fluorescent light condition at pH ranging from 2.0 to 12.0. The respective removal capacities measured were plotted (figure 2a). A statistically significant increase in the removal

capacities was observed with increase in pH from 2.0 to 7.0, after which it steadily decreased. Thus the maximum removal capacity ( $75.47 \text{ mg g}^{-1}$ ) was observed at pH 7.0. The changes in removal capacity with increasing pH from 7.0 to 12.0 were also found to be statistically significant by one-way ANOVA analysis. At lower pH 7.0 Cr(VI) predominantly exists in the form of oxyanions  $\text{HCrO}_4^-$  and  $\text{CrO}_4^{2-}$ .<sup>23</sup> These anions, being negative in nature tend to interact with the positively charged nanotitania. Thus at this pH range removal capacity was comparatively high due to the columbic force of attraction between the metal ion and the nanoparticle. This result is clearly in trend with the zeta potential measurements (zeta potential charge on



**Figure 1.** Image obtained by TEM of nanotitania.



**Figure 2.** The plots of the removal capacities at different (a) pH, (b) contact time, (c) nanoparticle dosage and (d) initial Cr(VI) concentration.

nanotitania discussed in section 3.6). pH 7.0 was considered as the optimum pH for further experiments.

Experiments were carried out for determining the optimum contact time for removal ranging from 5 to 45 min. As the contact time increased from 5 to 30 min, the removal capacity increased from  $40.56 \text{ mg g}^{-1}$  to a maximum of  $79.24 \text{ mg g}^{-1}$  (figure 2b). However, the change in removal capacity observed beyond 30 min observed to be statistically not significant by one-way Anova and Tukey's multiple comparison test ( $p$ -value: 0.3285). This study shows that 52.5% of maximum removal observed took place in the first 5 min of interaction. At this stage, the surface of nanotitania does not contain Cr(VI) molecule. Absence of chromium in the surface of un-interacted nanotitania was proved by FT-IR studies in section 3.7. Therefore, the large percentage of Cr(VI) removal observed at the initial 5 min interval may have occurred due to the high Cr(VI) concentration gradient between the Cr(VI) aqueous phase and nanotitania solid phase in this time interval. With increase in time, more Cr(VI) moves to the solid phase and the concentration gradient decreases between the solid and aqueous phase.<sup>24</sup> Beyond 30 min, the removal capacity was almost constant. This indicates the attainment of equilibrium, with no active sites promoting Cr(VI) removal. Further experiments with nanotitania were carried out with the optimum contact time at 30 min.

A range of nanotitania dosage [ $0.01$ – $0.5 \text{ g l}^{-1}$ ] was considered when experiments were carried out to determine the nanoparticle concentration at which maximum Cr(VI) removal obtained. The results obtained are provided in

figure 2c. Maximum Cr(VI) removal capacity of  $83.01 \text{ mg g}^{-1}$  was observed when  $0.1 \text{ g l}^{-1}$  of nanotitania was used. An increase in removal capacity was observed with the increase in nanotitania concentration from  $0.01$  to  $0.1 \text{ g l}^{-1}$ . This may be due to the increase in metal interacting surface sites with the increase in the concentration. Therefore, the metal removal is directly proportional to the specific surface area available. However, the removal capacity decreased with the further increase in the nanotitania dosage from  $0.1$  to  $0.5 \text{ g l}^{-1}$ . Meanwhile, the percentage removal of Cr(VI) remained constant ( $41.6 \pm 1.5\%$ ) for this range. With the increase in the nanoparticle dosage, the aggregation of nanoparticles may have occurred. This aggregation may have reduced the specific surface area of the nanoparticles thus exposing fewer functional groups for chromium binding. Moreover, the diffusivity of the Cr(VI) ions through the aggregates may not be sufficient enough to improve the removal capacity with the increase in the nanoparticle dosage, the aggregation of nanoparticles may have occurred. This aggregation may have reduced the specific surface area of the nanoparticles thus exposing fewer functional groups for chromium binding. Moreover, the diffusivity of the Cr(VI) ions through the aggregates may not be sufficient enough to improve the removal capacity. Therefore, the absence of increase in the Cr(VI) removal with the increase in nanoparticle dosage after  $0.1 \text{ g l}^{-1}$  may have resulted from the aggregation of nanoparticle and/or poor diffusion of the Cr(VI) ions within the aggregates when nanoparticle dosage increased.

The effect of initial Cr(VI) concentration on removal was analysed using Cr(VI) concentration from  $5$  to  $100 \text{ mg l}^{-1}$  at pH 7, constant nanoparticle dosage used ( $0.1 \text{ g l}^{-1}$ ) for 30 min. The removal capacity increased with an increase in Cr(VI) concentration up to  $20 \text{ mg l}^{-1}$  ( $85.85 \text{ mg g}^{-1}$ ) after which it remained constant (figure 2d). This may be due to the presence of sufficient amount of surface functional groups that helps in the binding of Cr(VI) molecules within this concentration. The removal capacities did not increase with further increase in Cr(VI) concentration, indicating the saturation of binding sites. This shows that there is constant amount of surface sites available for interaction for a definite amount of nanoparticles present. Therefore, further studies were carried out using  $20 \text{ mg l}^{-1}$  of initial Cr(VI) as the equilibrium metal ion concentration. The AAS analysis yielded total chromium of  $11.54 \text{ mg l}^{-1}$  in the solution after interaction and removal of nanoparticles. This was almost equivalent to the Cr(VI) observed by the DPC method ( $11.41 \text{ mg l}^{-1}$ ). This indicates the absence of reduced Cr(VI) species in the solution.

### 3.3 Removal studies at dark conditions

Studies were conducted at dark conditions to investigate the role of photocatalysis in the removal of Cr(VI). Optimized parameters (pH: 7.0, contact time: 30 min, initial Cr(VI) concentration:  $20 \text{ mg l}^{-1}$ , nanotitania dosage:  $0.1 \text{ g l}^{-1}$ ) were used to carry out the experiments for determining the percentage removal of Cr(VI) and removal capacity. The removal

percentage measured ( $27.35\%$ ) under dark condition was significantly less compared to that observed in the case of light condition ( $42.92\%$ ). Consequently, the removal capacity observed was measured to be  $54.71 \text{ mg g}^{-1}$ . This indicates that the comparatively high removal observed under light conditions may have photocatalytic removal of Cr(VI) from solution.

### 3.4 Equilibrium modelling

Equilibrium data obtained from the above experiment were modelled using Langmuir, Freundlich and Dubinin–Radushkevich isotherms at  $27 \pm 1^\circ\text{C}$ . The various isotherm parameters obtained are given in table 1. The nanotitania followed Langmuir model isotherm with best fit under both light and dark conditions with the highest regression coefficient,  $r^2$ . The  $q_0$  value obtained by removal experiments were comparable to that obtained theoretically from the Langmuir plot. The Langmuir model proves a monolayer mode of binding of Cr(VI) molecules on nanotitania at equilibrium.

### 3.5 Removal kinetics

The rate of removal of metal ions on the adsorbent was investigated by removal kinetics. Pseudo-first-order and pseudo-second-order kinetics were modeled for this study for initial Cr(VI) concentrations ( $5$ – $100 \text{ mg l}^{-1}$ ). The corresponding rates  $k_1$  and  $k_2$  are presented in table 2. Under light condition, a pseudo-second-order reaction was observed. This indicates that the rate of removal is depending upon the reaction sites present in excess on the surface of nanotitania. Here, Cr(VI) concentration is the rate determining step. The correlation coefficient  $r^2$  value suggests that the under dark condition, system fit best for pseudo-first order than the pseudo-second order. This indicates that, in the absence of sufficient reaction sites, solute will be in excess. Therefore, the capacity of nanotitania for removal becomes the rate limiting step.

**Table 1.** Comparison of  $q_{\text{max}}$  from Langmuir, Freundlich and Dubinin–Radushkevich isotherms for nanotitania under light and dark conditions.

Parameter	Light	Dark
<i>Langmuir constants</i>		
$q_0$ ( $\text{mg g}^{-1}$ )	88.495	55.55
$b$ ( $\text{l mg}^{-1}$ )	0.58	1.8
$r^2$	0.998	0.999
<i>Freundlich constants</i>		
$K_f$ ( $\text{mg g}^{-1}$ )	37.15	35.48
$n$ ( $\text{l mg}^{-1}$ )	4.78	9.09
$r^2$	0.775	0.751
<i>D–R constants</i>		
$q_D$ ( $\text{mg g}^{-1}$ ) <sup>2</sup>	77.62	61.65
$B_D$ ( $\text{mol}^2 \text{kJ}^{-2}$ )	0.0005	0.0006
$E_D$ ( $\text{kJ mol}^{-1}$ )	78.85	24.47
$r^2$	0.909	0.959

### 3.6 Zeta potential study

The surface charge of nanotitania in dispersion was studied by zeta potential measurements. They were conducted at different pH ranges (pH 5–9). The positive zeta potential values were obtained for all the pH. The highest was observed at pH 7.0 ( $32 \pm 1.7$  mV). This indicates that nanotitania had a higher stability at pH 7.0. The zeta potential values observed for pH 5.0 and 9.0 are  $28 \pm 1.3$  and  $27 \pm 0.7$  mV. The differences in the zeta potential values observed for the media with pH 5 and 9 were found to be statistically insignificant when tested by one-way ANOVA followed by Tukey's multiple comparison test. The zeta potential measurements indicates the presence of columbic force of attraction between the positively charged adsorbent surface and the negatively charged oxyanionic chromate ions through columbic interactions.<sup>25</sup> The decrease in the removal capacity at pH 5.0 and 9.0 compared to that at 7.0 can be therefore related to the lowering of reaction site density in terms of the positive charge present on the surface.

**Table 2.** Pseudo-first-order and pseudo-second-order kinetic models parameters for nanotitania.

Models	Light	Dark
<i>Pseudo-first order</i>		
$k_1$ ( $1 \text{ min}^{-1}$ )	0.010	0.015
$q_e$ ( $\text{mg g}^{-1}$ )	100	55.55
$r^2$	0.860	0.993
<i>Pseudo-second order</i>		
$k_2$ ( $1 \text{ g min}^{-1}$ )	0.015	0.011
$q_e$ ( $\text{mg g}^{-1}$ )	74.21	48.97
$r^2$	0.942	0.741

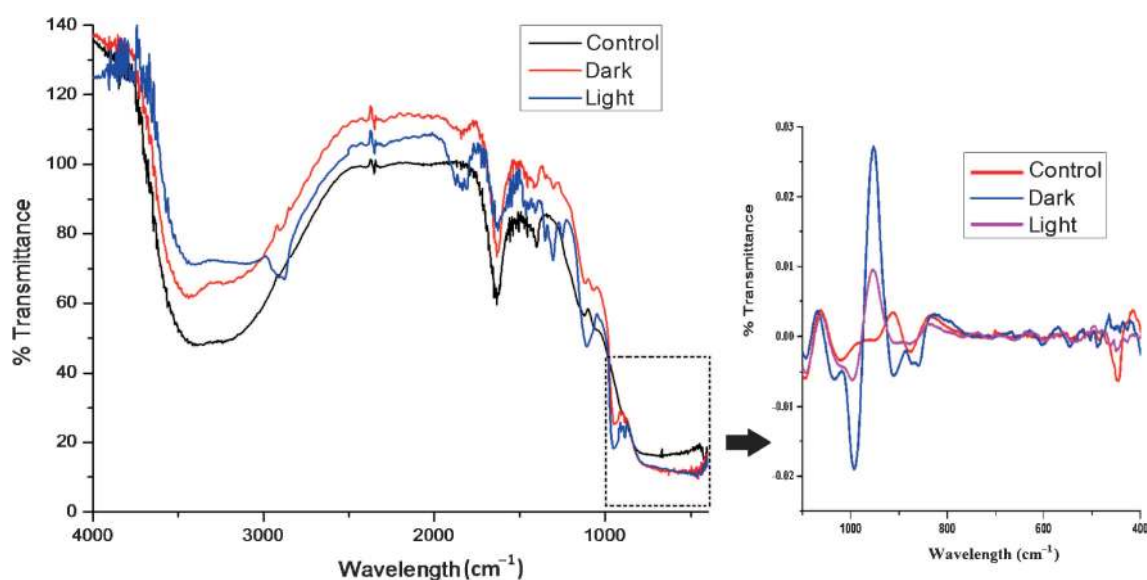
### 3.7 Surface chemical analysis by FT-IR spectroscopy

The FT-IR spectra of un-interacted and Cr(VI) interacted nanotitania under light and dark conditions were obtained (figure 3). In the spectrum of un-interacted nanotitania, the peak observed at  $3456 \text{ cm}^{-1}$  ( $-\text{OH}$  stretching vibration).<sup>26</sup> The major bands observed can be assigned as follows:  $2927 \text{ cm}^{-1}$  ( $-\text{CH}$  stretching vibrations),  $1634 \text{ cm}^{-1}$  ( $-\text{NH}_2$  bending vibrations),  $1420 \text{ cm}^{-1}$  (stretching vibration of  $\text{C}-\text{O}$ ). These peaks may represent the functional groups present on the surface of the nanotitania like carboxyl and amide. The peak at  $420 \text{ cm}^{-1}$  corresponds to the  $\text{Ti}-\text{O}-\text{Ti}$  stretching vibrations which is evident from the secondary derivative of transmittance spectra (figure 3 (inset)).<sup>27</sup>

Upon interaction with Cr(VI), under both the conditions, new sharp peaks corresponding to  $\text{Cr}-\text{O}$  vibrations at  $921$  and  $870 \text{ cm}^{-1}$  were formed. The absorbance intensity of these bands under light condition was higher than that under dark condition, indicating more binding under light condition. In addition, the intensity of peak at  $2927 \text{ cm}^{-1}$  increased while that at,  $1634$  and at  $1420 \text{ cm}^{-1}$  decreased. This indicates the probable involvement of the surface functional groups in the interaction with Cr(VI). The peak at  $420 \text{ cm}^{-1}$  was almost negligent in the secondary derivative spectra obtained for light and dark studies. This indicates the active involvement of this bond in interaction with chromium ions and their probable complexation on the surface.

### 3.8 Effect of Cr(III) on Cr(VI) removal

The effect of Cr(III) on Cr(VI) removal was analysed by carrying out synthetic mixtures of Cr(VI) and Cr(III) in different concentration ratios under visible light conditions. The total Cr removed estimated by AAS and the reduction in



**Figure 3.** FT-IR spectra of un-interacted nanotitania, Cr(VI) interacted nanotitania at light conditions and at dark conditions. Insight: Secondary derivative spectra from  $1100$  to  $400 \text{ cm}^{-1}$ .

**Table 3.** Effect of Cr(III) on Cr(VI) removal carried out on nanotitania.

Initial concentration of Cr(VI) (mg l <sup>-1</sup> )	Initial concentration of Cr(III) (mg l <sup>-1</sup> )	Removal capacity in the presence of Cr(III) (mg g <sup>-1</sup> )	Removal capacity in the absence of Cr(III) (mg g <sup>-1</sup> )	Reduction in removal capacity (%)
5	95	7.2	34.9	79.3
10	90	21.3	53.3	60.1
20	80	42.2	85.8	50.8
50	50	50.5	83.2	39.3

**Table 4.** Cr(VI) removal capacities obtained for nanotitania in different real water matrices.

Sample ID	Location	Removal capacity (mg g <sup>-1</sup> )
LW	Lake water, VIT University, Vellore	75.41
GW	Ground water, Suthipet, Vellore	69.78
GW	Ground water, Sulur, Vellore	71.83

removal capacity are tabulated (table 3). The % reduction in Cr(VI) removal capacity decreased with the decrease in the Cr(III) concentration in the mixture. It was the highest (79.37%) when the mixture of 95 mg l<sup>-1</sup> of Cr(III) and 5 mg l<sup>-1</sup> of Cr(VI) was studied, which decreased with the decrease in the Cr(III) concentration in the binary mixture. A decrease in Cr(III) concentration to 50 mg l<sup>-1</sup> increased the Cr(VI) removal capacity by 87.31%. This variation was proved statistically significant by one-way ANOVA. The results show that nanotitania binds to the chromium (III) as well as Cr(VI) non-specifically.

### 3.9 Application and reusability of adsorbent

The efficiency of nanotitania for the removal of Cr(VI) in the natural water matrices was analysed by carrying out experiments in the water samples collected from three different sources namely, (1) lake water, VIT University, Vellore, (2) ground water, Suthipet, Vellore and (3) ground water, Sulur. The experiments were conducted by spiking the water samples with 20 mg l<sup>-1</sup> of Cr(VI) under visible light condition. The results obtained are provided in table 4. The removal capacity observed for the environmental samples were near to that observed for distilled deionized water at this initial Cr(VI) concentration. However, a statistically significant decrease in the removal capacities was observed in the case of both the ground water samples. This may have occurred due to the interference of inorganic ions in these samples which needs further study.<sup>28</sup>

Reusability of the nanotitania was analysed by conducting desorption studies using 0.1 N NaOH under visible light conditions and at pH 7.0. At 20 mg l<sup>-1</sup> initial Cr(VI) concentration, the total Cr removed from the solution was found to be 8.79 mg l<sup>-1</sup>. With the treatment of NaOH, the adsorbent system was regenerated by 92% leaving 0.71 mg g<sup>-1</sup> total Cr on the adsorbent. This shows that the reversible binding

nature of Cr(VI) and nanotitania due to the coulombic force of attraction, largely increases the reusability of the system.

## 4. Conclusion and implication

The results from the present study show the potential of nanotitania in chromium removal from aqueous solutions. The difference in removal capacities achieved by nanotitania under light and dark conditions was statistically significant indicating the photoassisted removal of chromium. A monolayer of binding of Cr(VI) to nanotitania was observed by the Langmuir isotherm irrespective of the lighting conditions. The zeta potential study suggests the chromium (VI) removal by means of oxy-anionic mode of binding through coulombic interactions. The involvement of surface functional groups as reactive sites is evident from the FT-IR study. In short nanotitania was able to remove Cr(VI) efficiently under light conditions by photoassisted adsorptive removal from contaminated waters. The details mechanism of removal needs further investigation.

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