ISSN: 0975-8585

Research Journal of Pharmaceutical, Biological and Chemical Sciences

Adsorption Behaviour of Lead Removal from Aqueous Solution on to NanoTitanium Dioxide.

Gowri V[1*] and Thenmuhil D[2].

[1]Department of Civil Engineering, St. Josephs Insitute of Technology, OMR Road, Chennai, 600119, Tamilnadu, India.
[2]Department of Ceramic Engineering, A.C Tech, Anna University, Chennai, 600025, India.

ABSTRACT

Clean and safe water to meet human needs is essential. Water resource gets polluted due to human interventions. The removal of toxic heavy metals from ground water is a matter of paramount importance due to the fact that their high toxicity causes major health problems. Removal of heavy metals is often ineffective and expensive in developing countries like India. Adsorption is an emerging technique for water treatment utilizing nano materials. The focus of this study is the removal of lead ions from aqueous solution by nano titanium dioxide coated over clay pellet. The synthesis and characterisation of nano titanium dioxide was studied by X-ray diffraction (XRD), scanning electron microscope (SEM), and Fourier transform infrared spectroscopy (FITR). SEM image showed that TIO_2 nanoparticles were porous structure. FTIR confirms the presence of hydroxyl and carboxyl groups which were the main functional groups involved in the adsorption. The availability of negatively charged functional groups has the ability to absorb heavy metals present in the aqueous solution. The effect of initial concentration of metal ions and effect of contact time on the removal process was investigated. It was found such that the removal efficiency remained constant after an optimum time interval. The removal efficiency was found to be ranging from 85%-95%.
Keyword-Nano materials, Heavy Metals, Lead removal, Titanium dioxide

Corresponding author
Email id: gowrisenthilkumar@gmail.com

ISSN: 0975-8585

1. INTRODUCTION

The hydrologic cycle is an important natural process. The greatest challenge in the globe is to provide clean affordable water to meet human needs under the fast growing demand. Ground water is a major source of water for human population and even today more than half the world's population depends on ground water. In developing countries like India, due to rapid industrialization various pollutants enter the environment and by this means ground water also gets polluted. Contaminants are mostly found mixed in air, water and soil. The removal of toxic metal from water is important to sustain an ecological balance in environment. The major concern of environmental issue of heavy metal is that even at low concentration there is a high toxic effect of heavy metal contamination in water streams and waste water. The toxic metals can be removed from water and waste water by adsorption technique. Nanotechnology provides a platform to monitor, detect, remove and improve the quality of the environment. In this study an attempt has been made to remove heavy metal from aqueous solution by using clay pellets surface with nano titanium dioxide.

1.1 Heavy Metals

Due to anthropogenic activities within the ecosystem various pollutants like heavy metals enter into the ecosystem and cause pollution. The heavy metals enter into the groundwater from variety of sources either by natural or manmade activities. Natural sources include chemical weathering of rocks and soils, decomposing vegetation and animal matter, wet and dry fallout of atmospheric particulate matter. However, manufacturing processes act as the major sources of metals in many industrial urban areas. Table 1 describes the heavy metals employed in industries.

Table 1. Heavy Metals Employed in Industries

INDUSTRY	Cd	Cr	Cu	Fe	Hg	Mn	Ni	Zn	Pb
Paper mills	-			-		-			
Organic and Petro chemicals			-			-	-		
Alkalis, Chlorine and inorganic chemicals			-			-	-		
Fertilizers						-			
Petroleum refining					-	-			
Steel plants						-			
Vehicle industry				-		-		-	-
Glass, asbestos and cement industry	-		-	-	-	-	-	-	-
Textile mills	-		-	-	-	-	-	-	-
Power plants	-		-	-	-	-	-		
Leather industry	-		-	-	-	-	-	-	-

Table 2.Permissible Limit and Effects of Heavy Metals

Heavy metal	Permissible limit according to BIS (mg/lit)	Effects due to variance from limits
Lead	0.05	Cumulative poisoning and increase in blood pressure
Chromium	0.05	Results in haemolysis, renal and liver failure
Cadmium	0.01	Can cause severe lung damage and irritation, with shortness of breath tc.,
Iron	1	Leads to heart disease, liver problems and diabetes
Zinc	5	Extensive exposure to zinc can cause respiratory disorders

Heavy metal contamination affects the health of human beings by directly influencing the behaviour by impairing mental and neurological function, influencing neurotransmitter production and utilization, and altering numerous metabolic body processes [1], [2]. Table 2, discusses about the permissible limits for heavy metals prescribed as per BIS (IS1172:1993) and their effects due to deviation from their limits.

1.2 Treatment of Heavy Metals

The treatment of wastewater processes includes chemical precipitation, adsorption, ion exchange, electrolytic techniques, and evaporation exist for removing heavy metals from water [3]. The application of these technologies have limitations that restrict the applications in which they can be used. The drawback of these technologies are that they create sludge that must be disposed as hazardous waste and are pH sensitive, so they cannot target specific metals and cannot remove extremely low or high concentrations of metals [4]. The nanomaterials are used in the removal of heavy metals due to its enhanced affinity, capacity and selectivity for heavy metals and other contaminants. The advantages of using nanomaterials are their higher reactivity, larger surface contact and better disposal capability [5]. The treatment of heavy metals has been attempted since it gives better efficiency and has less drawbacks compared to conventional methods.

2. NANO TECHNOLOGY

2.1 Nano Materials

Nanomaterial are particle with size between 1nm to 100 nm and the ratio of surface area to volume ratio is high which helps in detecting sensitive contaminants [6]. Basic unit of measure for nanomaterial called a "nanometer" (abbreviated nm). Derived from the Greek word "nano" is a metric prefix and indicates a billionth part (10^{-9}). Nanotechnology is also used to prevent the formation of pollutants or contaminants by applying the material technology, industrial processes and others. The nanotechnology applications in the field of environ,ment may be classified as restoration and purification of contaminated material, pollution detection and pollution prevention [7],[8],[9].

Nanoparticles are either naturally occurring or engineered. The natural process like volcanic ash, soot from forest fire, by-products of combustion process are that are naturally occurring (e.g., volcanic ash, soot from forest fires) are physically and chemically heterogeneous and often termed ultrafine particles. Engineered nanoparticles are intentionally produced and designed with very specific properties related to shape, size, surface properties and chemistry. These properties are reflected in aerosols, colloids, or powders. The behaviour of nanomaterial may depend more on surface area than particle composition.

Relative-surface area enhance its reactivity, strength and electrical properties. The nano particles may be bought from commercial vendors or generated via experimental procedures by researchers in the laboratory. Examples of engineered nanomaterials include: carbon buckey balls or fullerenes; carbon nanotubes; metal or metal oxide nanoparticles (e.g., gold, titanium dioxide); quantum dots, among many others. [10].

2.2 Different Types of Nano Materials

1. *Carbon Based Materials:* These nanomaterials are composed mostly of carbon, taking the form of a hollow spheres, ellipsoids, or tubes. Spherical and ellipsoidal carbon nanomaterials are referred to as fullerenes, while cylindrical ones are called nanotubes.
2. *Metal Based Materials:* These nanomaterials include quantum dots, nanogold, nanosilver and metal oxides, such as titanium dioxide.
3. *Dendrimers:* These nanomaterial are nanosized polymers built from branched units. The surface of a dendrimer has numerous chain ends, which can be tailored to perform specific chemical functions which is useful in catalysis. Also, because three-dimensional dendrimers contain interior cavities into which other molecules could be placed, they may be useful for drug delivery.
4. *Composites:* Composites combine nanoparticles with other nanoparticles or with larger, bulk-type materials.

2.2.1 Nano Metal Oxides (NMO)

Nanomaterials are used as adsorbents for removal of heavy metal ions. The nanomaterial should be nontoxic, should posses high sorption capacity and easily removed from surface of nanomaterial. . The nano sized metal oxides most widely studied NMO's include Iron Oxides, Manganese Oxides, Aluminum Oxides, and Titanium Oxides which are present in different forms, such as particles, tubes and others. The adsorption performance is affected by the size and shape of NMO's [10].

1. *Titanium Dioxide (TiO_2):* Titanium dioxide (TiO_2) is a common material that has been used in products like paints and cosmetics because of its stable brilliant white color. Anatase, rutile and brookite are the crystal structures of TiO_2 (11). Rutile is thermodynamically stable at room temperature. Anatase is kinetically stable and will not readily transform to the rutile phase at room temperature. The anatase phase of TiO_2 has been used as a photocatalyst to oxidize heavy metal pollutants in water.
2. *Nano Titanium Dioxide:* Nano titanium dioxide is commercially available in market as degussa-P25 in a powder format (resembles like talcum powder) of size ranging from 23nm – 40nm.

2.3 TiO2 for Water Purification

Chemical precipitation, ion exchange, adsorption, membrane filtration and electrochemical technologies are few methods that have been proposed for efficient heavy metal removal from waters. The conventional methods consume high quantities of chemicals and generate effluents and large amounts of residual sludge [4]. The flexibility in design and operation provides an advantage in case of adsorption technique. Due to the reversible nature of most adsorption processes, the adsorbents can be regenerated by desorption processes. The desorption processes are easy to operate, high efficient and has low maintenance cost [11]. Since the adsorption process has become a major techniques for heavy metal removal from water/wastewater.

Hua et al., [12] studied the removal efficiency, adsorption and the process underlying the removal property of various metal oxides under varying conditions. The removal efficiency of nano metal oxides with the porous host supported metal oxides were compared and found that the later was found to be more useful for commercial purpose than the regular nano metal oxides. The solar water purification using the Titanium dioxide with improved binding agents was studied and different binding agents were used for the study and it was found that the sodium acetate was most efficient and safe to use [10]. The same can be prepared easily in remote areas using baking soda and vinegar.

The effect of the nano titanium dioxide on the human health and environmental impact were studied in a step wise analysis and a comprehensive environmental assessment of nano titanium dioxide on water treatment was presented [11]. It was found that the environmental impact of the titanium di oxide was negligible and only when particle size of less than 20 nm was found to be carcinogenic.

From the earlier studies undertaken with heavy metal removal using nano material absorbance, it was found that TiO_2 was used successfully to remove heavy metals from water such as Lead, Iron, Zinc, Chromium, Copper, Cadmium and Mercury with an efficiency of 82%-85% with low sludge production [4]. In this study the sorption based on photocatalytic properties of titanium dioxide the sorption of the heavy metal is reduced. The surfaces of the nanosized TiO_2 promotes the adsorption of lead

3. MATERIALS AND METHODS

The study was conducted by batch experiment to determine the efficiency of adsorption of lead using titanium dioxide coated clay pellet. The efficiency in reducing of lead concentration from the prepared synthetic solution would provide the direction to treat lead from the contaminated water.

3.1 Clay Pellet Preperation

The clay pellets were prepared by mixing 80% of commercial ball clay of particle size 2µm and 20% of quartz (to strengthen the clay pellet). The mixture was made into a plastic mass by adding appropriate quantity of water by weight of clay. The mixture was then introduced into a mechanical extruder for deriving a bar of clay mix of diameter 1cm (approx.).The clay bar was then cut to make clay pieces of size varying from 1 to 1.25 cm and rolled into the shape of ball. The clay balls were drilled with a hole for ease in handling purpose during the doping of Titania. The resultant wet clay pellets were dried in oven at 120◦C for 24 hours and fired at 1100◦C for 3 hours in an electric furnace. The resultant clay pellet weight was recorded to be 4.0 to 4.5g.

3.2 Synthesis of Nano Titanium Dioxide

1) *Sol-gel Synthesis of Titanium Dioxide:* Titanium tetra–isopropoxide and iso-propanol in the volume ratio of 17:40 was added drop-wise to solution containing acetic acid, iso-propanol and water in the volume ratio of 15:60:5 to obtain titanium dioxide sol. It was then stirred well using magnetic stirrer for 24 hours to get titanium dioxide gel [13-14].

2) *Coating of Nano Titanium Dioxide Over Clay Pellet: The resultant gel is applied as a thin layer of film over the clay pellet by dipping the clay pellet in the resultant gel. A thin layer of gel will be formed over the pellet and was dried at 110◦C for 24 hours and fired at 1100 ◦C for 3 hours.*

3.3 Characterization of TiO2 nanoparticles

Surface morphology of TiO2 was carried out on a Scanning Electron Microscope. X-ray diffraction was also recorded. Fourier Transform Infrared spectroscopy was recorded to study the functional group with a Perkin Elmer Fourier Transform Infrared Spectrometer.

3.4 Test Procedure

The working aqueous solutions were prepared for the known concentrations such as 5, 10 and 15 ppm using lead nitrate ($PbNO_3$) mixture. 1.598 g of $PbNO_3$ was dissolved in 100ml of distilled water with constant stirring to a beaker containing distilled water to make up a volume of 1 litre which would contribute as a 1000ppm stock solution. The prepared stock solution was used to prepare the working solutions of 5ppm, 10ppm and 15ppm concentration. The clay pellet coated with titanium dioxide was then put into the aqueous solution. The aqueous solution was tested for different lead concentration at 30, 60, 120 and 180 min after the start of batch mixing. The batch experiment was conducted in mechanical shaker at 150rpm. The final concentration of the lead was analyzed using atomic absorption spectrophotometer. By comparing the results of concentration of lead before and after the mixer operation with pellet the efficiency of the treatment was arrived.

3.5 Removal Efficiency

Batch experiments were conducted and the removal efficiency was computed using the formula:

$$\% \text{ Removal} = ((C_i – C_f)/C_i) \times 100$$

Where,

C_i- initial concentration of lead and C_f –final concentration of lead

4. RESULTS AND DISCUSSION

4.1 IR characterization of TIO_2

The FT-IR spectra of sol-gel derived TiO_2 were collected by a Fourier Transform Infrared Spectroscopy to gain a better insight into the functional groups available on the surface of the nano titaniuim dioxide coated over the clay pellet. Fig 4 shows the FTIR spectra of TiO_2. The spectrum shows peaks at 3560.58 cm-1, 3509.86 cm-1, 3429.96 cm-1, 3358.02 cm-1, 3304.15 cm-1 and 3088.07 cm-1. The bands at 3560.58 cm-1 and 3509.86 cm-1is attributed to the surface O-H group. The high concentration of O-H is attributed at the peaks of 3429.96 cm-1, 3358.02 cm-1, 3304.15 cm-1 and 3088.07 cm-1. The bands at around 1629.05 cm-1 can be assigned to C=C stretching. The hydroxyl and carboxyl stretching were the main functional groups involved in the adsorption.

ISSN: 0975-8585

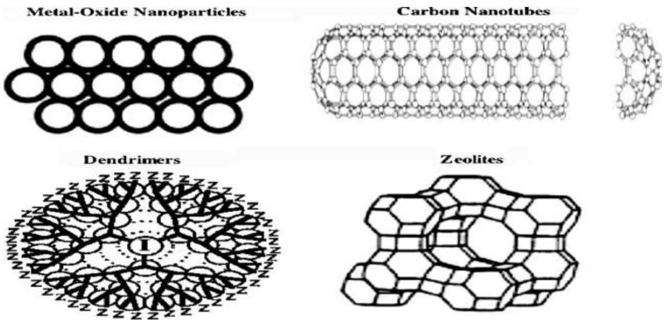

Figure 1. Selected nanomaterials currently being evaluated as functional materials for water purification (Courtesy: Savage and Diallo 2005)

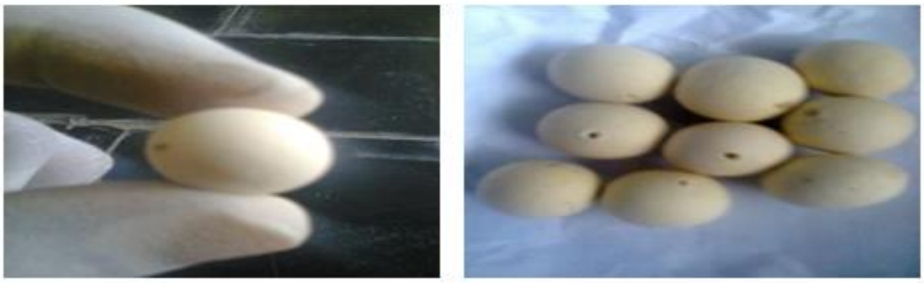

Figure.2. Clay Pellets

Figure. 3 Coating of Titanium Dioxide Gel Over Clay Pellet

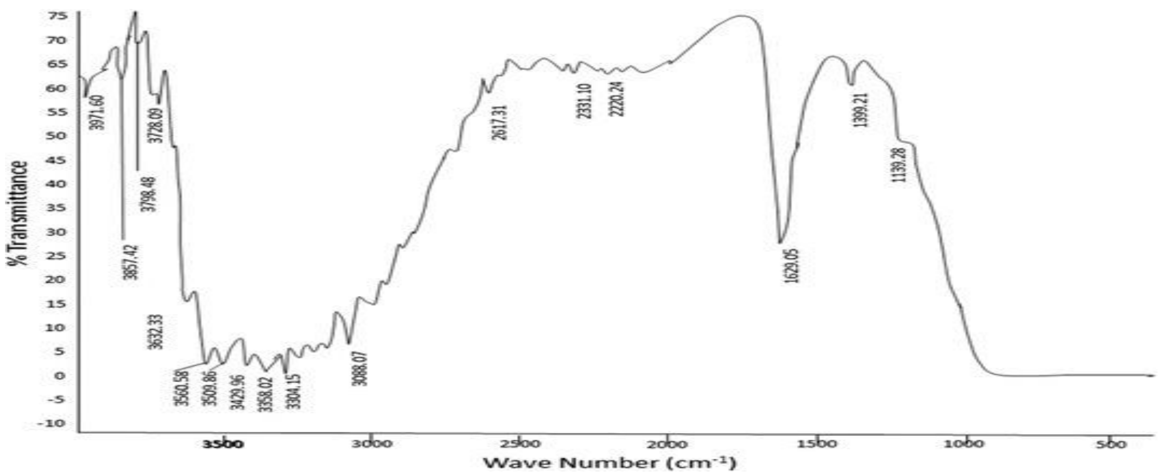

Figure 4. FTIR spectra of TiO2

An increased participation of these groups would explain a more stable bond and higher equilibrium constant. The importance of carboxyl groups in heavy metal binding has been extensively confirmed. These groups provide negative charges to attract divalent metal cations. Fourest and Volesky observed that cadmium and lead uptake decreased with the partial or total sterilization of carboxyl groups.

The specific surface area is known to be an important property for characterizing adsorptivity of adsorbents. (12 lead pellet). The clay pellets had a density of 1.58 g/cc with 6.1% porosity. The surface of titanium dioxide coated clay pellets is given in the optical microscope image (Fig.5). The Scanning Electron Microscope (SEM) image of titanium dioxide particles are given in Fig. 6.

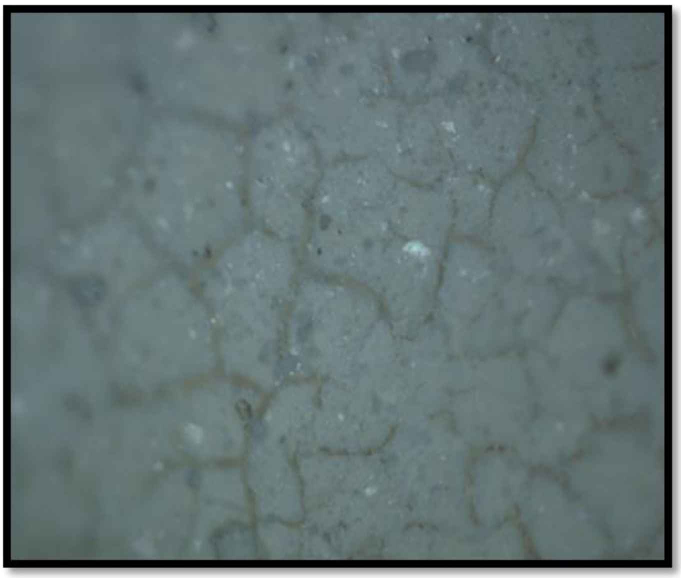

Figure. 5 Optical Microscope Image of Titanium dioxide Coated Clay Pellet Surface

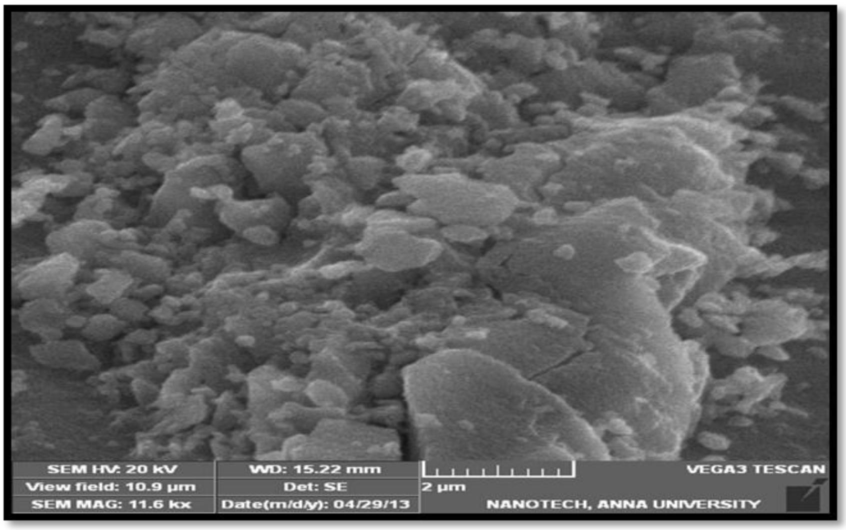

Figure.6 SEM Image of Titanium Dioxide Particles

4.2 Batch Experiment

The batch experiments were conducted by using the mechanical orbital shaker for varying interval of detention time and varying initial lead concentrations. The process of removal was the adsorption of the metal ions to the surface of the titanium ions by weak van der waal's force of attraction between the molecules. This process was enhanced by the photo catalytic property of the titanium metal oxide [15].

ISSN: 0975-8585

After conducting the batch experiment, resultant samples were analysed for lead concentration with atomic absorption spectrophotometer. A blank sample for varying concentration was also analysed for determining the initial concentration of lead before the experiment. The variation of final lead concentration with respect to the initial concentration of lead present in blank sample results in removal efficiency of lead. The initial pH of the stock solution was varied from 5.15 to 5.45. Table 3 describes the results of batch experiment and the removal efficiency of lead.

Table 3.Test Results of Batch Experiment

Time of Experiment (Hours)	Initial Concentration (ppm)	Final Concentration (ppm)	% Removal
	5 ppm		
0.5	4.88	0.213	95.64
1	4.88	0.218	95.53
2	4.88	0.179	96.33
3	4.88	1.164	76.15
	10ppm		
0.5	8.63	0.883	89.77
1	8.63	0.544	93.70
2	8.63	0.162	98.12
3	8.63	1.497	82.65
	15ppm		
0.5	14.27	0.559	96.08
1	14.27	0.530	96.29
2	14.27	0.231	98.38
3	14.27	2.225	84.41

4.2.1 Effect of Contact Time

The batch experiments were conducted for varying time of contact from 0.5 hrs to 3 hrs. The variation of removal efficiency of lead for various time intervals was studied (Fig 7). It was found that the efficiency varied only a negligible percent with respect to time. The final concentration of the lead was found to decrease after a contact time of 2 hrs because the layer of titania on the pellet adsorbs maximum lead and then becomes saturated that no more transfer of ions take place in the equilibrium. At 30 min time and 1 hr time interval the concentration is almost stable hence the equilibrium time is taken as 1 hr.

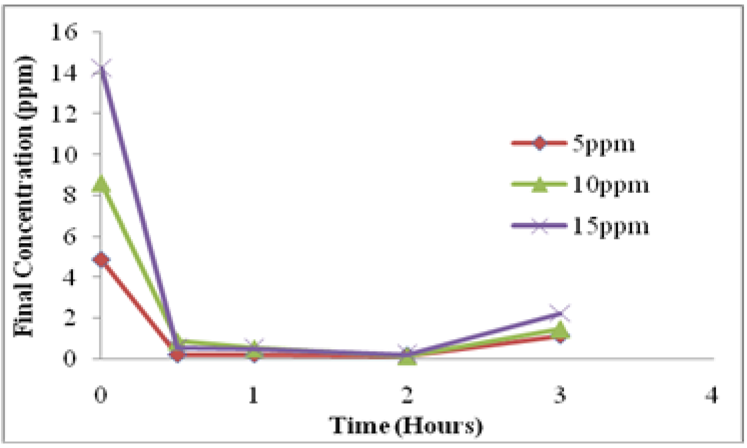

Figure. 7. Variation of final concentration of lead with respect to time

4.2.2 Effect of Initial Concentration

The effect of initial concentration was studied by adding 2.5, 5 and 7.5 ml of stock solution to the 250 ml of working solution. The initial concentrations of the solution were estimated as 4.88, 8.63 and 14.27 ppm.

The variation of removal efficiency of lead for various initial concentrations was studied using a scatter plot (Fig.8). It is observed that at lower initial concentration the removal was efficient and as concentration increases the removal efficiency decrease. This shows that with the increased availability of lead concentration there is high amount of lead available for adsorption but with time difference the adsorption decreases.

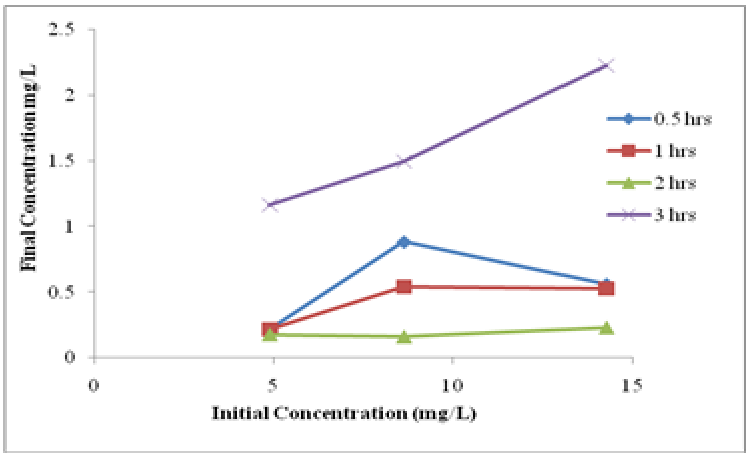

Figure.8. Variation of final concentration of lead with respect to initial concentration of lead

4.2.3 Percentage Removal of Lead

The efficiency was found to be high in comparison to the conventional methods of heavy metal treatment. Fig.9 shows the percentage efficiency of lead removal for the three different concentration of lead at varying contact time. By undergoing the batch experiment the efficiency of removal of lead was determined to be 85%-95% using titanium dioxide coated clay pellet.

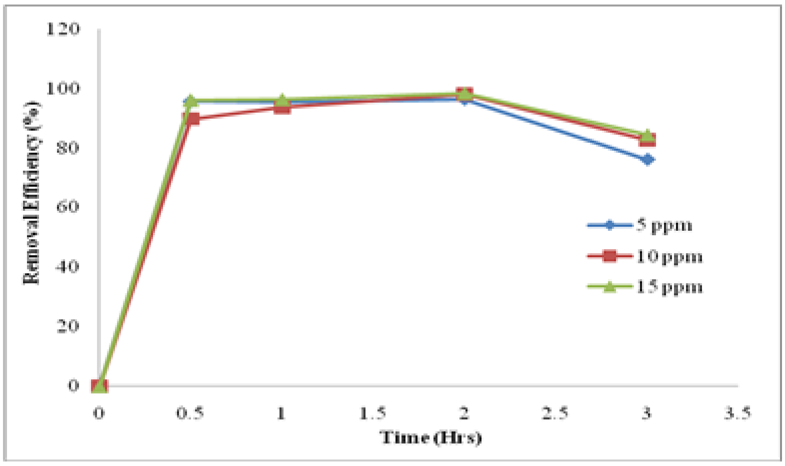

Figure.9. Variation of removal efficiency of lead with respect to time

The efficiency of removal of the lead from the water using titanium dioxide was affected by the process of adsorption of the lead on to the titanium dioxide. The photo catalytic and chelating property of the titanium dioxide affects the property of adsorption. The adsorption process takes place as the two electrons in the excited state get adsorbed with valence bond of the lead atom.

5. CONCLUSION

The efficiency of the removal of lead under various concentrations of the lead was determined. The efficiency of the removal of lead process against time and initial concentration were inferred such that the removal efficiency remained a constant after an optimum time interval. The removal efficiency of lead was found to be ranging from 85%-95% and optimum time of contact for optimal removal was 1 hour.. The aqueous solution shall be stirred at the rate of 150 rpm with detention time of the pellets in the solution for 1 hour. The pellets placed for adsorption in the tanks must be well ventilated and should be made of glass so as to permit sunlight which helps in photo catalytic activity.

The amount of sludge produced is less when compared to the conventional method. The efficiency of the process is higher than the other methods. There is no organometallic compound formed hence the purification process is simple [16]. The effect of increasing titanium dioxide concentration on the lead removal efficiency study can be taken up. Further attempts can be done for the treatment of waste water and industrial effluents.

6. REFERENCES

[1] Georgaka A, and Spanos N. Global NEST Journal 2010; 12: 239-247.
[2] Sajil Kumar PJ, Davis Delson P, Thomas Babu P. Bull Environ Contam Toxico. 2012; 1: 793–798.
[3] Savage and Diallo. Journal of Nanoparticle Research 2005; 7: 331–342.
[4] Azevedobertrand Z. Removal of Lead, Cadmium and zinc from industrial effluents using Nanofiltration and reverse osmosis membrane. Procs. of 13th international conference on Heavy metals in the environment, Brazil, 2005.
[5] Yunus IS, Harwin IS, Kurniawan AD, Adityawarman, Indarto A. Environmental Technology Reviews 2012; 1: 136–148.
[6] Lu GQ and Zhao XS. Nanoporous Materials : Science and Engineering, in Nanoporous Materials-an Overview, World Scientific, Singapore, 2004.
[7] Royal Commission on Environmental Pollution (RCEP),"Novel materials in the environment: the case of nanotechnology," [online] Available: http://www.defra.gov.uk/ 2008.
[8] Hyder MAH., "Nanotechnology and environment: potential application and environmental implications of nanotechnology," Master thesis, Technical University of Hamburg- Harburg, Germany, 2003.
[9] Indarto A, Choi JW, Lee H, Song HK. Environ. Chem. Lett. 2008; 6: 215–222.
[10] Morgan M. Environmental Biology 2008; 3: 27-163.
[11] Michael Davis J, "Comprehensive Environmental Assessment of Nanomaterials: A Meta-Assessment Approach," National Center for Environmental Assessment, U.S. Environmental Protection Agency, 2010.
[12] Hua M, Zhang S, Pan B, Zhang W, Lv L, Zhang Q Journal of Hazardous Materials 2012; 211: 317-331.
[13] Han F, Kambala VSR, Srinivasan M, Rajarathnam D, Naidu R, Water Science Technology 2007; 2: 180-196.
[14] Chen and Mao. Journal of Chemistry 2007; 107: 2891-2959.
[15] Sharmaa YC, Srivastava V, Singh V.K, Kaul S.N, Weng C.H. Environ. Technol. 2009: 30: 583–609.
[16] Fourest, E, Volesky, B. Environ. Sci. Technol. 1996; 30: 277–282.