Chapter 4

Green Synthesized TiO_2 nanoparticles for photo-catalytic removal of lead (Pb) from explosive industry wastewater

In this chapter, green synthesized titanium dioxide nanoparticles (TiO_2 NPs) as mentioned in chapter 3 are used to evaluate the photo-catalytic performance of nanoparticles for removal of lead from industrial wastewater. Photo-catalytic studies are performed in a self-designed reactor. Inductive coupled plasma spectroscopy (ICP) is used to determine the lead concentration before and after treatment. The results conclude that around 75.5% chemical oxygen demand (COD) removal and 82.53% lead (Pb^{2+}) removal is obtained. This is the first report on the removal of lead through photo-catalytic action of green synthesized TiO_2 NPs.

4.1 Introduction

Environmental safety is currently a prime global challenge. In particular, deteriorating water quality is an alarming global concern. Various types of wastewater discharges bearing pollutants like heavy metals, dyes, and pesticides enter different water bodies and contaminate them. Among these contaminants, heavy metals being non-biodegradable and hazardous are posing serious threat to humans and other living beings. Due to their high aquatic solubility and easy access to living body through the food chain they are causing various health disorders (Abdel et al., 2003, Acharya et al., 2013, Dhir, 2014, Dong et al., 2010, Hu et al., 2011, Mondal, 2009, Singha et al., 2012,). Among the heavy metals, lead (Pb) is a priority pollutant and is widely present in environment (Mondal, 2009). Electroplating, mining, metal finishing, lead smelting and lead based chemical

manufacturing units are some of the sources from which lead enters the water bodies (Halim et al., 2003). As per the World Health Organization (WHO) and Environmental Protection Agency, USA, the maximum permissible limit of lead in the drinking water is 0.05 ppm (Goe et al., 2005; Ucun et al., 2003). So, it is of prime importance to restrict the lead concentration in the range of 0.05-0.10 ppm before discharge to local water bodies (Ucun et al., 2003; Vilar et al., 2005).

Explosive industries which use highly explosive compounds in its detonators, mines, rocket boosters, etc., due to their improper disposal practices often contaminate surrounding land and water bodies (Lee et al., 2002). One such contaminant, lead (Pb), which is primarily used as lead azide in the detonators is often detected as lead ion pollutant in the water bodies. Plenty of efforts are being made globally to eliminate the problem of lead pollution through regulatory as well as technological measures.

Conventional approaches like physical, chemical and biological processes are being used for waste water treatment including removal of heavy metals (Neppolian et al., 2002). The efficacy of each of these processes depends on factors like technological feasibility, efficiency, and economics (Sin et al., 2012).

Photo catalysis is a kind of chemical method which is being considered due to its simplicity, low cost, non-toxic, high degradation efficiency and excellent stability (Nakata et al., 2012). In the process of photo-catalysis, oxidation is induced by UV light and carried out by photo-catalysts such as TiO_2, ZnO, etc. (Nakata et al., 2012). Among these, TiO_2 with band gap energy of 3-3.5 eV possesses excellent photo-catalytic behaviour (Lijuan et al., 2012). The electron transfer mechanism in TiO_2 from valance band to conduction band

during exposure to UV or visible light generates a hole (h^+), which further contacts with water to form an OH radical. This OH radical will act as a strong oxidizing agent and is responsible for removing organic pollutants, pesticides and heavy metals like lead (Pb) (Chen et al., 2001) from the waste water through photo oxidation mechanism. The generation of electron and OH radicals takes place as shown below:

$$TiO_2 + h\nu \rightarrow TiO_2 (e_{CB}^- + h_{VB}^+) \quad (4.1)$$

$$TiO_2 (h_{VB}^+) + H_2O_{ad} \rightarrow TiO_2 + {}^{\cdot}OH_{ad} + H^+ \quad (4.2)$$

$$TiO_2 (h_{VB}^+) + {}^{-}OH_{ad} \rightarrow TiO_2 + {}^{\cdot}OH \quad (4.3)$$

$$TiO_2 (e_{CB}^-) + O_2 \rightarrow TiO_2 + {}^{\cdot}O_2^- \quad (4.4)$$

$${}^{\cdot}O_2^- + H^+ \rightarrow HO_2^{\cdot} \quad (4.5)$$

$${}^{\cdot}O_2^- + HO_2^{\cdot} \rightarrow {}^{\cdot}OH + O_2 + H_2O_2 \quad (4.6)$$

$$2HO_2^{\cdot} \rightarrow O_2 + H_2O_2 \quad (4.7)$$

$$TiO_2 (e_{CB}^-) + H_2O_2 \rightarrow TiO_2 + {}^{-}OH + {}^{\cdot}OH \quad (4.8)$$

Thus, the photocatalytic degradation of lead proceeds by photooxidation induced by positive radicals given by TiO_2 nanoparticles. Here, Pb (II) ion oxidizes to Pb (IV) to finally form PbO_2 (Wahyuni et al., 2015).

$$Pb^{2+} \rightarrow Pb^{4+} + 2e \quad (4.9)$$

$$Pb^{4+} + 2\ OH^- \rightarrow PbO_2 + 2H^+ \quad (4.10)$$

Nano-particle synthesis through chemical route is generally expensive and polluting due to the use of synthetic chemicals which are detrimental to the living ecosystem (Devatha et al., 2016). On the other hand, synthesis through green route using extracts of plants, microbes,

enzymes, etc. is simple, less toxic, economical and eco-friendly way to synthesize nanoparticles (Ajitha et al., 2015). Few works on green synthesized nano-particles and their usage in wastewater treatment are already reported (Wang et al., 2014). Nano-particles of TiO_2 can be produced using physico-chemical methods like chemical vapour deposition, sol-gel processes etc. As mentioned earlier in chapter 3, these methods are costly, require harsh conditions (high pressure, temperature, and pH) and are also highly polluting. These problems have encouraged researchers to produce TiO_2 through eco-friendly and cheaper methods. Literature on synthesis of TiO_2 NPs using various plant extract like *Glycosmis cochinchinensis* (Rosi et al., 2018), *Jatropha curcas* (Goutam et al., 2018), *Moringa oleifera* (Patidar et al., 2017), *Aloe barbadensis Miller* (Rao et al., 2015), and *Psidium guajava* (Santhosh et al., 2014) is summarised in Table 4.1.

Table: 4.1 Synthesis of TiO_2 nanoparticles from different plant extract

SL. No.	Plant used for synthesis of TiO_2 NPs	Plant Image	Particle size(nm)	Reference
1	***Glycosmiscochin chinensis***		**35- 45**	(Rosi et al., 2018)
2	***Jatropha curcas***		**75**	(Goutam et al., 2018)
3	***Moringa oleifera***		**12.22**	(Patidar et al., 2017)

4	***Aloe barbadensis Miller***		**20**	(Rao et al., 2015)
5	***Psidium guajava***		**32.58**	(Santhosh et al., 2014)

In this chapter, already synthesized titanium dioxide nanoparticles are used for the removal of lead present in the explosive industry waters. Less literature availability in relation to treatment of explosive industry disposal waters combined with coincidental visit to explosive industry has inspired me to consider this waste water as a source. Experimental methodology and obtained results are elaborately discussed in the following sections.

4.2 Experimental

4.2.1 Materials

Synthesized TiO_2 nanoparticles (18±6nm and $105 m^2 g^{-1}$) are taken for this experiment. Industrial waste water having lead is collected from a commercial explosive manufacturing industry, Gomia, Jharkhand, India. It is used directly without any purification and stored in a glass bottle and kept in the refrigerator for use.

4.2.2 Photo catalytic Properties

The photo-catalytic activity of the synthesized TiO_2 nano-particles is directly tested using industrial wastewater collected from explosive manufacturing industry, situated at Gomia,

Jharkhand, India. The industrial wastewater samples are collected and stored at 6-7°C for further physicochemical analysis. Collected sample (500 mL) without altering the pH is treated photo-catalytically using the TiO_2 NPs (0.3 g) for 12 h in a self-designed and fabricated photo catalytic reactor (Figure 4.1). The reactor consists of three UV lamps of 15 W each placed at equal intervals around a centrally placed reaction vessel. Initially, to establish the adsorption equilibrium between lead in wastewater and TiO_2 nanoparticles, 0.3g TiO_2 nanoparticles are kept in 100ml of wastewater in the dark (without UV) for 30 min and analysed for decrease, if any, in the lead concentration. The UV lamps were then switched on and the wastewater samples (2mL) are taken out from the UV reactor at a regular interval of time and are centrifuged at 9000 rpm for 10 min to obtain a clear supernatant of industrial wastewater which was stored in sample bottles for analysis.

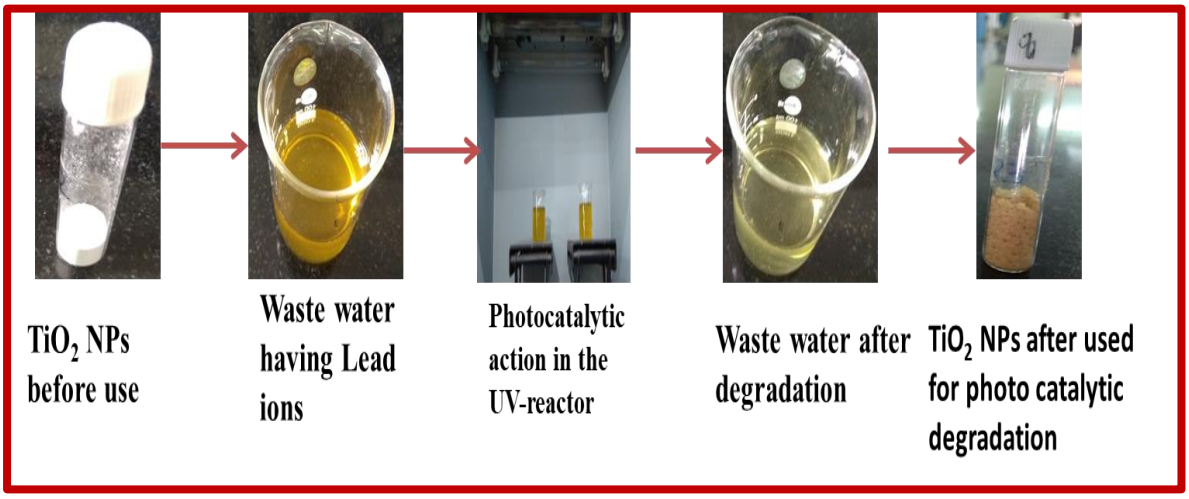

Figure 4.1 TiO_2 used as photo catalyst for removal of lead (Pb)

The lead concentrations are analysed by inductive coupled plasma spectroscopy (Thermo Scientific, USA). The operating conditions of the ICP instrument before analysis was set as: camera temperature: −45.65°C, optics temperature: 38°C, pump rate = 45 rpm, gas flow rate =1.5 L/min (argon) and wave length (λ) = 220.353 nm. Standards taken for calibration

plot are 1.25 ppm, 2.5ppm, 5ppm, and 10ppm. A control sample without nanoparticle is also taken as reference for the photo-catalytic degradation study. For a comparative study, another experiment is done in the dark with TiO_2 nanoparticles in the sample and samples are collected at a regular interval for analysis.

The change in chemical oxygen demand (COD) is also monitored to determine the overall removal efficiency of pollutants. The COD analysis is carried out using a UNIPHOS COD analyser (Uniphos Envirotronic Pvt Ltd, Gujarat, India). Uniphos COD Analyser is a microprocessor based instrument for the determination of COD in the range of 50-2000 mg/L in water sample. The analysis involves the measurement of absorbance of the digested samples using COD analyser. The digestion of the sample water involves the water sample being treated with Mercuric Sulphate to remove the interference of chloride ions and subsequently mixing it with an appropriate amount of oxidizer mixture viz. potassium dichromate, silver sulphate catalyst and sulphuric acid and digesting the mixture in a closed vial at 150° C for 2h as shown in the Figure 4.2 and also the reagents used in this process are prepared as

Reagent A: 2.3g $K_2Cr_2O_7$, 20ml conc.H_2SO_4 and 3.34g $HgSO_4$ were added to 50ml of distilled water, allowed to cool and diluted to 100ml.

Reagent B: 1g Ag_2SO_4 was added to 100ml of conc. H_2SO_4, stir until dissolved.

Also with the help of colorimeter, the true and apparent colour in water and wastewater in 0 to 500 PCU range was measured (Hanna Instruments, USA, HI 96727).

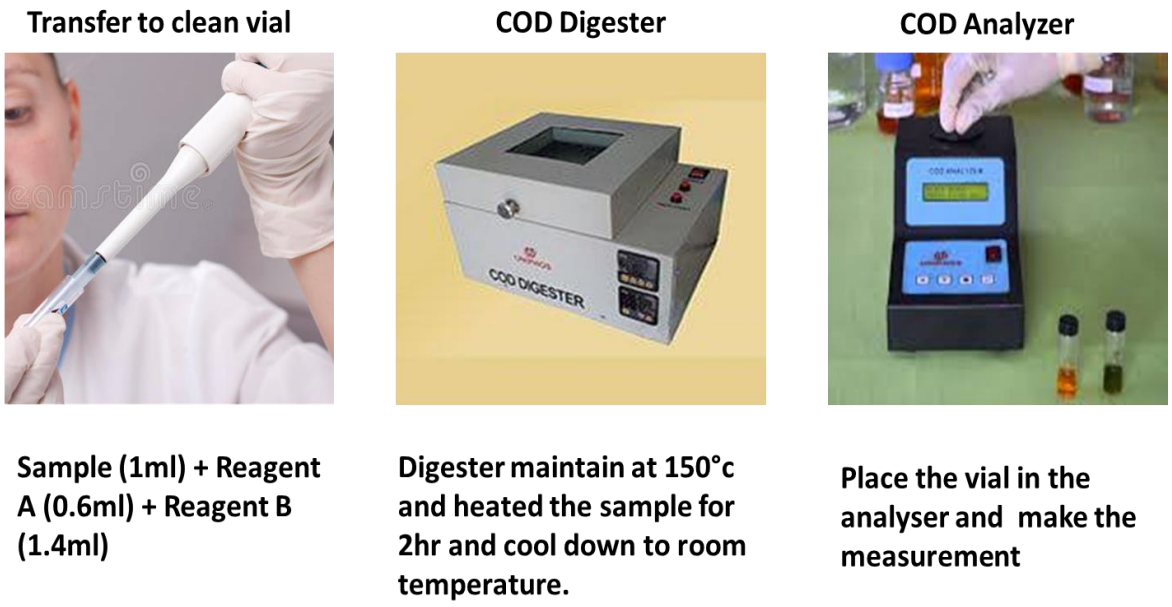

Figure 4.2 COD analysis measurement steps

4.3 Results and discussion

4.3.1 Photo catalytic Activity

The performance of synthesized nanoparticles is tested for the photo catalytic treatment of lead-contaminated explosive industrial wastewater. The physicochemical properties of waste water before and after treatment are presented in Table 4.2.

Table: 4.2 Water characteristics before and after treatment

Physico-chemical parameter	**Before treatment**	**After treatment**
pH	7.6	7.8
Lead (ppm)	8.621	1.5
COD (mg/L)	8450	2004
Color (a.u.)	Yellow(0.15)	Light Yellow(0.07)

The degree of treatment of wastewater is analysed by measuring the concentration of Pb as a function of time. At the same time, it is also significant to carry out a blank test (without NPs) to ascertain that removal is mainly due to the photo catalytic reaction of TiO_2 NPs. The effectiveness of the treatment process is evaluated by calculating the removal efficiency using the equation (4.11).

$$R\ (\%) = Pb_0 - Pb_t / Pb_0 \times 100 \qquad (4.11)$$

where Pb_0 and Pb_t are the initial and final concentrations of lead in wastewater before and after the photo catalytic treatment. The values of lead concentration obtained from the ICP analysis are given in Table 4.3.

Table: 4.3 ICP and COD values at different condition

Time (h)	**Pb Concentration (ppm) in absence of TiO_2 NPs + UV**	**Pb Concentration (ppm) in in presence of TiO_2 NPs + dark**	**Pb Concentration (ppm) in presence of TiO_2 NPs + UV**	**COD (mg/L) in presence of TiO_2 NPs + UV**
0	8.621	8.621	8.621	8450
2	8.621	8.560	7.844	6300
4	8.598	8.412	7.397	5500
6	8.598	8.35	5.325	4900
8	8.595	8.35	4.713	3800
13	8.595	8.35	2.170	3187
16	8.595	8.35	1.506	2187
17	8.595	8.35	1.500	2004

It is seen that as time changed from 0 to 17 h, a sharp decrease in Pb concentration from 8.6 ppm to 1.5 ppm in the presence of TiO_2 + UV is observed compared to experiments carried in dark condition where the concentration decreased is only up to 8.35 ppm. This sharp decline in concentration is attributed to the photo-catalytic activity of TiO_2 NPs on lead ion present in the water sample, whereas in dark condition the minor change in concentration is attributed to the adsorption of Pb on TiO_2 surface (Lee et al., 2002). The decrease in the Pb concentration in the photolysis condition (only UV light) was due to the photo-degradation of Pb by the strong UV wavelength. Comparative results as shown in Figure 4.3(a) for un-catalyzed and TiO_2-catalyzed change with time (12 h) reveal that the transformation rate is about 82.53% in TiO_2-catalyzed and only 3.14% in un-catalyzed condition. This not only supports but also proves the role of TiO_2 NPs in the photo catalytic removal of Pb**.** Effect of Pb concentration on the photo catalytic transformation rate is also investigated and results are presented in Figure 4.3(a). The first-order kinetic model as shown in the equation (4.12) is used to analyse the photo catalytic degradation of Pb (Murruni et al., 2007)

$$r_{Pb} = -dC_{Pb}/dt = k_{app} C_{Pb} \quad (4.12)$$

After integrating Equation 4.12 can be rewritten as

$$\ln (C_{Pbo}/C_{Pb}) = k_{app}\, t \quad (4.13)$$

where C_{Pbo} and C_{Pb} are the initial and final concentrations of Pb (ppm), k_{app} represents the pseudo first-order constant (h^{-1}), and t is the time (h).

The graph between ln (C_{Pbo}/C_{Pb}) versus time (t) is observed to be linear (Figure 4.3(b)) and the rate constant 0.097 h^{-1}. The R^2 value being greater than 0.96, indicates a good

correlation with the first order kinetics. The large surface area of TiO_2 NPs provides more active sites which are responsible for the effective removal of Pb from the aqueous solution.

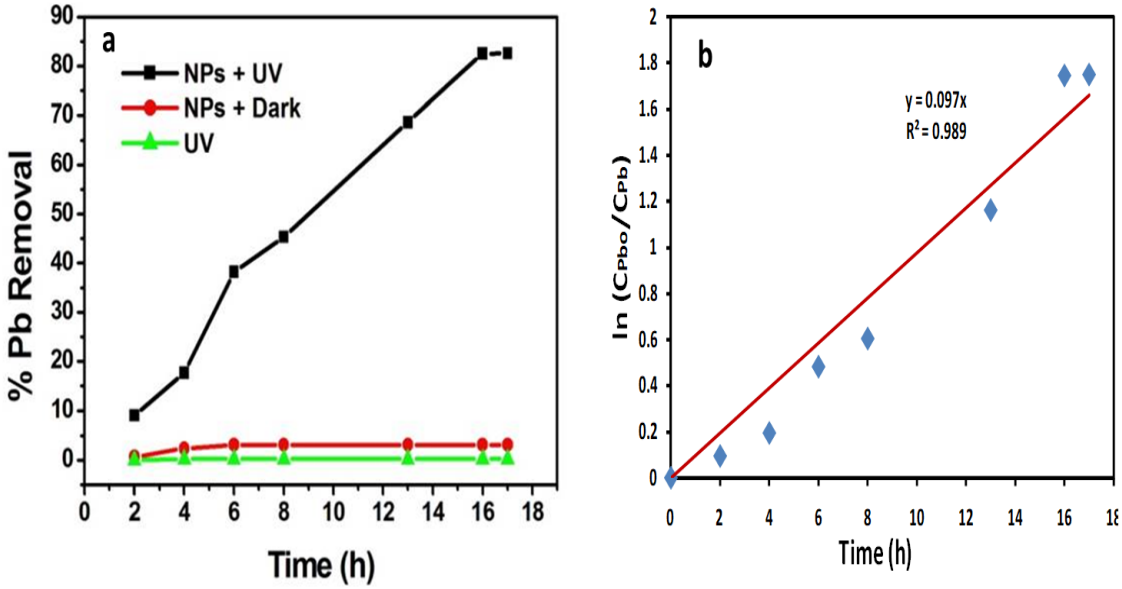

Figure 4.3 (a) Pb removal profile in UV and dark condition in the presence of synthesized TiO_2 NPs; (b) Kinetic data for Pb removal with synthesized TiO_2 NPs.

The chemical oxygen demand (COD) of the original sample is 8450 mg/L, which is greater than the permissible limit. Water bodies with high loading of COD disturb the ecological functions which lead to adverse effect to aquatic life (Saxena et al., 2016). However, a considerable decrease (75.5 %) in the chemical oxygen demand (COD) is observed after the photo-catalytic treatment of wastewater using synthesized nanoparticle i.e. TiO_2 NPs. The COD removal profile is shown in Figure 4.4(a). The COD removal as shown in Figure 4.4(b) also shows a good agreement with the first-order kinetic with R^2>0.95 and rate constant 0.121 h^{-1}.

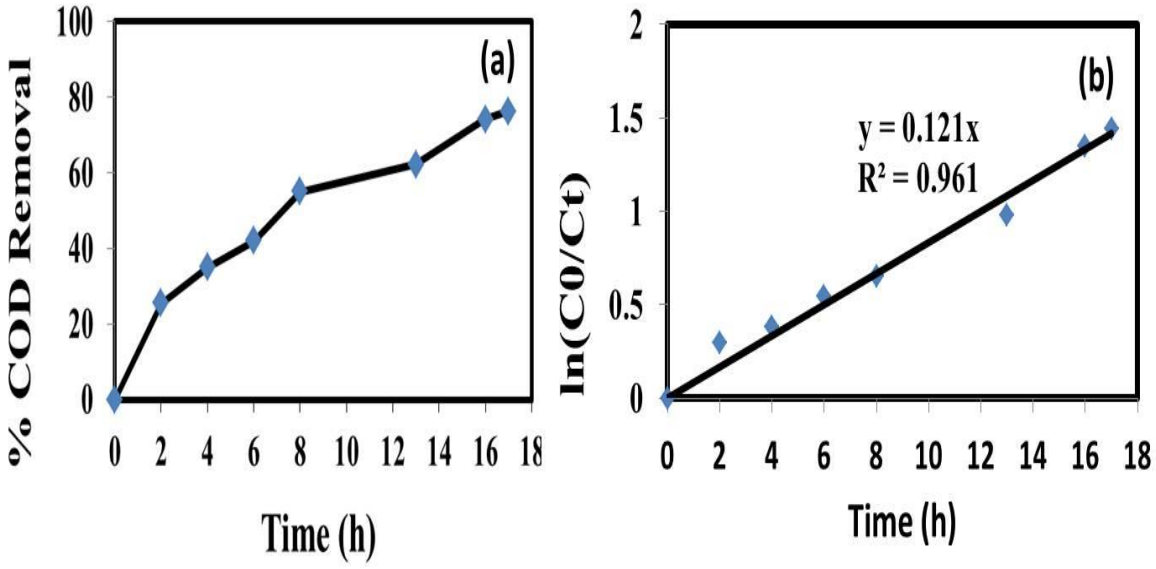

Figure 4.4 (a) COD removal profile in UV light; (b) First order kinetics plot for COD removal with the synthesized TiO_2 nanoparticles.

The lead ion removed in the form of PbO_2, settles over the surface of the nano catalyst which reduces the active sites for further reaction. Also, the nano catalyst being used in dispersed form makes recovery and reusability a tedious task. Treatments like water spray followed by acid treatment can be used to recover the spent TiO_2 nanoparticles, however the process costs stand un-economical and the by-products formed during the process attracts further pollution. To overcome this issue with dispersed nano catalyst, usage of nano particles in immobilized form by means of a support can be explored.

4.4 Conclusion

In this work, the performance of the green synthesized TiO_2 nano particles is evaluated in a self-made photo reactor. The concentration of heavy metal ions is analysed by inductive

coupled plasma spectroscopy as well as the overall removal efficiency of pollutants is monitored by COD analyser. Here the synthesized nanoparticles are successfully used as a photo-catalyst for removal of lead from explosive industry waste water in a cost-effective way with 75.5 % removal of chemical oxygen demand (COD) and 82.53 % removal of lead (Pb^{2+}). Kinetic study reveals that 1^{st} order kinetics is followed for photo-catalytic removal of lead as well as the COD removal. Thus, utilization of TiO_2 nanoparticles as an effective photo catalyst for the in-situ remediation of lead containing waste water is shown in this chapter and these nanoparticles might also be helpful for other environmental remediation studies as well.