International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

Optimization of Variable parameters in the Photocatalytic Reduction Of Cadmium(II) Using Iron Oxide (α-Fe_2O_3) Nanoparticles by using Taguchi

Dr Shrikrishna H Gurlhosur[1*], Srinivas Halemani[2], Dr V M Patil[3]

1*. Department of Engineering Chemistry, , R. T. E. Society's Rural Engineering college Hulkoti, Gadag, Karnataka , India-582205

2. Department of Civil Engineering ,R. T. E. Society's Rural Engineering college Hulkoti, Gadag, Karnataka , India-582205

3. Department of Engineering Chemistry, R. T. E. Society's Rural Engineering college Hulkoti, Gadag, Karnataka , India-582205

*Corresponding Author Email: krishg.libra@gmail.com

Abstract

Synthesized iron oxide α-Fe_2O_3 (Haematite) crystalline size of 11.55nm was used in the study of photo catalytic reduction of Cadmium(II) .Different parameters like Metal concentration, Dosage of Nanoparticles, Contact time and pH were studied. pH maintained for the solutions of different concentrations were 4,5,6,7 and 10.Concentration of cadmium solution taken for the study were 2,4,6,8 and 10ppm. Keeping concentration and dosage constant, pH was varied. Then concentration was varied by keeping dosage and pH constant. Then dosage was varied by keeping concentration and pH constant. Dosage of iron oxide taken was 50 mg, 75mg, 100mg, 125 mg and 150mg. It was observed that photo catalytic reduction by Iron oxide nanoparticles (IONP) was more effective at metal concentration 4ppm, IONP dosage 100mg, pH 5, and contact time of 150 min with 97.02% reduction of Cadmium (II). For Metal concentration of 4ppm ,optimization of parameters using Taguchi method confirmed the best results that were obtained from experiments.

Keywords: Iron Oxide Nanoparticles, X-ray diffraction, Scanning Electron Microscope, Cadmium (II) , UV-Vis Spectrophotometry, Photocatalytic reduction

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

INTRODUCTION

Heavy metals are known to be toxic for living organisms even if they are present at low levels. The presence of heavy metals and other pollutants in water continues to be a major concern. Among different heavy metal ions present in industrial wastewater, Cadmium(II) is acutely carcinogenic and toxic. Cadmium (II) contamination may originate from various agricultural practices and chemical industries, including metallurgical alloying, ceramics, pigment manufacture, electroplating, and textile and such effluents must be treated to convert it to the less toxic form before discharging into the sewer.

This heavy metals are potentially toxic to humans and aquatic life, create an oxygen demand in receiving waters, and impart taste and odour to drinking water. Heavy metals in high levels possess serious health problems in humans and animals, in extreme cases can cause death.

Cadmium (II) is accumulated in the kidneys, the filtering mechanism is damaged resulting in the elimination of vital proteins and sugars from the body promoting kidney damage. Some of the many other influences of human exposure to cadmium are; diarrhoea, bone fracture, damage to the central nervous system, damage to the immune system, and cancer development.According to Indian standards the permissible limits for cadmium is 0.003mg/l. There are various techniques for treating heavy metals in water and wastewater. Such as electroplating, evaporating, chemical precipitation, flotation, membrane filtration, oxidation, reduction, ion exchange and adsorption.

Photoreduction is one of the techniques for remediation of heavy metals in wastewater. Oxidation of organic pollutants has been widely studied in connection with the treatment of drinking water and industrial water. However, the reducing capacity of photocatalyst, which can be profitably used, is less explored. The method has the advantage of destroying pollutants or transforming them into less toxic forms. This is an essential characteristic of photocatalytic technology for water treatment because the toxicity of inorganic substance depends on their oxidation states.

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

Experimental Description

Preparation of Cadmium (II) stock solution

2.3049 gm of Cadmium sulphate octahydrate ($3CdSO_4 .8H_2O$) was weighed and was diluted in 1000ml of distilled water in volumetric flask up to the mark to get 1000ppm solution. All the required solutions were prepared with analytical grade reagents and distilled water. Synthetic samples of different concentrations 2,4,6,8 and 10 ppm of Cadmium (II) were prepared from this stock solution. The pH of aqueous solution was adjusted to the desired value by adding 0.05N H_2SO_4 or 0.1N NaOH solution.

Procedure for Reduction of Cadmium (II)

2, 4, 6, 8 and 10ppm solutions prepared were taken for U.V analysis to know the absorbance. And the absorbance was used as reference.100ml of stock solution with predetermined Cadmium (II) concentration and pH was taken in quartz tube.100mg of iron oxide nanoparticles which was synthesized were added into the solution.Cadmium (II) solutions in quartz tubes were placed in photo catalytic reactor. Where the solution was exposed to visible light source.After every 30min. 1ml of sample was collected and the collected samples were centrifuged using microcentrifuge, later 1ml of alizarin red s indicator solution and 0.1 ml of acid were added **.**The solution was taken for U.V analysis to know the absorbance**.**

VARIATION OF PARAMETERS:

pH maintained for the solutions of different concentrations were 4,5,6,7 and 10. Concentration of cadmium solution varied were 2,4,6,8 and 10ppm.Keeping concentration and dosage constant, pH was varied. Then concentration was varied by keeping dosage and pH constant Then dosage was varied by keeping concentration and pH constant. Dosage of iron oxide taken was 50 mg, 75mg, 100mg, 125 mg and 150mg.

Methodology

CHEMICALS USED: For Preparation of Cadmium Solution.

Cadmium sulphate ($3CdSO_4.8H_2O$) Alizarin red s indicator, Sulphuric Acid, Sodium Hydroxide–All the Chemicals used were of analytical grade samples.

Equipment Used: For Reduction of Cd(II)

pH Meter, Photo catalytic Reactor, UV Visible Spectrometer

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

Results and discussion

REDUCTION OF Cd (II) TO Cd (0) USING IRON OXIDE NANOPARTICLES

The chemistry behind the photo catalytic reduction is that, iron oxide nano particles having Fe^{2+} oxidation state converts to Fe^{3+} oxidation state .

$$2Fe^{2+} \xrightarrow{\text{Visible light}} 2Fe^{3+} + 2e^{-}$$

$$2e^{-} + Cd^{+2} \longrightarrow Cd^{+0}$$

During this conversion it donates electron to cadmium heavy metal ions and cadmium ion get reduced to non-toxic form i.e. from Cd^{2+} to Cd^{+0} states. The reduction can be identified by UV-vis spectrophotometry. For the photo reduction of cadmium heavy metal photo catalytic reactor is used under visible spectrum. The photo catalytic reactor used was of 125 watts. Experiments are done on various parameters such as time, dosage, concentration and pH and optimum results are found at which maximum removal took place.

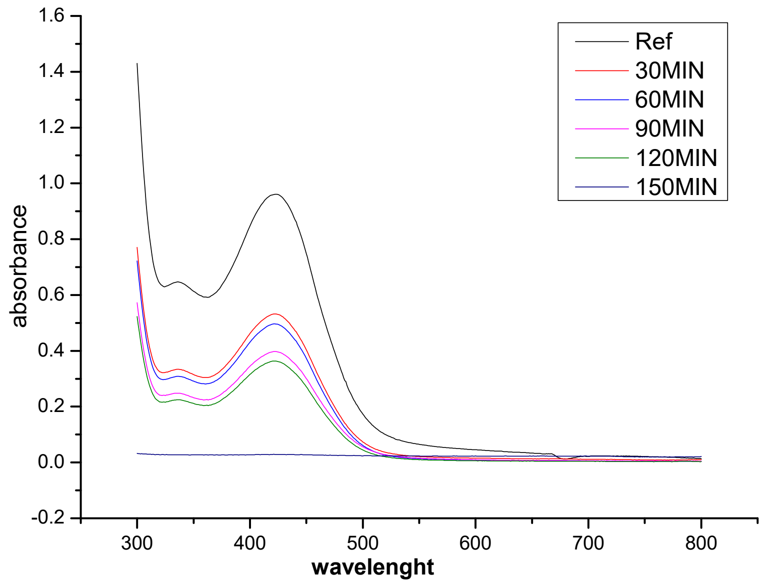
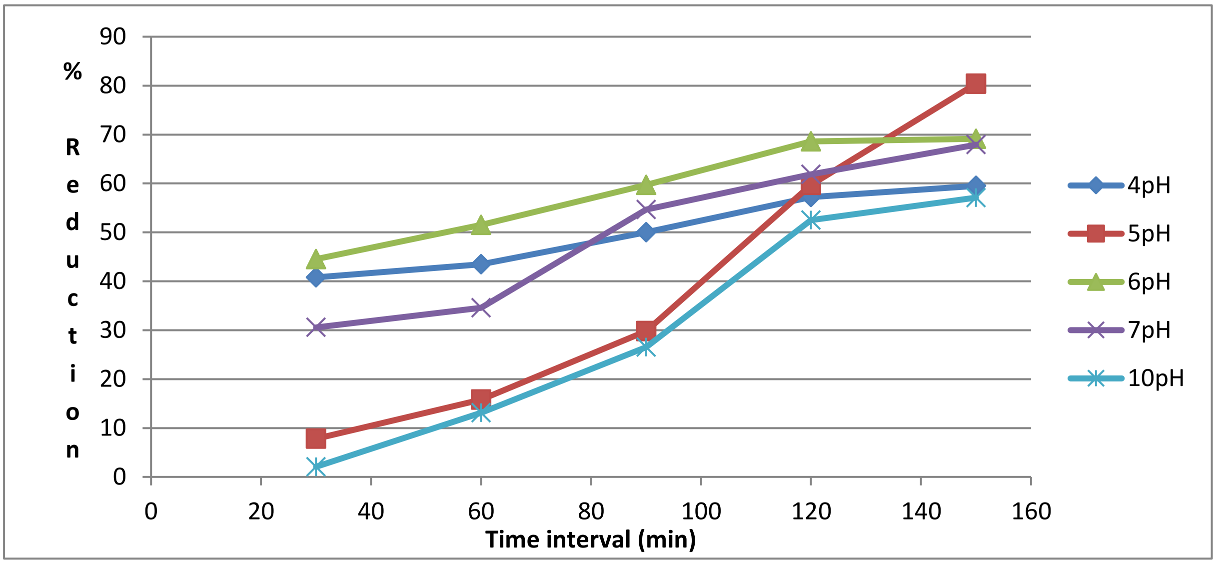
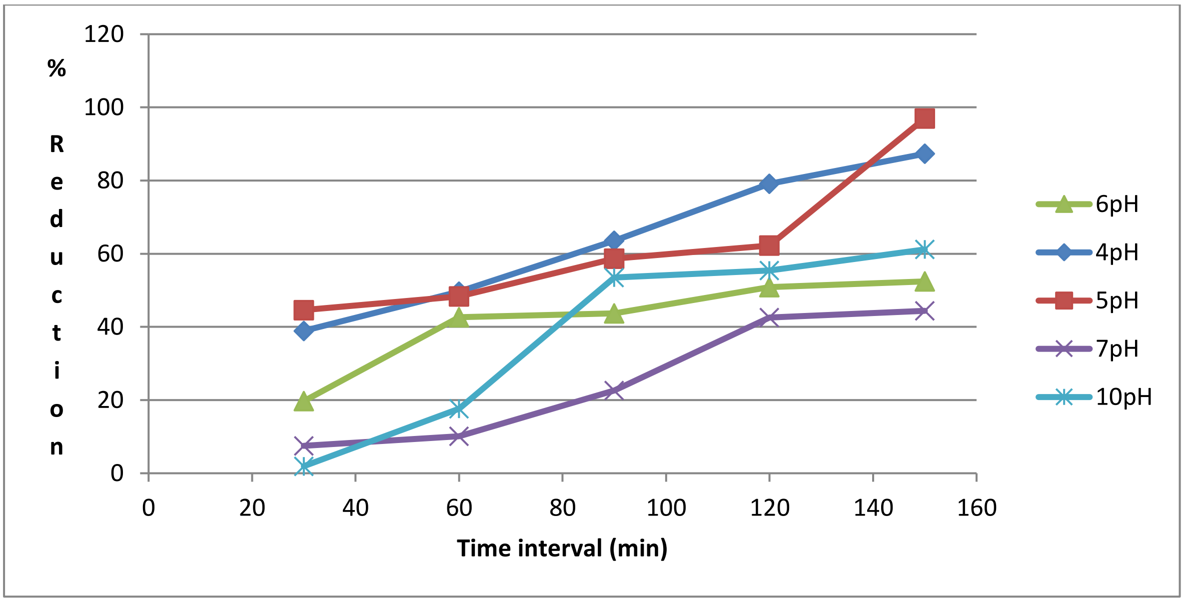


Fig1: UV-Vis absorbance graph (4ppm, 100mg dosage, 5pH)

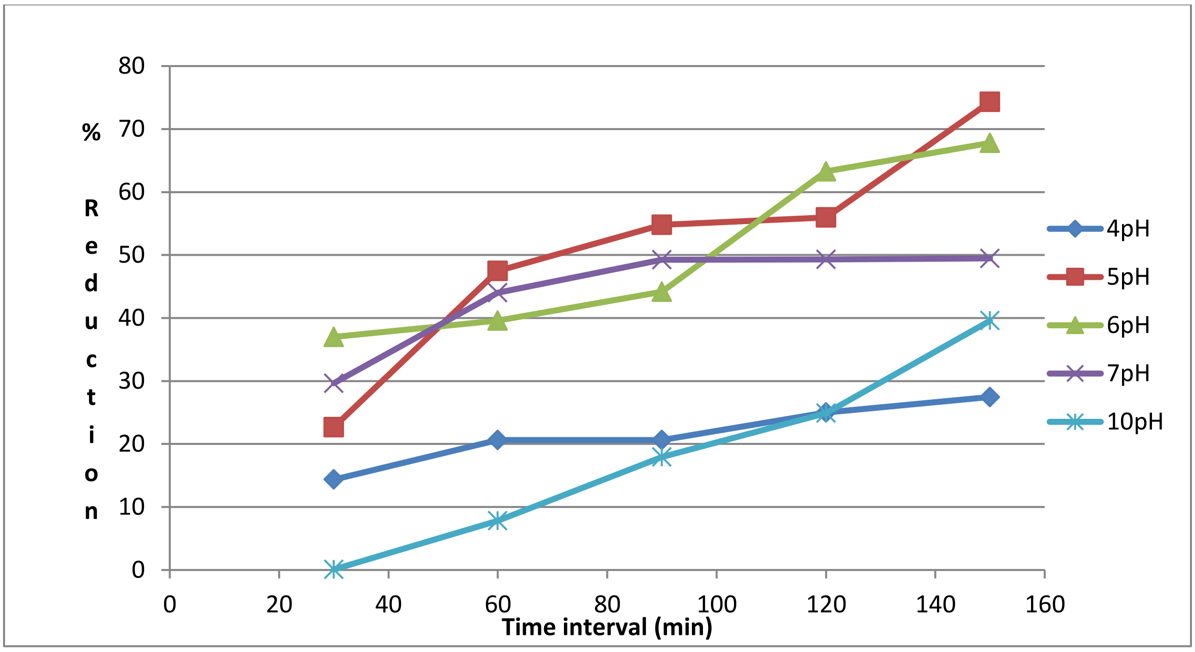


Graph 1: % Reduction vs time interval at dosage 100mg INOP and 2ppm concentration for different pH.

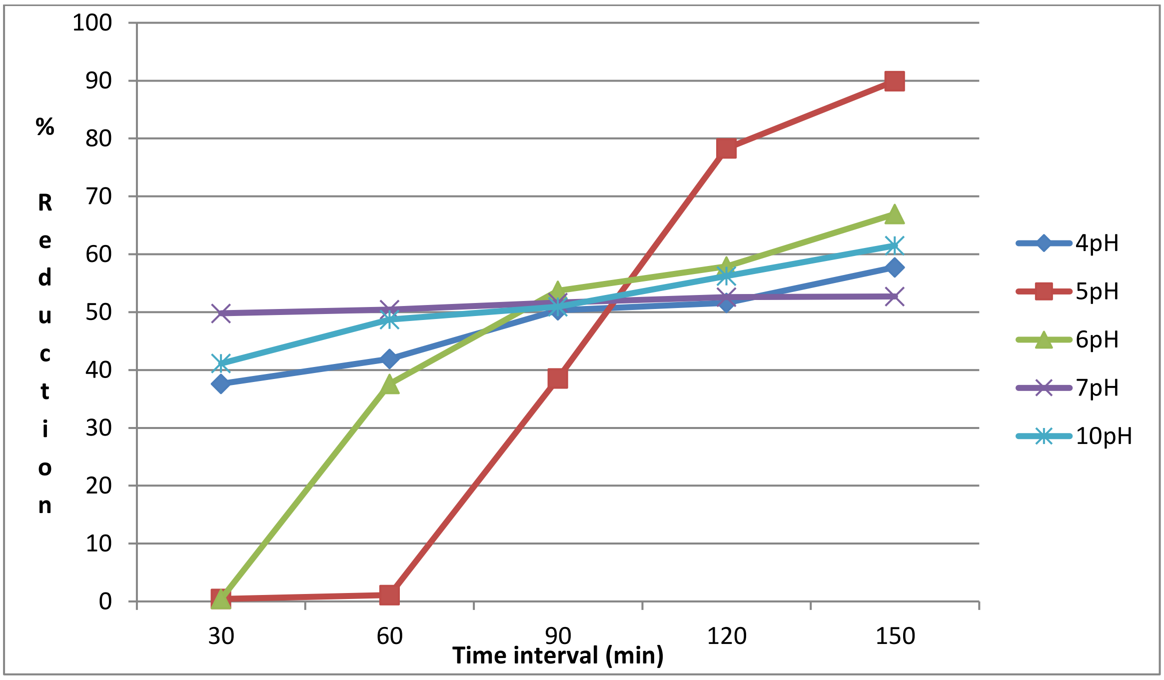


Graph.2: % Reduction vs time interval at dosage 100mg and 4ppm constant at different pH

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

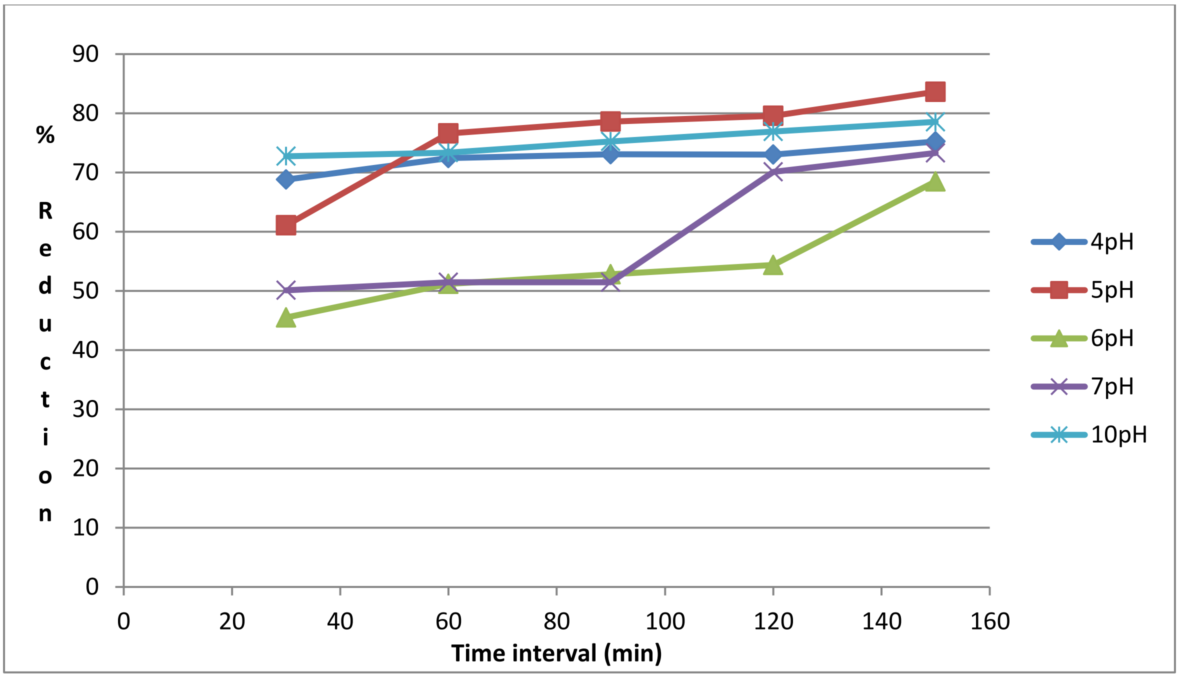


Graph.3: % Reduction vs time interval at dosage 100mg and 6ppm constant at different pH

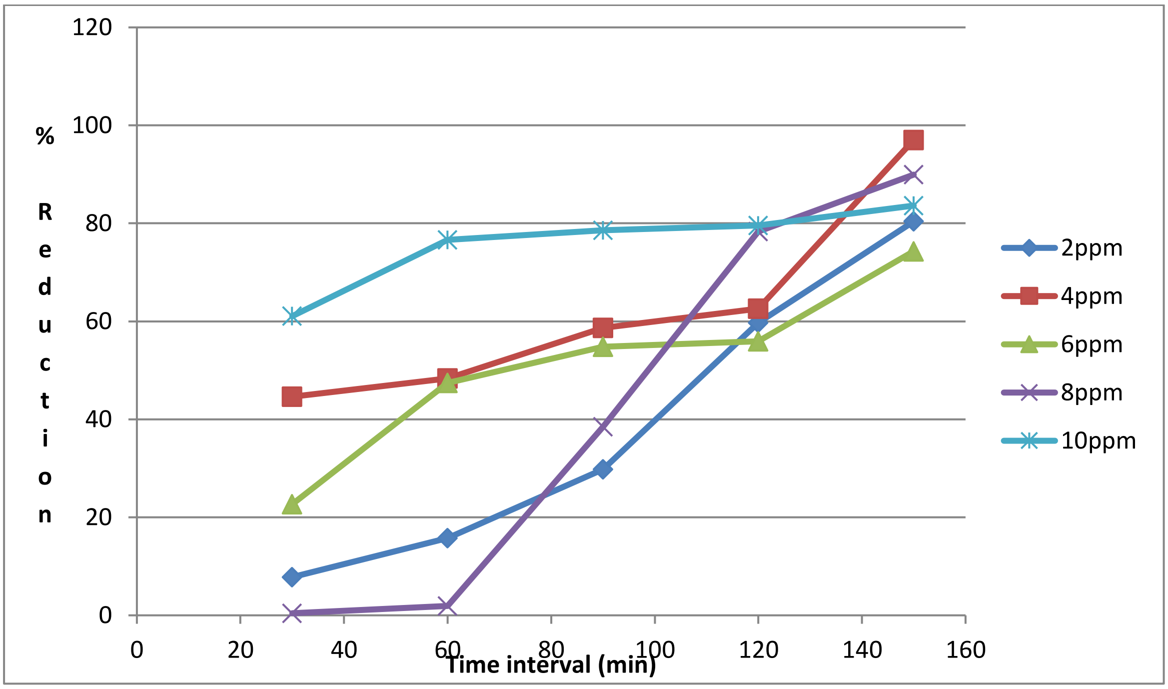


Graph.4: % Reduction vs time interval at dosage 100mg and 8ppm constant at different pH

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

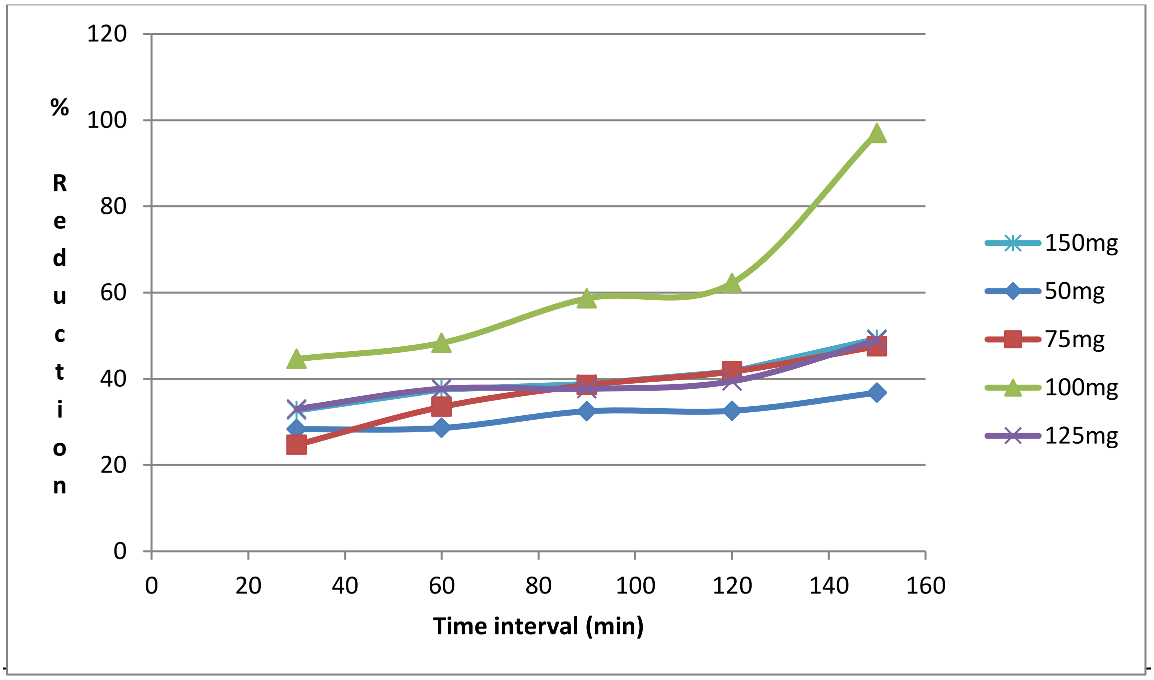


Graph.5: % Reduction vs time interval at dosage 100mg and 10ppm constant at different pH



Graph.6: % Reduction vs time interval at dosage 100mg and 5pH constant at different concentration (ppm).

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018



Graph.7: % Reduction vs Time interval at 4ppm and 5pH constant at different dosage.

In graph.1, 2, 3, 4 and 5 keeping dosage 100mg and concentration 2ppm, 4ppm, 6pmm, 8pmm and 10ppm constant respectively with variation in pH the highest reduction of 80.39%, 97%, 74.3%, 89.95% and 83.63% were found respectively. Therefore, we can conclude that the maximum reduction was obtained at 5pH. Graph.6 shows that at 5pH and 100mg dosage constant at different concentration maximum reduction of 97% was found at 4ppm.Since, best results were found at 4ppm 5pH keeping them constant variation in dosage were made and the maximum reduction was obtained at 100mg of dosage.

OPTIMISATION USING TAGUCHI METHOD

Taguchi design of Experiments for variation in ppm and pH:

Here L-25 orthogonal array is used for conducting the experiment. As per the Table-1 the varying time test was carried out with two variables ppm and pH, and altering them for four levels. The standard L-25 orthogonal array consists of 25 tests. PPM and pH are assigned first and second column. And for Smaller the better quality characteristic the varying time is studied as response to signal to noise ratio. In this 2,4,6,8 and 10 PPM concentration are taken as 1,2,3,4 and 5units respectively in PPM column and 4,5,6,7 and 10 pH are again taken as 1,2,3,4 and 5 units respectively in pH column.

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

Code	Control factors	levels				
		I	II	III	IV	Units
C1	concentration	1	2	3	4	PPM
C2	pH	1	2	3	4	----

Table 1: Control factors and their levels

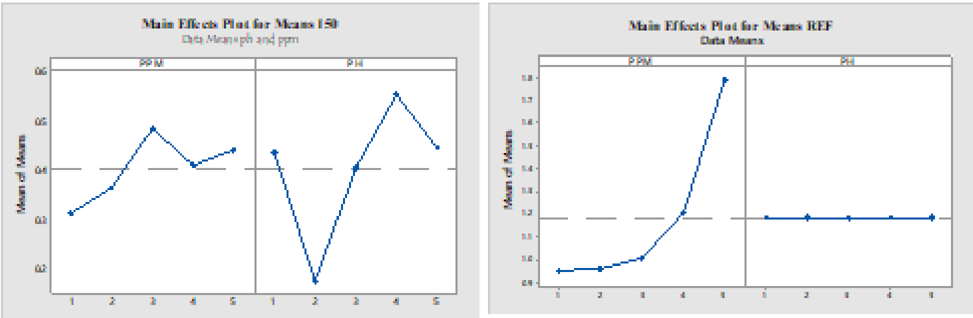


Fig.1 -Main effects plot of Means (a) 150 (b) reference

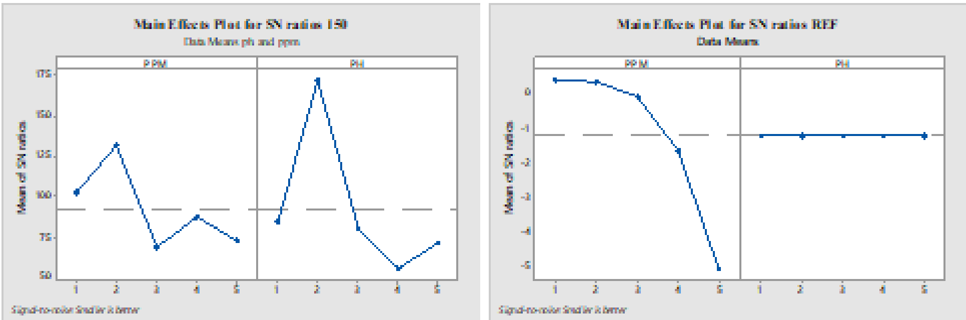


Fig. 2-Main effects plot for S/N ratios (a) 150 (b) reference

Response Table for Means

Level	PPM	pH Level
1	0.3169	0.4390
2	0.3687	0.1780
3	0.4872	0.4082
4	0.4131	0.5571
5	0.4448	0.4484
Delta	0.1702	0.3791
Rank	2	1

Response Table for Signal to Noise Ratios (smaller is better)

PPM	pH	
1	10.289	8.430
2	13.162	17.223
3	6.869	8.022
4	8.736	5.540
5	7.271	7.113
Delta	6.293	11.682
Rank	2	1

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

Table 2: Response table of varying time 150 for mean and S/N ratio (smaller is better)

Response Table for Means

Level	PPM	pH
1	0.9550	1.1855
2	0.9609	1.1855
3	1.0091	1.1855
4	1.2073	1.1855
5	1.7954	1.1855
Delta	0.8404	0.0000
Rank	1	2

Response Table for Signal to Noise Ratios (smaller is better)

Level	ppm	pH
1	0.39966	-1.21046
2	0.34644	-1.21046
3	-0.07886	-1.21046
4	-1.63630	-1.21046
5	-5.08322	-1.21046
Delta	5.48288	0.00000
Rank	1	2

Table 3: Response table of varying time Ref for mean and S/N ratio (smaller is better)

Taguchi analysis:

According to the orthogonal array L-25, experiments were conducted for different combinations of process parameters. The experimental value were remodeled into S/N quantitative for measuring the standard characteristics using MINITAB-17

Analysis of control factors:

In Taguchi method, the desirable value (mean) for the output characteristics is termed as signal and the undesirable value for the output characteristics is termed as noise. Taguchi uses S/N ratio to measure the characteristics deviating from the desire values. The Delta statistic is the maximum minus the minimum average of S/N ratio and mean for each factor. The minitab 17 assigns ranks based on Delta values, highest delta value is rank 1 and second highest is rank 2. As per Taguchi experiments, the S/N ratio is always maximized. The S/N ratios with high values in the response The main effect plot is the plot of means at each level. And by these plots one can use and compare the magnitude and relative strength of the various main effects across factors. Also it is important to evaluate significance by looking at the effects in the analysis of variable table.

IRJGES

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

Analysis of variance (ANOVA):

Sir Ronald Fisher introduced analysis of variance (ANOVA) and was performed using statistical software MINITAB 17.The investigation is carried out and the level of confidence is 5% i.e. 95 %level of confidence. The principle of ANOVA is to analyze the percentage of contribution of variance over the response parameter and to find the influence of wear parameters. For statistically significant model the P-value should be less than 0.05. The pooled error related in the ANOVA table was approximately about 44.524% for 150 and 10.010% for reference sample as per 150.

Source	DF	Adj SS	Adj MS	F-Value	P-Value	p%
ppm	4	0.08732	0.02183	0.88	0.497	10.010
pH	4	0.38851	0.09713	3.92	0.021	44.524
Error	16	0.39672	0.02479			45.466
Total	24	0.87255				100.000

Table 4: Analysis of Variance for 150

Source	DF	Adj SS	MS	Fvalue	Pvalue	P%
PPM	4	2.53562	0.63391	**	100	
PH	4	0.00000	0.00000	**		
Error	16	0.00000	0.00000			
Total	24	2.53562				100

** Denominator of F-test is zero or undefined.

Table 5: Analysis of Variance for Ref

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

Regression analysis and confirmation test:

Statistical software MINITAB 17 is used to develop the linear regression equation. A correlation is established between the significant parameters.

The linear regression equation developed for 150 is:
150 = 0.197 + 0.0300 PPM + 0.0398 pH

The linear regression equation developed for for reference is:

Ref = 0.607 + 0.1927 PPM + 0.0000 pH

As compared with the above two relation, the coefficient related with ppm and ph is positive. This shows as ppm and pH increases, varying time also increases and if the coefficient related with the ppm and pH is negative it shows increase in time.

Expt no	PPM	pH
1	1	1
2	2	2
3	3	3
4	4	4

Table 6: Confirmation experiment

Expt No	REF			150		
	Exp value	REG value	Error	Exp value	REG value	Error
1-1	0.9553	0.7997	0.1553	0.3866	0.2668	0.1198
2-2	0.9609	0.9924	-0.0315	0.0286	0.3366	-0.308
3-3	1.00912	1.1851	-0.1759	0.325	0.4064	-0.0814
4-4	1.2073	1.3778	-0.1705	0.5709	0.4762	0.0947
5-5	1.7954	1.5705	0.2249	0.3848	0.5460	-0.1612

Table 7: Results of confirmation experiment

Pooled error for ref varies from -0.1759 to 0.2249 = 0.049
Pooled error for 150 varies from -0.308 to 0.1198 = -0.1882

Taguchi design of Experiments for variation in Dosage and Time

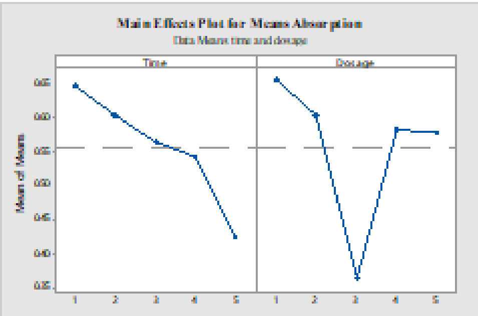
Here L-25 orthogonal array is used for conducting the experiment. As per the Table-1 the varying time test was carried out with two variables time and dosage, and altering them for four levels. The standard L-25 orthogonal array consists of 25 tests. TIME and DOSAGE are assigned first and second column. And for Smaller the better quality characteristic the varying time is studied as response to signal to noise ratio.in this dosage 50,75,100,125 and

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

150 mg are taken as 1,2,3,4and 5 respectively in dosage column and time 30,60,90,120 and 150 min are taken as 1,2,3,4 and 5 respectively in time column. Table 6 readings are used from Appendix B

Code	Control factors	levels				
		I	II	III	IV	Units
C1	Time	1	2	3	4	min
C2	Dosage	1	2	3	4	mg

Table 1: Control factors and their levels



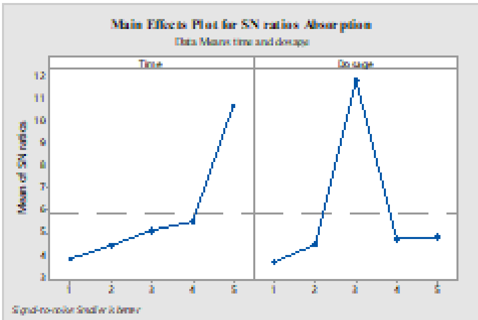


Fig 1: Main effects plot of Means and S/N ratios for Dosage vs Time

Response Table for Means			Response Table for Signal to Noise Ratios (smaller is better)		
Level	Time	Dosage	Level	Time	Dosage
1	0.6467	0.6555	1	3.831	3.678
2	0.6036	0.6031	2	4.433	4.457
3	0.5644	0.3635	3	5.088	11.851
4	0.5427	0.5824	4	0.5427	0.5824
5	0.4448	0.4484	5	10.697	4.802
Delta	0.2220	0.2920	Delta	6.866	8.173
Rank	2	1	Rank	2	1

Table 2: Response table of varying time Dosage for mean and S/N ratio (smaller is better)

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

Taguchi analysis:

According to the orthogonal array L-25, experiment were conducted for different combinations of processparameters.The experimental value were remodeled into S/N quantitative for measure the standard characteristics using MINITAB-17

Analysis of control factors:

In Taguchi method, the desirable value (mean) for the output characteristics is termed as signal and the undesirable value for the output characteristics is termed as noise. Taguchi uses S/N ratio to measure the characteristics deviating from the desire values. The Delta statistic is the maximum minus the minimum average of S/N ratio and mean for each factor. The minitab 17 assigns ranks based on Delta values, highest delta value is rank 1 and second highest is rank 2 As per Taguchi experiments, the S/N ratio is always maximized. The S/N ratios with high values in the response The main effect plot is the plot of means at each level. And by these plots one can use and compare the magnitude and relative strength of the various main effects across factors. Also it is important to evaluate significance by looking at the effects in the analysis of variable table.

Analysis of variance (ANOVA):

Sir Ronald Fisher introduced analysis of variance (ANOVA) and was performed using statistical software MINITAB 17.The investigation is carried out and the level of confidence is 5% i.e. 95 %level of confidence. The principle of ANOVA is to analyze the percentage of contribution of variance over the response parameter and to find the influence of wear parameters. For statistically significant model the P-value should be less than 0.05. The pooled error related in the ANOVA table was approximately about 16.39% for for time vs dosage.

Analysis of Variance:

Source	DF	Adj SS	Adj MS	F-Value	P-Value	p%
Time	4	0.13993	0.034982	7.29	0.002	29.88
Dosage	4	0.25167	0.062918	13.12	0.000	53.74
Error	16	0.07675	0.004797		16.39	
Total	24	0.46835				100.00

Table 3:Response table of varying dosage and time for mean and S/N ratio (smaller is better).

International Research Journal in Global Engineering and Sciences. (IRJGES)
ISSN : 2456-172X | Vol. 3, No. 3, Sep.-Nov 2018
Pages 174-189 | Cosmos Impact Factor (Germany): 5.195
Received: 02.10.2018 Published: 28.11.2018

Regression analysis and confirmation test:

Statistical software MINITAB 17 is used to develop the linear regression equation. A correlation is established between the significant parameters.

The linear regression equation developed for
Regression Equation-

Absorption = 0.7608 - 0.0505 Time - 0.0176 Dosage

As compared with the above two relation, the coefficient related with time and dosage is positive. This shows as time and dosage increases, varying time also increases and if the coefficient related with the time and dosage is negative it shows increase in time

Expt No	Dosage vs Time		
	Exp value	REG value	Error
1-1	0.6884	0.6927	-0.004
2-2	0.6382	0.6246	0.0136
3-3	0.3973	0.5565	-0.1592
4-4	0.58196	0.4884	0.09356
5-5	0.4928	0.4203	0.0725

Table: Pooled error for Time vs Dosage ranges from -0.1592 to 0.09356

Conclusion The iron oxide nanoparticles prepared by Sol-Gel method was found to be haematite. Synthesized Iron oxide Nanoparticles with the particle size was found to be 11.5nm..Batch studies were conducted for the reduction of toxic Heavy metal Cadmium (II).

In this work, Iron Oxide Nanoparticles were used as an effective photo catalyst for the reduction of Cd (II) under UV-vis radiation (125 watts) source. The Nanoparticles with small crystalline size and strong visible-light absorption were appropriate for the photo catalytic reduction of Cd (II). The effect of pH was investigated in reduction. The catalyst showed high reduction in acidic medium that is appropriate for the complete reduction at 5pH. Reduction increases with Contact time above 30min of UV-vis spectrum irradiation in acidic medium.The increase of Nanoparticles dosage beyond the optimum of 100mg resulted in the agglomeration of IONP, hence particle surface become unavailable for photo absorption, and reduction.According to the results, maximum metal reduction Efficiency (%) for Cd(II) were obtained at: pH 5; Contact time of 150minutes; Fe_2O_3 dosage 100mg; Metal concentration 4ppm.Optimization of parameters using Taguchi method confirmed the best results that were obtained from experiments.

Aknowledgement The authors thankfully acknowledge the Management of Rural Engineeering College Hulkoti for their support extended to carry out research at SIT Tumkur. Authors are also in depth thankful to the Principal & staff of Department of Chemical Engineering SIT Tumkur for providing the lab facilities to carry out the research work.

Referrences

1. Hu, Jin-Song, et al. "Synthesis of hierarchically structured metal oxides and their application in heavy metal ion removal." *Advanced Materials* 20.15 (2008): 2977-2982.
2. Barakat, M. A. "New trends in removing heavy metals from industrial wastewater." *Arabian Journal of Chemistry* 4.4 (2011): 361-377.
3. Kakavandi, Babak, et al. "Enhanced chromium (VI) removal using activated carbon modified by zero valent iron and silver bimetallic nanoparticles." *Journal of Environmental Health Science and Engineering* 12.1 (2014): 115.
4. Ilankoon, Nirmala. "Use of iron oxide magnetic nanosorbents for Cr (VI) removal from aqueous solutions: A review." *Journal of Engineering Research and Applications* 4.10 (2014): 55-63.
5. Xu, Piao, et al. "Use of iron oxide nanomaterials in wastewater treatment: a review." *Science of the Total Environment* 424 (2012): 1-10.
6. Zulmajdi, S. L. N., et al. "Kinetics of Photocatalytic Degradation of Methylene Blue in Aqueous Dispersions of TiO2 Nanoparticles under UV-LED Irradiation." *American Journal of Nanomaterials* 5.1 (2017): 1-6.
7. Parvin, Tabasom, et al. "Photocatalytic degradation of municipal wastewater and brilliant blue dye using hydrothermally synthesized surface-modified silver-doped ZnO designer particles." *International Journal of Photoenergy* 2012 (2012).
8. Park, Hyunwoong, et al. "Surface modification of TiO2 photocatalyst for environmental applications." *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 15 (2013): 1-20.
9. Hu, Jin-Song, et al. "Synthesis of hierarchically structured metal oxides and their application in heavy metal ion removal." *Advanced Materials* 20.15 (2008): 2977-2982.
10. Barakat, M. A. "New trends in removing heavy metals from industrial wastewater." *Arabian Journal of Chemistry* 4.4 (2011): 361-377.
11. Kakavandi, Babak, et al. "Enhanced chromium (VI) removal using activated carbon modified by zero valent iron and silver bimetallic nanoparticles." *Journal of Environmental Health Science and Engineering* 12.1 (2014): 115.
12. Ilankoon, Nirmala. "Use of iron oxide magnetic nanosorbents for Cr (VI) removal from aqueous solutions: A review." *Journal of Engineering Research and Applications* 4.10 (2014): 55-63.
13. Xu, Piao, et al. "Use of iron oxide nanomaterials in wastewater treatment: a review." *Science of the Total Environment* 424 (2012): 1-10.
14. Zulmajdi, S. L. N., et al. "Kinetics of Photocatalytic Degradation of Methylene Blue in Aqueous Dispersions of TiO2 Nanoparticles under UV-LED Irradiation." *American Journal of Nanomaterials* 5.1 (2017): 1-6.