

Adsorption of Cadmium Ions from Aqueous Solution Using MnO_2 and TiO_2 Monoliths

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Abstract - Till now, the excessive release of Cd^{2+} ions in water became a foremost concern by way of threatening human health seriously. Therefore, for removal of heavy metal ions from waste water, adsorbent with high efficacy and low-cost technologies is most needed to alleviate the situation. In this work, robust, synthesized Metal-oxide monoliths (MnO_2 and TiO_2) by nanocasting process and their performance as an adsorbent for removal of heavy metal (Cd^{2+}) ions from aqueous water was successfully evaluated. The adsorption data shows better fit at pH 6.5, metal ion concentration of 30mg/l and contact time of 47.5 minutes. The maximum adsorption efficacy of Cd^{2+} ions by monoliths was found to be 94.5% and 90.92 % respectively.

Key Words: Titanium di-oxide (TiO_2), Manganese di-oxide (MnO_2), Cadmium, adsorption, Monolith, dosage.

1. INTRODUCTION

In Asia around 4.4 billion i.e. 60% of the world population lives, 1.2 billion in Africa (16%), 738 million i.e. 10% in Europe, the Caribbean and Latin America (634 million) 9%, and remaining 5% (358 million) in Northern America and 39 million Oceania. One and half billion from China & one billion in India are the 2 major nations of the globe signifying 19% and 18% of the world's population. WHO-World Health Organization in 2015 reported that 663 million (9%) of the globe's residents have no access to pure drinking water. 48% sub-Saharan Africa region population will have no access to pure water, 20% (134 million) people of Southern Asia being the 2nd highest. The rural areas population mainly affect without access to fresh drinking water & sanitation. [1].

The presence of heavy metals like zinc, mercury, nickel, arsenic, chromium, cadmium in waste water is increasing day by day due to growth of industry and human activities, e.g., mining, use of batteries, use of bio reactors etc. Cadmium [is one such heavy metal which results from such activities. [2] The maximal permissible limit for Cd (cadmium) is 0.003mg/L. The above concentration is the threshold limit for the maintenance of an ecological equilibrium and public health. Study concentrates in removal of Cd from waste water with the process of adsorption. Removal of cadmium from waste water by using titanium di-oxide and manganese

oxide as nano adsorbents have shown better results as a very good adsorbents. [3]

1.1 NANOTECHNOLOGY AND NANOMATERIALS

Nanotechnology is the use of nano science, which is the study of nano scale constituents that demonstrate remarkable functionality, properties and phenomena due to the effect of small sizes. Nanotechnology depends on the operation, control, and settlement of particles & atoms to shape things, constructions, segments, gadgets, and frameworks at the nano scale. Some of the capable water treatment methods/tools presented by nanotechnology are Nano-sorbents (Adsorption), Nano-filtration (Membranes and membrane processes), Photocatalysis [4].

- Metal Oxide Based Nano materials: Nano sized metaloxide have extraordinary properties, with great removal capacity and selectivity to heavy metals. So, they offer promising capable adsorbents for heavy metals. Metaloxides nano constituents comprises of nano sized zinc oxide, iron oxide, titanium oxide, manganese oxide, zirconium oxide and aluminum oxide etc. [5]
- Manganese Oxides Based Nano materials: Nano crystalline manganese oxide with large surface area shows excellent adsorption capacity. [6]
- Titanium Oxides Based Nano materials: Titanium oxide, degrades the organic impurities and hence used for the heavy metal removal. [7].

Advantages

The advantages of using Nanotechnology in wastewater treatment are:

- Cost saving on materials and less waste on raw material, i.e. Huge number of sample testing done on a lowest scale, hence raw material usage will be more effective. Use of catalysts (Nano scale chemical reagents) enhances rate of chemical reaction. [8]
- Cleaner, more effective industrial practices.

- Enhanced capability to identify and remove contamination by refining water, air and soil quality.
- Great accuracy manufacturing by decreasing quantity of waste.
- Refecilitating environmental damages.[9]

Disadvantages

The disadvantages/probable hazards need to be considered using nano particles:

- The main disadvantages of nano particle is analysis method, as nanotechnology progresses, new and unique nano materials are steadily established. The materials size & shape plays a vital role in defining the toxicity.
- Also, data of the chemical configuration is a basic element to decide how poisonous the material is, and slight variations of chemical set would certainly result in feature change.[10]
- High risk evaluation on environmental impact & life has to be forced to be assessed in the least phases of engineering. The chance evaluation ought to embody the contact risk and its probability of exposure, toxicological analysis, transport risk, persistence risk, transformation risk and skill to recycle.[11]
- Large vitality required for blending nano particles causing high vitality demand.
- Lack of skilled workers & engineers affecting further concerns [12].

1.2 Objectives of present study

- To study adsorption by using metal oxide monoliths MnO₂ and TiO₂ In removal of Cd.
- To study the internal structure of monolith using SEM.
- To study the adsorbent capacity by varying various factors adsorbent dosage, initial concentration, contact time, pH of the solution
- To study adsorption with Design Software by using RSM (Response Surface Methodology) by design of Central composite.

2. ADSORPTION

Adsorption is a surface attrition where in toxins are adhered to solid surface. A particle (pollutant) sticking to the surface is adsorbate, and surface is adsorbent. This phenomena, occurs by physisorption or chemisorption. The significant models are Freundlich, Langmuir, Halsey, and Smith,

Henderson, Elovich fluid film dissemination, intra molecule dispersion, and Lagergren.[13]

The Langmuir and Freundlich models are most broadly utilized.

Langmuir Model: Adsorption happens uniformly on the dynamic spots of the adsorbents, and when the every single adsorptive spot are involved by the adsorbates, no further adsorption exercises on these locales. The mathematical representation of Langmuir model is expressed as:

$$\frac{C_s}{q_s} = \frac{1}{b_s q_l} + \frac{C_s}{q_m}$$

Where Cs represents equilibrium adsorbate concentration (mg/l), qs represents equilibrium adsorption capacity of adsorbent (mg/g), b_s represents adsorption equilibrium constant & ql represents saturated solo layer adsorption capacity (mg/g)[11].

Freundlich Model: It defines the heterogeneous adsorption process on surface and at specific active sites through discrete energy formed on multilayer adsorption. This model provides estimation of sorption efficiency of adsorbate on an adsorbent. The mathematical representation of Freundlich Model is expressed as:

$$\log q_t = \log k_f + \frac{1}{n} \log C_s$$

Where Cs = equilibrium concentration of the adsorbate (mg/l), ql = equilibrium adsorption capacity of the adsorbent (mg/g), n= constant i.e adsorption index & Kf = Freundlich constant [14].

3. MATERIAL AND METHODOLOGY

3.1 Materials used

- Synthesized Titanium di oxide and Manganese di oxide monoliths were used as adsorbents prepared from silica monoliths, with diameter of 0.5cm and length of 0.8cm with 99% purity purchased from NANOSHEL.
- Cadmium carbonate CdCO₃ was used as adsorbate.
- The solution pH was adjusted with Sodium hydroxide and Hydrochloric acid of 1N.
- Equipments needed for experiment were AAS (Atomic absorption spectroscopy), pH meter, rotary shaker and weighing balance.

3.2 Adsorbate

Preparation of Aqueous cadmium solution:

Synthetic Cadmium sample will be prepared by dissolving 1.533g Cadmium carbonate (Analytical Reagent) in one litre of double distilled water.

3.3 Adsorbents

Monoliths of metal oxide with progressively permeable structures can be set up by utilizing nano casting process. In this method, pores of the parental silica have been immersed with desired salts of metal ion solution. Then by further heating, the metal salt is changed over to relating metal oxides. Toward the end, silica part gets evacuated by either KOH or NaOH. The use of prepared monoliths of metal oxide is a function of pore diameter along with surface properties. The porosity of metal oxide monoliths can be modified by modifying the pore size. Integrated different pore size controlled TiO₂ and MnO₂ by a nano casting technique utilizing guardian mesoporous silica have been utilized as adsorbents.

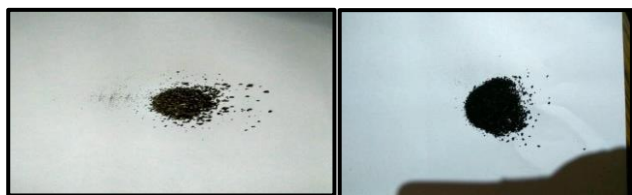


Fig. 3.1(a). TiO₂ Monolith

(b). MnO₂ Monolith

3.4 Experimental designs.

The tables 3.1 are the independent variables whose values range between lower and higher value. The experiments are conducted in 30 runs, with each run with varying variables and Response of each run is calculated. The independent variables for pH varies from 3-10 (i.e 0.5, 3, 6.5, 10,13.5), adsorbent dosage from 10-20 mg(5,10,15,20,25),

initial concentration 10-50 mg/l(i.e 10, 30,50,70) and contact time from 15-80 minutes (15, 47.5, 60,80, 112.5) . Each run will be conducted with the combination of different variables and response is calculated for each run.

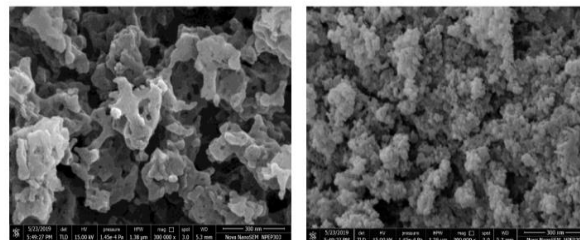
TABLE 3.1

FACTORS WITH INDEPENDENT VARIABLES WITH LOWER AND HIGHER RANGE.

Factors	Ranges	
	lower	higher
pH	3	10
Dosage (mg)	10	20
Initial Concentration(mg/l)	10	50
Contact Time (minutes)	15	80

4. RESULTS AND DISCUSSIONS

4.1 Characterization study



4.1 FESEM images of TiO₂ (i) before and (ii) after adsorption for Cadmium.

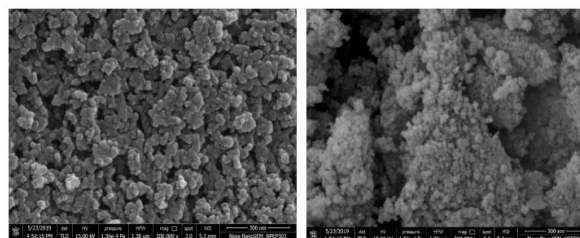


Fig 4.2 FESEM images of MnO₂ (i) before and (ii) after adsorption for Cadmium.

4.2 Adsorption method (Batch process)

Metal-oxide monoliths (MnO₂ and TiO₂) were used to conduct batch trials by using Response surface approach by designing with centre composite strategy. The test were performed for each set of runs for different pH, contact time, metal concentration and agitation speed of 200 rpm. The independent variables for pH varies from 3-10 (i.e 0.5, 3, 6.5, 10,13.5), adsorbent dosage from 10-20 mg(5,10,15,20,25), initial concentration 10-50 mg/l(i.e. 10, 30,50,70) and contact time from 15-80 minutes (15, 47.5, 60,80, 112.5) . AAS was used to study the broke down Cd from a standard arrangement of cadmium carbonate individually. The adsorption is determined by the below formulae.

$$\% \text{Removal} = \frac{C_i - C_f}{C_i} \times 100$$

Where, C_i = initial concentration (mg/l).

C_f = Final (equilibrium) concentration (mg/l).

4.3 Adsorption of cadmium using TiO₂ monolith

Removal % = -54.19267+8.19432* pH +11.81291*Dosage+0.474595*Concentration +0.655846*ContactTime-0.008071* pH * Dosage +0.011161* pH *Concentration +0.003516*pH*Contact Time- 0.000437*Dosage*Concentration -0.008077*Dosage* Contact Time -0.003188*Concentration * Contact Time - 0.572279* pH² -0.365667* Dosage² -0.005885* Concentration² -0.003273* Contact Time².

The above expression gives the response for each run, considering each factor with different factor combination.

Table 4.1 Fit Statistics

Std. Dev.	2.63	R ²	0.9772
Mean	76.93	Adjusted R ²	0.9558
C.V. %	3.42	Predicted R ²	0.8684
		Adequate Precision	21.7873

The Predicted R² of 0.8684 is close to Adjusted R² of 0.9558; i.e. difference being 0.2. Adequate Precision value with 21.787 is acceptable, hence can be used for design.

4.3.1 Effect of pH on removal efficiency of TiO₂:

To examine adsorption of Cadmium by monoliths of metal oxide, 15mg of TiO₂ was added to 30 mg/l of 100ml Cadmium solution at pH 6.5. HCl or NaOH was added to alter the pH of Cadmium solution.

Table 4.2 Effect of pH on Removal of Cd by TiO₂ Monolith

pH	Dosage, mg	Concentration, mg/l	Contact Time, Minutes	Removal %
0.5	15	30	47.5	60.5
6.5	15	30	47.5	94.5
13.5	15	30	47.5	74

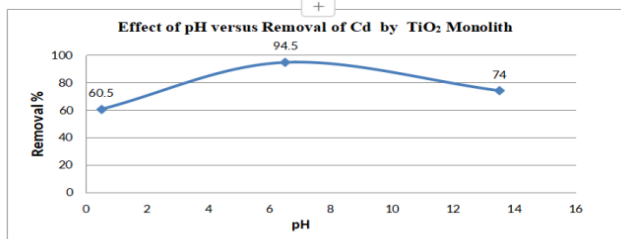


Fig. 4.3 Effect of pH versus Removal of Cd by TiO₂ Monolith

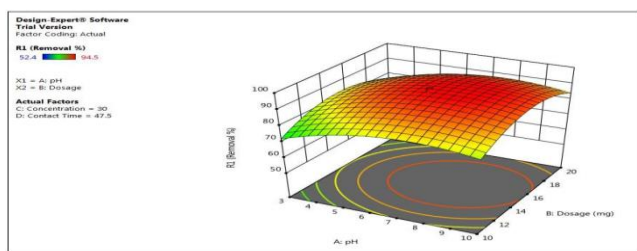


Fig. 4.4, 3D graph with factors A: pH and B: Dosage (mg) & their mutual effect.

Fig.4.3 illustrates the removal efficiency of Cd by TiO₂ monolith of 94.5% at pH of 6.5. Fig.4.4, shows 3D graph showing interaction of parameters at optimum dosage of 15mg, and contact time of 47.5 minutes.

pH effect on adsorption of Cd²⁺ showed maximum removal at pH 6.5 and decreased significantly as the pH increases. At lesser pH, the adsorbent surface exhibits positive charge due to increase in H⁺ ions and hence the material to be adsorbed i.e., Cd ions being positive experiences a repulsive force and

thus hindering the adsorption process and further H⁺ along with Cadmium ions will also compete for the adsorption sites present thus opposing the uptake of adsorbate by the adsorbent. On other hand, at higher pH, surface of the adsorbent will be charged negatively thus enhancing the adsorption process of positive charged metal ions. Precipitation of metal ions as its hydroxide occurs with further increase in pH.

4.3.2 Effect of dosage on adsorption

Dosage effect was studied on surface of TiO₂ monolith for Cadmium, adsorption experiments were performed at different dosages of (10-20) mg.

Table 4.3 Effect of Dosage on Removal of Cd by TiO₂ Monolith

pH	Dosage, mg	Concentration, mg/l	Contact Time, Minutes	Removal %
6.5	5	30	47.5	56.25
6.5	15	30	47.5	94.5
6.5	25	30	47.5	61.2

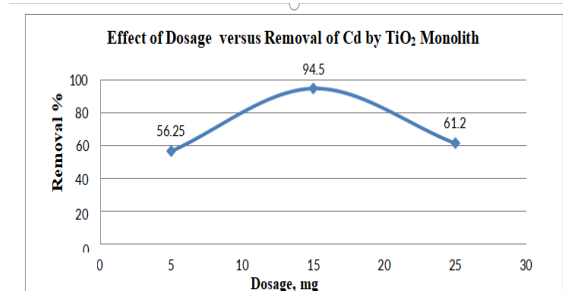


Fig. 4.5 Effect of Dosage versus Removal of Cd by TiO₂ Monolith

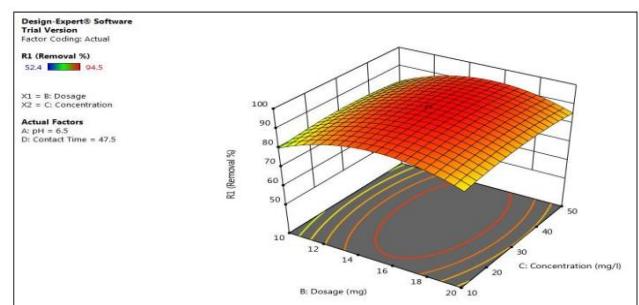


Fig. 4.6, 3D graph with factors B: Dosage (mg) and C: Concentration (mg/l) & their mutual effect.

Fig.4.5 illustrates the removal of Cd by TiO₂ monolith of 94.5% at adsorbent dosage of 15mg. Fig.4.6, 3D graph showing mutual effect of parameters at 6.5 pH and concentration of 30mg/l. The above figure represents adsorbent dosage has increased from 15 to 25mg; removal efficiency goes on decreasing, though the number of active sites present may be more. This may be mainly due to Agglomeration of TiO₂ monolith or unsaturation of sites during the process.

4.3.3 Effect of concentration on adsorption

To examine the effect of concentration on the surface of TiO₂ for Cd adsorption experiments were performed at different concentration (10-50)ppm.

Table 4.4 Effect of concentration on Removal of Cd by TiO₂ Monolith

pH	Dosage, mg	Concentration	Contact Time	Removal %
6.5	15	10	47.5	67
6.5	15	30	47.5	94.5
6.5	15	70	47.5	86.25

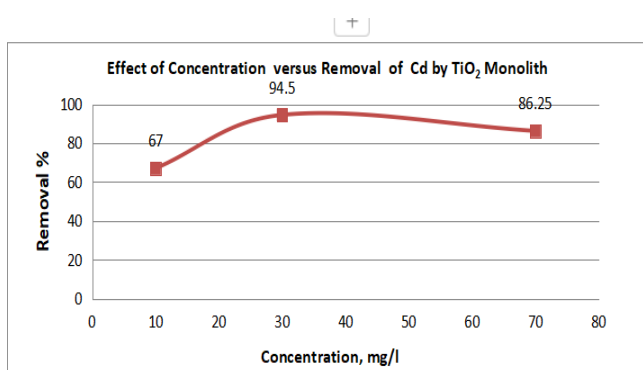


Figure 4.7 Effect of concentration versus Removal of Cd by TiO₂ Monolith

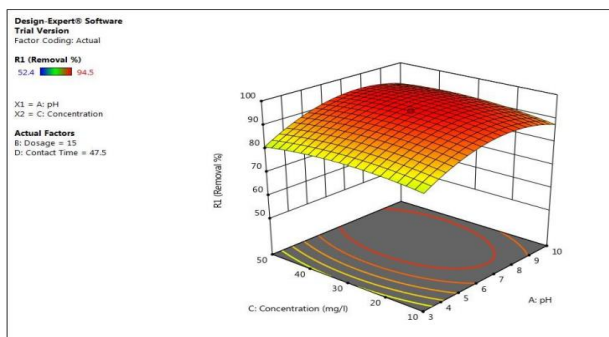


Fig. 4.8, 3D graph with factors C: Concentration (mg/l) and A: pH & their mutual effect.

4.3.4 Effect of contact time on adsorption

To examine effect of contact time on surface of TiO₂ monolith for Cd adsorption experiment was performed for contact time (15-80) minutes.

Table 4.5 Effect of contact time on Removal of Cd by TiO₂ Monolith

pH	Dosage, mg	Concentration	Contact Time	Removal %
6.5	15	30	17.5	72.6
6.5	15	30	47.5	94.5
6.5	15	30	112.5	90.33

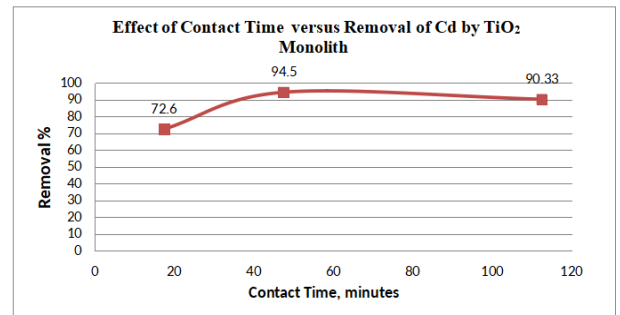


Fig. 4.9 Effect of Contact Time versus Removal of Cd by TiO₂ Monolith

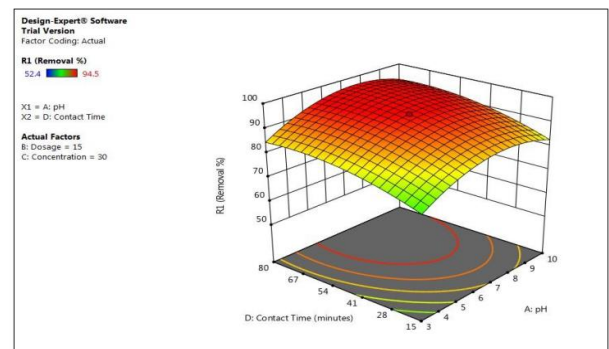


Fig. 4.10, 3D graph with factors D: Contact Time (minutes) and A: pH & their mutual effect.

Fig.4.9 illustrates removal Cd by TiO₂ monolith of 94.5% at contact time of 47.5minutes. Fig. 4.10 , 3D graphs showing interaction of parameters at optimum dosage of 15mg and pH of 6.5. The above graphs represent that once the equilibrium is reached i.e saturation of active sites by Cadmium ion occurs within 47.5 minutes; further increased efficiency cannot be obtained by increasing the contact time. This may be mainly due to desorption once the sites are saturated. TiO₂ monolith has shown removal efficiency of 94.5% with optimum pH of 6.5, dosage of 15 mg, concentration of 30mg/l with contact time of 47.5 minutes.

4.4 Adsorption of cadmium using MnO₂ monolith

$$\text{Removal \%} = -47.22855 + 4.14756 \cdot \text{pH} + 10.78810 \cdot \text{Dosage} + 1.24944 \cdot \text{Concentration} + 0.458851 \cdot \text{Contact Time} + 0.056250 \cdot \text{pH} \cdot \text{Dosage} + 0.003366 \cdot \text{pH} \cdot \text{Concentration} + 0.018599 \cdot \text{pH} \cdot \text{Contact Time} - 0.042781 \cdot \text{Dosage} \cdot \text{Concentration} + 0.000781 \cdot \text{Dosage} \cdot \text{Contact Time} + 0.001774 \cdot \text{Concentration} \cdot \text{Contact Time} - 0.385213 \cdot \text{pH}^2 - 0.307404 \cdot \text{Dosage}^2 - 0.009100 \cdot \text{Concentration}^2 - 0.005636 \cdot \text{Contact Time}^2.$$

The above equation exhibits, relation between each factors considered for each run where removal can be obtained with influence of each factor on each run.

Table 4.6 Fit Statistics

Std. Dev.	3.81	R ²	0.9502
Mean	72.60	Adjusted R ²	0.9037
C.V.%	5.24	Predicted R ²	0.7130
		Adequate Precision	13.9660

The Predicted R² value 0.7130 is in sensible concurrence with the Adjusted R² value 0.9037; i.e difference is less than 0.2. Adequate Precision 13.966 is approved, therefore can be used in design.

4.4.1 Effect of pH on adsorption:

pH influence on adsorption of Cadmium by monoliths of metal oxide, dosage of 15mg (MnO₂) was added to 30 mg/l of 100ml Cadmium solution at 6.5 pH. HCl or NaOH was added to alter the pH of Cadmium solution.

Table 4.7 Effect of pH on Removal of Cd by MnO₂ Monolith

pH	Dosage, mg	Concentration, mg/l	Contact Time, Minutes	Removal %
0.5	15	30	47.5	64.75
6.5	15	30	47.5	90.2
13.5	15	30	47.5	80.12

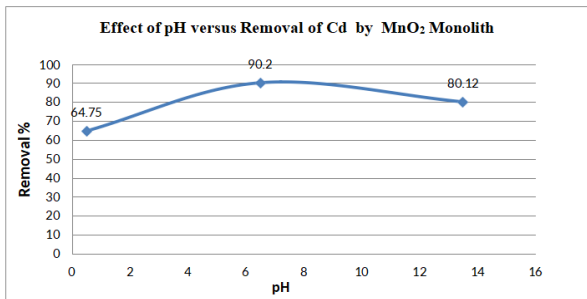


Fig. 4.11 Effect of pH versus Removal of Cd by MnO₂ Monolith

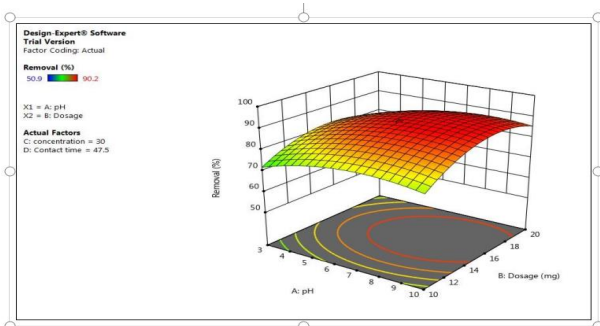


Fig. 4.12, 3D graph with factors A: pH and B: Dosage (mg) & their mutual effect.

Fig.4.11 illustrates removal of Cd by MnO₂ monolith of 90.2% at pH of 6.5. fig.4.12 is a 3D graph showing mutual effect of parameters at optimum dosage of 15mg and concentration of 30mg/l.pH influence on adsorption of Cadmium ions showed maximum removal efficiency pH 6.5 and decreased significantly as the pH increases. At acidic condition Cadmium

with positive charge and Manganese with negative charge, adsorption occurs by electrostatic attraction. At higher pH this attraction becomes weak and hence efficiency decreases.

4.4.2 Effect of dosage on adsorption

Table 4.8 Effect of Dosage on Removal of Cd by MnO₂ Monolith

pH	Dosage, mg	Concentration, mg/l	Contact Time, Minutes	Removal %
6.5	5	30	47.5	50.9
6.5	15	30	47.5	90.2
6.5	25	30	47.5	70.24

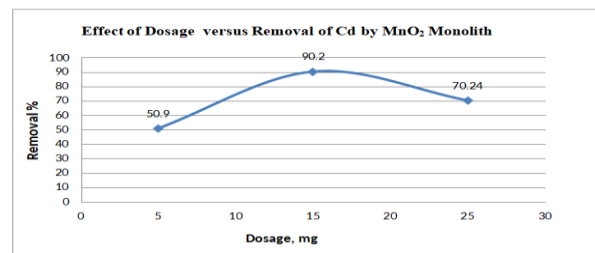


Fig. 4.13 Effect of Dosage versus Removal of Cd by MnO₂ Monolith

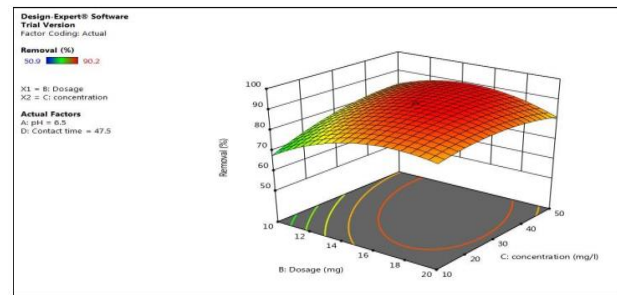


Fig.4.14, 3D graph with factors B: Dosage (mg) and C: Concentration (mg/l) & their mutual effect.

Fig.4.13 illustrates removal of Cd by MnO₂ monolith of 90.2% at adsorbent dosage of 15mg. Fig.4.14, 3D graph showing interaction of parameters at pH 6.5 and concentration of 30mg/l.The above figure shows that adsorbent dosage is raised from 15 to 25mg; removal efficiency goes on decreasing, though the number of active sites present may be more. This may be mainly due to Agglomeration of TiO₂ monolith or unsaturation of sites during the process.

4.4.3 Effect of Concentration on adsorption

Influence of concentration was noticed by adding dosage of 15mg, pH 6.5 with contact time of 47.5minutes.

Table 4.9 Effect of concentration on Removal of Cd by MnO₂ Monolith

pH	Dosage, mg	Concentration	Contact Time	Removal %
6.5	15	10	47.5	72.5
6.5	15	30	47.5	90.2
6.5	15	70	47.5	81

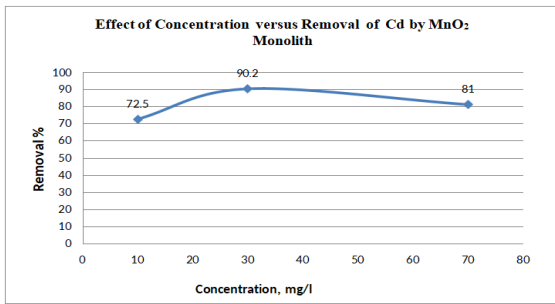


Fig. 4.15 Effect of Concentration versus Removal of Cd by MnO₂ Monolith.

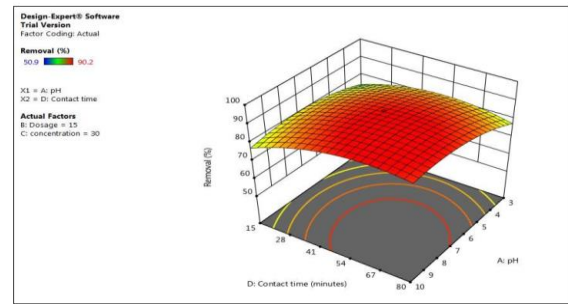


Fig. 4.18, 3D graph with factors D: Contact Time (minutes) and A: pH & their mutual effect.

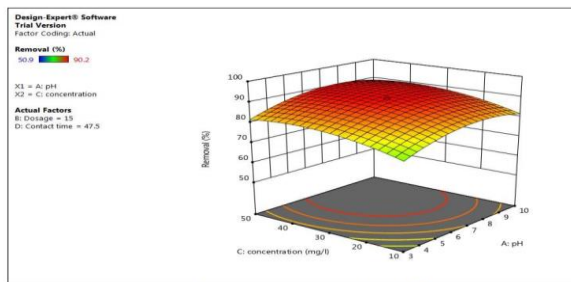


Fig. 4.16, 3D graph with factors C: Concentration (mg/l) and A: pH & their mutual effect on Cadmium removal.

Fig.4.17 illustrates removal efficiency of Cd by MnO₂ monolith of 90.98% at concentration of 30mg/l. Fig.4.18, 3D graph showing mutual effect of parameters at optimum dosage of 15mg and pH of 6.5. The above graphs show that adsorption increases with increased Cadmium ion concentration upto 30mg/l. Increase in Cadmium ion concentration, the removal efficiency decreases due to limiting amount of adsorbent dosage. MnO₂ monolith has shown removal efficiency of 90.2% with optimum pH of 6.5, dosage of 15 mg, concentration of 30mg/l with contact time of 47.5 minutes.

Fig.4.15 illustrates removal of Cd by MnO₂ monolith of 90.98% at concentration of 30mg/l. Fig.4.16, 3D graph showing mutual effect of parameters at optimum dosage of 15mg, and pH of 6.5. The above graphs show that adsorption increases with increased lead ion concentration upto 30mg/l. With increase in Cadmium ion concentration, the removal efficiency decreases due to less active sites and surface area.

4.5 Comparison study on removal of cadmium by using TiO₂ and MnO₂ monolith

4.5.1 Effect of pH on Removal efficiency of Cd Using TiO₂ and MnO₂

Influence of pH is noticed by drawing comparative graph of both metal oxide at constant time, dosage and concentration.

4.4.4 Effect of Contact Time on adsorption

Table 4.10 Effect of Contact Time on Removal of Cd by MnO₂ Monolith

pH	Dosage, mg	Concentration	Contact Time	Removal %
6.5	15	30	17.5	58.5
6.5	15	30	47.5	90.2
6.5	15	30	112.5	76.5

Table 4.11 Effect of pH on removal of Cd by monoliths

pH	Dosage, mg	Concentration, mg/l	Contact Time, Minutes	(TiO ₂)Removal %	(MnO ₂)Removal %
0.5	15	30	47.5	60.5	64.75
6.5	15	30	47.5	94.5	90.2
13.5	15	30	47.5	74	80.12

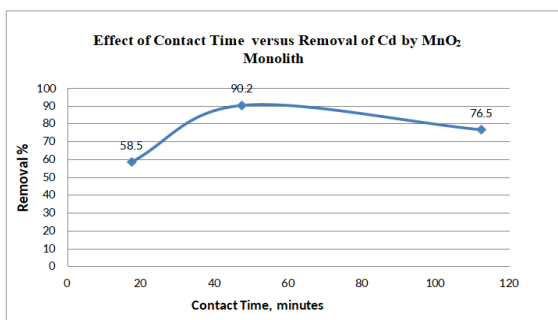


Fig.4.17 Effect of Contact Time versus Removal of Cd by MnO₂ Monolith.

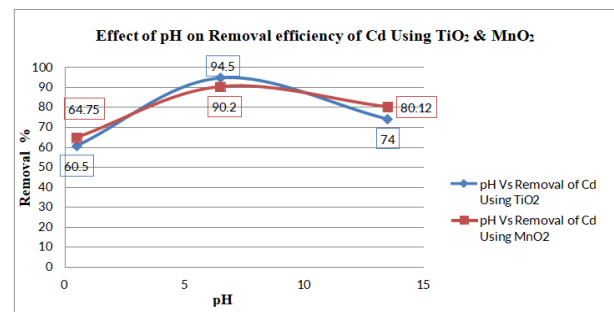


Fig 4.19 Effect of pH on Removal efficiency of Cd Using TiO₂ & MnO₂

The above fig.4.19 shows the comparative graph of removal of Cd by TiO₂ and MnO₂ monoliths with varying pH from 0.5 to 13.5. TiO₂ has highest removal efficiency of 94.5% as compared with MnO₂ with 90.2% at optimum pH of 6.5.

4.5.2 Effect of Dosage on Removal efficiency of Cd Using TiO₂ & MnO₂

Dosage effect for both monoliths was noticed by plotting a comparative graph at fixed concentration, time & pH.

Table 4.12 Effect of Dosage on removal of Cd by monoliths

pH	Dosage, mg	Concentration, mg/l	Contact Time, Minutes	(TiO ₂)Removal %	(MnO ₂)Removal %
6.5	5	30	47.5	56.25	50.9
6.5	15	30	47.5	94.5	90.2
6.5	25	30	47.5	61.2	70.24

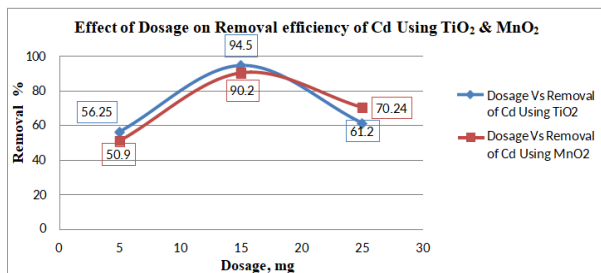


Fig. 4.20 Effect of Dosage on Removal efficiency of Cd Using TiO₂ & MnO₂.

Fig. 4.20 shows a comparative graph on removal of Cd by TiO₂ and MnO₂ monoliths with varying Dosage from 5 to 25mg. TiO₂ has highest removal efficiency of 94.5% as compared with MnO₂ with 90.2% at optimum dosage of 15mg.

4.5.3 Effect of Concentration on Removal efficiency of Cd Using TiO₂ & MnO₂

Table 4.13 Effect of Concentration on removal of Cd by monoliths

pH	Dosage, mg	Concentration, mg/l	Contact Time, Minutes	(TiO ₂)Removal %	(MnO ₂)Removal %
6.5	15	10	47.5	67	72.5
6.5	15	30	47.5	94.5	90.2
6.5	15	70	47.5	86.25	81

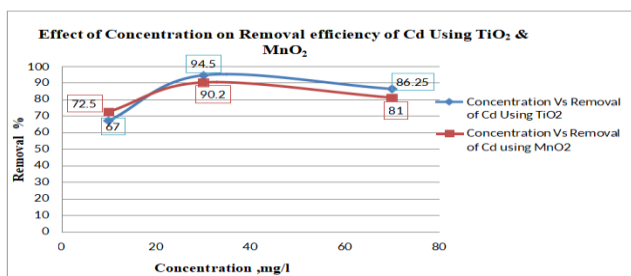


Fig. 4.21 Effect of Concentration on Removal efficiency of Cd Using TiO₂ & MnO₂

The above fig. 4.21 represents a comparative graph of removal efficiency of Cd by TiO₂ and MnO₂ monoliths with varying Concentration of 10 to 70mg/l. TiO₂ has highest removal efficiency of 94.5% as compared with MnO₂ with 90.2% at optimum Concentration of 30mg/l.

4.5.4 Effect of Contact Time on Removal efficiency of Cd Using TiO₂ & MnO₂

Comparative graph of varying contact time is drawn to observe the removal of Cd by monoliths.

Table 4.14 Effect of Contact Time on removal of Cd by monoliths

pH	Dosage, mg	Concentration, mg/l	Contact Time, Minutes	(TiO ₂)Removal %	(MnO ₂)Removal %
6.5	15	30	17.5	72.6	58.5
6.5	15	30	47.5	94.5	90.2
6.5	15	30	112.5	90.33	76.5

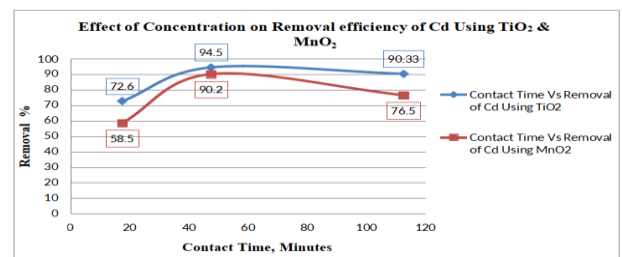


Fig. 4.22 Effect of Contact Time on Removal efficiency of Cd Using TiO₂ & MnO₂

The above fig. 4.22 exhibits a comparative graph of removal of Cd by TiO₂ and MnO₂ monoliths with varying Contact Time of 17.5 to 112.5minutes. It is observed that TiO₂ has highest removal efficiency of 94.5% as compared with MnO₂ with 90.2% at Contact Time of 47.5 minutes.

Batch experiment conducted with varying pH, dosage, concentration and contact time TiO₂ proved to be more efficient in removal of cadmium with 94.5 % than MnO₂ monolith with 90.2%.

5. CONCLUSIONS

In this work, TiO₂ and MnO₂ monolith synthesized monolith were utilized as an adsorbent for adsorption of Cd²⁺ ions from aqueous solution. For adsorption process of metal ions, all the experiments were executed in different batches in precise environment with varying pH, optimum dosage, metal ion concentration, and contact time. Experiments verified that removal of cadmium by using TiO₂ and MnO₂ monolith as adsorbents showed removal efficiency with 94.5% and 90.92 % with optimum dosage of 15mg with pH of 6.5, metal ion concentration of 30mg/l and contact time of 47.5 minutes. TiO₂ proved to be more effective in the removal of cadmium. Response surface methodology showed effective results in determining the optimum conditions for cadmium removal of cadmium from aqueous solution with monoliths as adsorbents. FESEM images before adsorption showed interlinked pores which were created by phase separation. After adsorption clusters of Cadmium deposit is seen on the surface of monolith forming a strong bond with monolith.

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