Removal of Phenol using ZnO Nanoparticle in Three Phase Fluidization

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Abstract: **Phenol is a wide spread persistent organic pollutant that is commonly present in industrial effluent streams such as those of the petrochemical industries, kraft pulp mills, olive oil production and other chemical industries. Since phenol is harmful to organisms even at low concentration and is difficult to be graded biologically, it has been classified as a priority pollutant in wastewater. There are many physical and chemical treatment methods available for the removal of phenol but all these methods have problem associated such as secondary effluent, hazardous and harmful end products, high energy consuming, non economic etc. These problems can be overcome by the use of nanotechnology which is simple when compared to the other methods and complete removal of the pollutants is possible. In this study, Zinc oxide nanoparticles was synthesized by the wet chemical process and used for the removal of phenol from pollutants. ZnO nanoparticles were characterized by X-Ray Diffraction (XRD) and Fourier Transform Infra Red spectroscopy (FTIR). Using fluidized bed reactor the characteristics of removal of phenol was studied. The parameter like pH was varied as 3, 7 and 11 phenol concentration was varied from 10 to 50 mg / l as case I, 20 to 100 mg / l as case II, 50 to 250 mg / l as case III and 100 to 500 mg / l as case IV in the difference of 10, 20, 50, 100 mg / l respectively and adsorbent dosage varied from 0.5 to 2.5 g / l for case I and case II, 2 to 10 g / l for case III and 4 to 20 g / l for case IV. The optimized parameter for the removal of phenol from pollutant was predicted by using Design Expert software.**

Keywords: ZnO nanoparticles, Fourier Transform Infra Red spectroscopy, wet chemical process, fluidized bed reactor and Minitab software.

I. INTRODUCTION

Phenol one of the most common organic water pollutants is highly toxic even in low concentrations. Besides, phenol leads further to the generation of substituted compounds during disinfection and oxidation processes in natural water (1, 2, 3). Phenol is also relevant in the field of environmental research, because it has been chosen frequently as a model pollutant and many data are available on its removal and destruction in particular with respect to wastewater treatment. Phenol exists in all industrial wastewater, such as refineries (6-500 mg/l), coke making operations (28-3900 mg/l), coal processing (9-6800 mg/l) and manufacture of petrochemicals (2.8-1220 mg/l) (4). Phenol is also the main organic constituents exist in condensate streams of coal gasification and liquefaction (5). Phenol exists in waste water of pharmaceutical, plastics, wood products, paint, pulp and paper industries (0.1-1600 mg/l).

Phenol containing wastewater must not drain into open water without treatment because of the toxicity of phenol. It also contributes to off-flavors in drinking and food processing water. Thus, lots of abatement technologies for phenol from wastewater were developed, whose primary mechanisms are separation and destruction. For separations, the solid-liquid-vapor state diagram for the water-phenol system to distillate the phenol contamination (6).

The best abatement technologies for removal of phenol from wastewater to be applied strongly depend on single cases, in particular on the concentration of phenol in the stream, the co-presence of other contaminants, the nature of the plant where this problem is found. Now, a number of strategies such as oxidation with ozone-hydrogen peroxide, biological methods, membrane filtration, ion exchange, electrochemical oxidation, photo catalytic degradation and adsorption have been used for the removal of phenol (7, 8). Review on available technologies for phenol removal from fluid streams has been recently published providing comparison of the experimental conditions and the performances of different techniques (9).

Nanotechnology involves the creation and manipulation of materials at the nanometre (nm) scale either by scaling up from single groups of atoms or by refining or reducing bulk materials. A nanometre is 1×10^{-9} m or one millionth of a millimetre. The properties of many conventional materials change when formed from nanoparticles. This is typically because nanoparticles have a greater surface area per weight than larger particles which causes them to be more reactive to some other molecules. Nanoparticles are used, or being evaluated for use, in many fields (10).

Up to now, ZnO has been synthesized by various techniques including sol-gel method, hydrothermal synthesis method, chemical vapor deposition, precipitation method, laser vaporization condensation method and spray-pyrolysis method (11). Among these techniques, spray-pyrolysis process has been successfully applied to synthesize a wide variety of inorganic and organic materials (12). It has many advantages, which were high purity of synthesized powders, regular shape of particles, a better control of stoichiometry and continuous working.

Process design is typically complex due to varying customer demands and technology advances. Several responses must generally be considered in complex product/process designs. Therefore, simultaneously optimizing multiple responses is of priority concern. Design of experiments (DOE) is extensively adopted in industry to improve processes, product design or obtain an optimal parameter setting for process parameters. When utilizing DOE, Response Surface Methodology (RSM) is frequently employed to obtain the optimal parameter setting following analysis of variance (ANOVA) for identifying significant factors (13). Through RSM, an equation representing the approximate relationship between a single response and control factors can be obtained based on experimental data. A contour plot is used to characterize the response surface graphically and determine the optimal parameter-setting. When multiple responses are considered, the optimal parameter setting is obtained by observing overlay contour plots (14). Because RSM constructs response surfaces for each response, the overlay contour plots are complex when many responses are considered. In this case, determining the optimal parameter-setting is difficult. A conventional means of optimizing multiple responses in DOE is to formulate a multi-response problem as a constrained optimization problem (15). The response surface of a concerned response is selected as the objective function, and the remaining response surfaces are selected as constraint functions. Mathematical programming is then utilized to acquire the problem solution.

II. EXPERIMENTAL SETUP AND PROCEDURE

2.1. Precipitation of ZnO from Aqueous Solution of Zinc Salts

A one-step wet-chemical process was employed for synthesis of ZnO nanoparticles as shown in equation (1).

$$ZnSO_4 + 2NaOH \rightarrow ZnO(s) + Na_2SO_4 + H_2O \qquad (1)$$

Around 250 ml of 0.05 M zinc sulphate was prepared and 150 ml of 1N NaOH was added slowly to the zinc sulpahte solution. A white precipitate obtained was stirred for 2hr to get a milky white solution. Then the solution was placed in an oven at 100 ^{0}C. After removal of the moisture content, the solid was crushed using sterilized mortar to get a powder. The solid was washed in double distilled water, then dried and crushed, followed by calcination at 800 ^{0}C.

2.2. Coating of Nanoparticle

Coating of nanoparticles on glass beads and ceramic rings were done by the following methods. 50 g of ZnO nanoparticles and 9 g of polyethylene glycol are mixed with 50 g of isopropanol and stirred at room temperature for 1hr. Then 4 ml of deionized water and 2 g of nitric acid was added slowly under vigorous stirring conditions. The glass beads were added to the solution and placed in an oven to remove the moisture content (16).

2.3 Characterization of ZnO Nanoparticle

Size of the nanoparticles were analyzed by XRD and confirmed by using FTIR spectroscopy.

2.4 Preparation Of Synthetic Effluent

To get a 1000 ppm of synthetic effluent , 0.93 ml of phenol was dissolved in 1000 ml water. Effluent was prepared by varying the concentration 10 ppm to 500 ppm. The solution was prepared and stored in a brown color glass container.

Fig 1. Glass beads and ceramic rings before coating

Fig 2. Glass beads and ceramic rings after coating

2.5 Analysis of Phenol Solution

The concentration of the phenol in the synthetic effluent was determined by spectrophotometry method. The absorbance of colored complex of phenol with 4-aminoantipyrene was read at wavelength 700nm. 4-aminoantipyrene solution was added to the effluent at a ratio of 15 ml in 1000 ml (17).

2.6 Experimental Procedure

Removal of phenol from the effluent was carried out using two methods, batch reactor and batch fluidized bed reactor. In the batch reactor, the effect of pH, effluent concentration and adsorbent dosage were studied. In batch fluidized bed reactor, the optimized pH value in batch stirring method was used to prepare synthetic effluent (18). In this method, the driving forces for the removal of phenol are gas flow rate, liquid flow rate, concentration of the effluent and adsorbent dosage, which are optimized using the software MINITAB17. The parameters varied are concentration (100-500 mg/l), adsorbent dosage (2.0-10.0 g/l), gas flow rate (0.025-0.125 cm^3/sec) and liquid flow rate (50-250 l/hr).

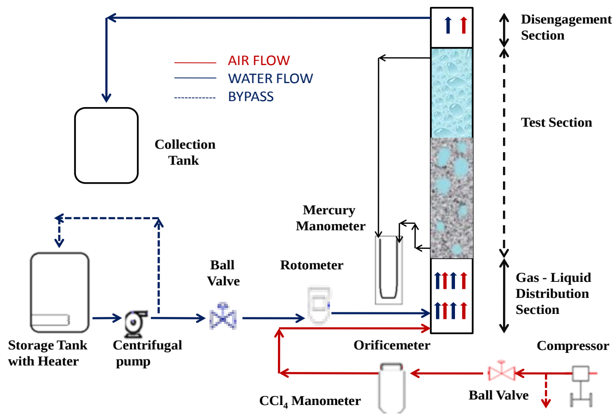

Fig 3. Fluidized COLUMN

III. RESULTS AND DISCUSSION

3.1 Characterization of Zinc-oxide Nanoparticle

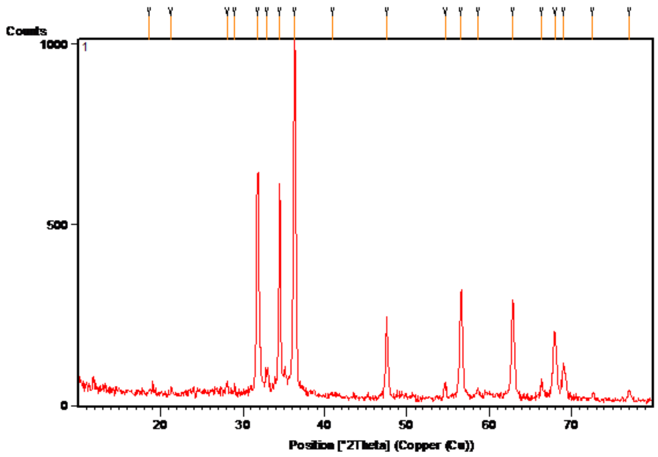

Fig 4. XRD analysis on Zinc oxide Nanoparticle

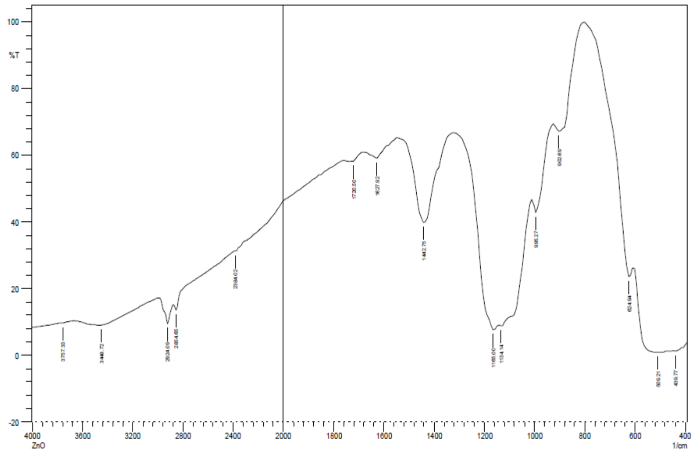

Fig 5. FTIR analysis of Zinc oxide Nanoparticle

The analyzed ZnO Nanoparticle obtained a size of 61.2nm calculated from the graph

3.2. Optimization of pH

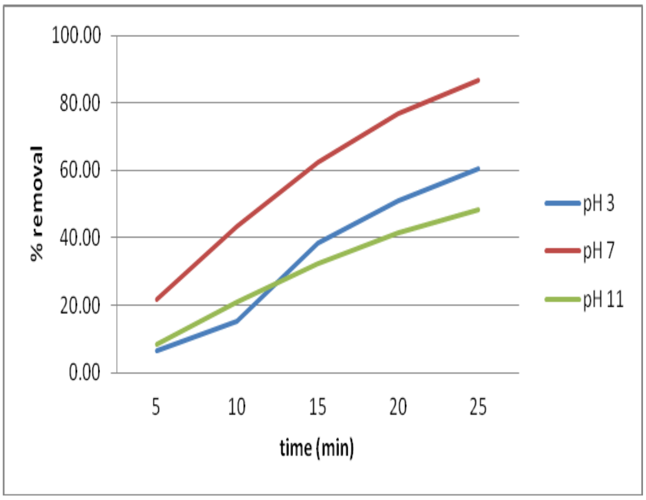

Fig 6. Removal efficiency of adsorbent at various pH values

To remove phenol from effluent, pH of the effluent was optimized. The pH of the solution was varied as pH 3, 7 and 11. To optimize the removal efficiency of phenol, the adsorbent dosage and initial concentration of phenol was kept constant. The adsorbent dosage of ZnO nanoparticles of 1.5 g/l and initial concentration of phenol of 30 mg/l was maintained at the beginning of the process. The percentage of phenol removal was good at pH 7, whereas pH 3 and 11 shows less removal compared to pH 7. From the below graph the optimized pH 7 effluent was used. This is due to high alkalinity and high acidity of the effluent (19).

3.3 Response Surface Method

RSM defines the effect of the independent variables, alone or in combination, on the processes. In addition to analyzing the effects of the independent variables, this experimental methodology also generates a mathematical model.

In the present study, the Box–Behnken experimental design was chosen for finding out the relationship between the response function variables. Box–Behnken design is rotatable second-order design based on three-level incomplete factorial designs [20]. The special arrangement of the Box–Behnken design levels allow the number of design points to increase at the same rate as the number of polynomial coefficients. For three factors, for example, the design can be constructed as three blocks of four experiments consisting of a full two-factor factorial design with the level of the third factor set at zero.

Design

Table 1. Parameters provided in Design Expert software

Factor	Name	Type	Low	High
A	Gas flow rate	Numeric	0.025	0.125
B	Liquid flow rate	Numeric	50	250
C	Concentration	Numeric	100	500
D	Adsorbent Dosage	Numeric	20	100

Table 2. Actual design of experiments and responses

Std	Run	Factor 1	Factor 2	Factor 3	Factor 4	Response 1
		A Gas flow rate	**B Liquid flow rate (l/hr)**	**C Conc. (mg/l)**	**D Adsorbent dosage (g/l)**	**Removal efficiency %**
4	1	0.125	250	300	60	77.38
6	2	0.075	150	500	20	65.84
24	3	0.075	250	300	100	76.53
23	4	0.075	50	300	100	94.28
29	5	0.075	150	300	60	85.67
20	6	0.125	150	500	60	76.45
14	7	0.075	250	100	60	81.23
22	8	0.075	250	300	20	69.85
25	9	0.075	150	300	60	79.81
13	10	0.075	50	100	60	89
18	11	0.125	150	100	60	82.71
21	12	0.075	50	300	20	74.05
7	13	0.075	150	100	100	96.09
8	14	0.075	150	500	100	81.57
26	15	0.075	150	300	60	84.63
16	16	0.075	250	500	60	67.81
5	17	0.075	150	100	20	71.49

9	18	0.025	150	300	20	72.07
2	19	0.125	50	300	60	74.92
28	20	0.075	150	300	60	80.67
27	21	0.075	150	300	60	83.95
3	22	0.025	250	300	60	70.26
15	23	0.075	50	500	60	79.36
10	24	0.125	150	300	20	60.17
12	25	0.125	150	300	100	74.41
17	26	0.025	150	100	60	79.92
11	27	0.025	150	300	100	79.93
1	28	0.025	50	300	60	84.75
19	29	0.025	150	500	60	74.32

Table 3. ANNOVA table

Source	Squares	D_f	Mean Square	F Value	p-value
Model	1539.96	8	192.49	15.38	< 0.0001
A-Gas flow rate	19.28	1	19.28	1.54	0.2289
B-Liquid flow rate	236.74	1	236.74	18.92	0.0003
C-Concentration	252.91	1	252.91	20.21	0.0002
D-Adsorbent dosage	665.14	1	665.14	53.14	< 0.0001
AB	71.83	1	71.83	5.74	0.0265
BD	45.9	1	45.9	3.67	0.0699
A^2	175.13	1	175.13	13.99	0.0013
D^2	105.71	1	105.71	8.45	0.0087
Residual	250.31	20	12.52		
Lack of Fit	224.03	16	14	2.13	0.2424
Pure Error	26.28	4	6.57		
C of Total	1790.27	28			

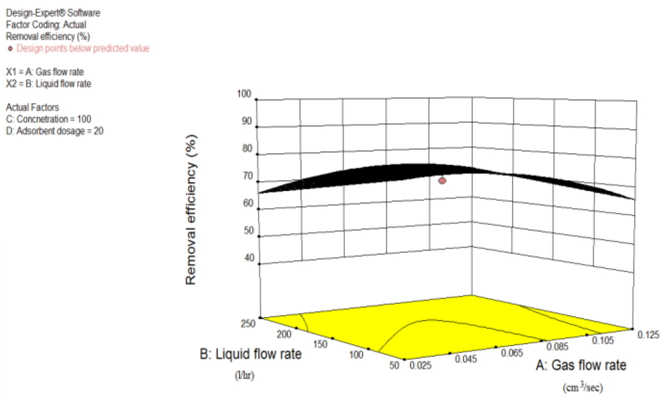

Fig 7. Combined effects of 100 mg/l of concentration and 20g/l adsorbent dosage on removal efficiency

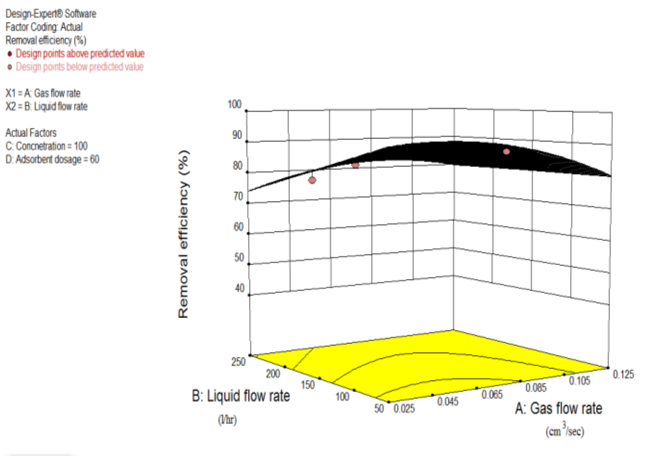

Fig 8. Combined effects of 100 mg/l of concentration and 60g/l adsorbent dosage on removal efficiency

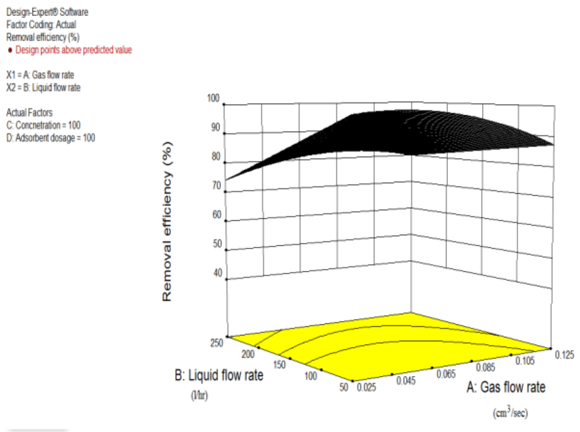

Fig 9. Combined effects of 100 mg/l of concentration and 100 g/l adsorbent dosage on removal efficiency

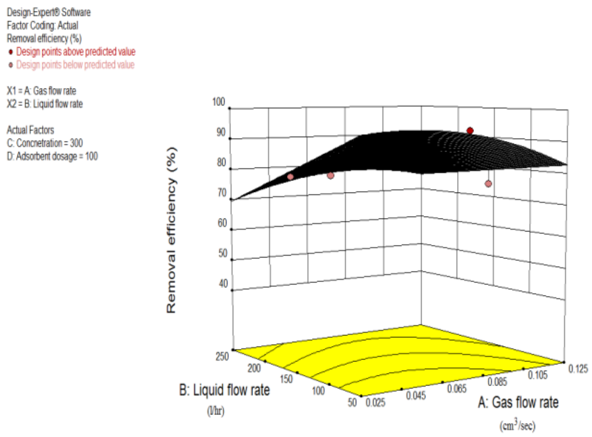

Fig 10. Combined effects of 300 mg/l of concentration and 100 g/l adsorbent dosage on removal efficiency

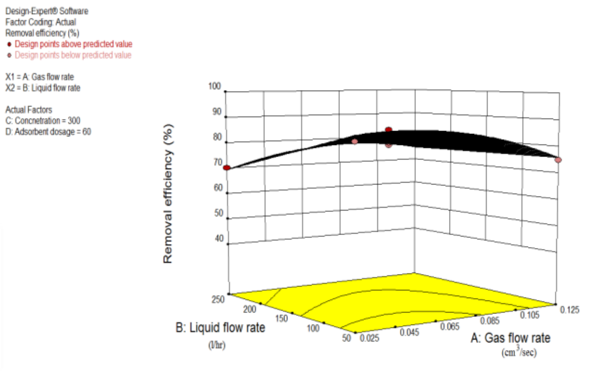

Fig 11. Combined effects of 300 mg/l of concentration and 60g/l adsorbent dosage on removal efficiency

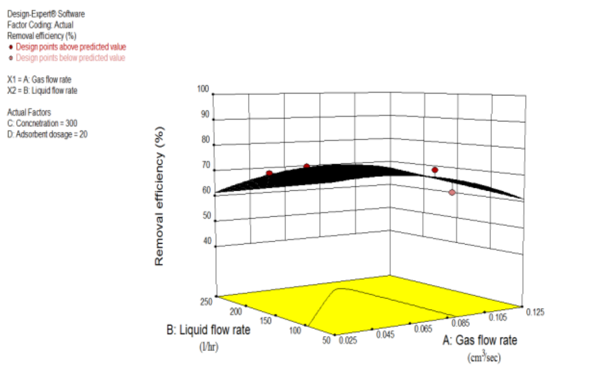

Fig 12. Combined effects of 300 mg/l of concentration and 20g/l adsorbent dosage on removal efficiency

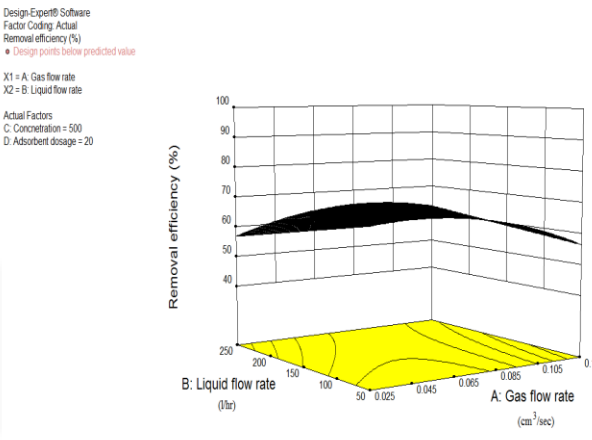

Fig 13. Combined effects of 500 mg/l of concentration and 20g/l adsorbent dosage on removal efficiency

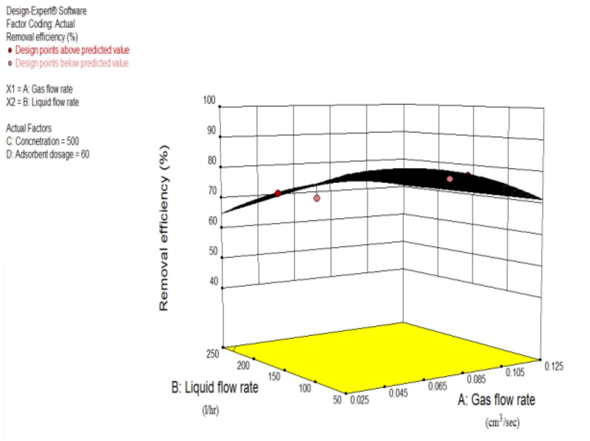

Fig 14. Combined effects of 500 mg/l of concentration and 60g/l adsorbent dosage on removal efficiency

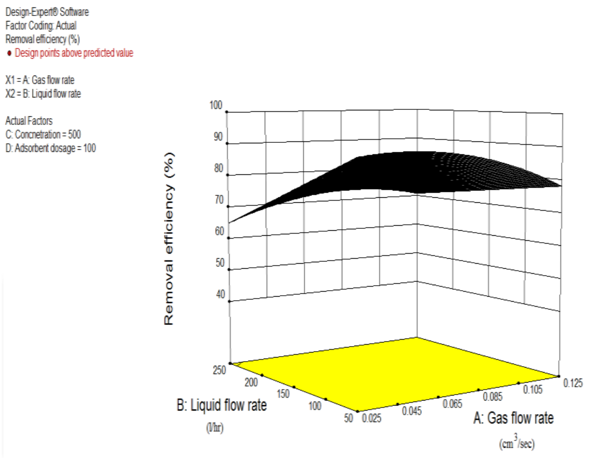

Fig 15. Combined effects of 500 mg / l of concentration and 100 g/l adsorbent dosage on removal efficiency

Final Equation in Terms of Actual Factors

Removal efficiency = 68.00490057 + 149.7630682 X Gas flow rate - 0.057166667 X Liquid flow rate - 0.022954167 X Concentration + 0.606672585 X Adsorbent dosage + 0.8475 X Gas flow rate X Liquid flow rate - 0.000846875 X Gas flow rate X Liquid flow rate - 2014.920455 X Gas flow rate^2 - 0.002445969 X Adsorbent dosage^2

Final Equation in Terms of Coded Factors

Removal efficiency = 81.94931818 - 1.2675 X A - 4.441666667 X B - 4.590833333 X C + 7.445 X D + 4.2375 X AB - 3.3875 X BD - 5.037301136 X A^2 - 3.913551136 X D^2

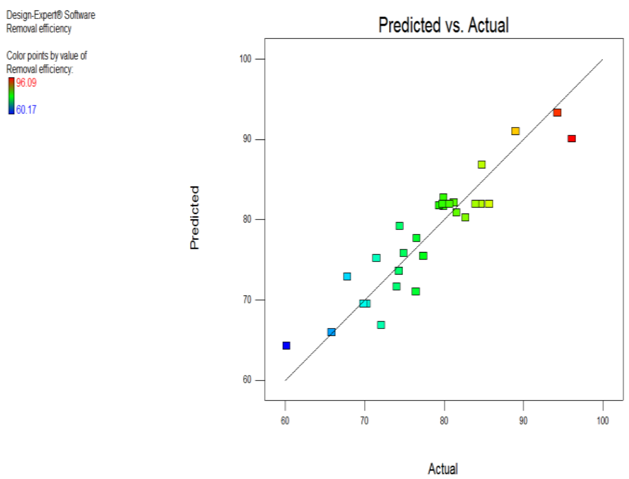

Fig 16. Linear plot for actual values versus predicted values

IV. CONCLUSION

The effect of phenol removal by using ZnO nanoparticles were studied. Synthesized nanoparticles were analyzed by using XRD and FTIR. From XRD image the size of ZnO nanoparticles was calculated as 61.2 nm. FTIR image shows that ZnO nanoparticles were found in the region between 400-600 cm^{-1}. The high adsorbent dosage of 2.5 g/l has the maximum removal efficiency for 40 mg/l and 80 mg/l respectively. The maximum adsorbent dosage of 8 g/l and 16g/l removes the minimum effluent concentration as 50 mg/l and 100 mg/l respectively. By using fluidized column, the effect of removal of phenol was optimized by using Design Expert software and Minitab software. Parameters such as gas flow rate, liquid flow rate, concentration of effluent and adsorbent dosage play a vital role in treatment of effluent. By using the software it was analyzed that the effluent concentration was affected with respect to the gas flow rate, liquid flow rate and adsorbent dosage in order. At low gas flow rate and liquid flow rate the removal efficiency of phenol was high. Adsorbent dosage and effluent concentration does affect the removal efficiency but not greater than the gas flow rate and liquid flow rate. ANNOVA table, fit summary table, removal efficiency equation, linear regression equation, interaction plot and actual value versus predicted value has been provided and plotted for Box–Behnken experimental design and factorial design. It was evident that the removal efficiency of phenol was good in fluidized bed column than the batch stirring method.

V. REFERNCES

1. A.P. Annachhatre et al., (1996) "Biodegradation of chlorinated phenolic compounds", Biotechnology Advances, Volume 14, Issue 1, pp 35–56.
2. Alexander M. Klibanov et al., (1983) "Peroxidase - Catalyzed Removal of Phenols from Coal-Conversion Waste Waters", Science,Vol. 221, no. 4607, pp. 259-261.
3. Al-SultaniKadhim F et al., (2012) "Characterization the Removal of Phenol from Aqueous Solution in Fluidized Bed Column by Rice Husk Adsorbent", Research Journal of Recent Sciences, Vol. 1, pp. 145-151.
4. AmitBhatnagar et al., (2006) "Conventional and non-conventional adsorbents for removal of pollutants from water – A review", Indian Journal of Chemical Technology, Vol 13, pp.203-217.
5. AntonijaVišekruna et Al., (2014) "The Use of Low Cost Adsorbents for Purification Wastewater", The Holistic Approach to Environment, vol. 1, pp.29-37.
6. Brian G. Prevo et al., (2004) "Controlled, Rapid Deposition of Structured Coatings from Micro- and Nanoparticle Suspensions", Langmuir, vol. 20, pp.2099-2107.
7. BrunaMartinelloSavi et al., "Synthesis Of Zno Nanoparticles By Solgel Processing", Castellón (Spain)., pp12.
8. Butenko E et al., (2014) "LDHs as Adsorbents of Phenol and Their Environmental Applications", American Journal of Environmental Protection, Vol. 2, No. 1, 11-15
9. D N Jadhav et al., (2004) "Removal of phenol from wastewater using sawdust, polymerized sawdust and sawdust carbon", Indian Journal of Chemical Technology., Vol.11, pp, 35-41.
10. Dada, A.O. et al., (2012) "Langmuir, Freundlich, Temkin and Dubinin–Radushkevich Isotherms Studies of Equilibrium Sorption of Zn2+ Unto Phosphoric Acid Modified Rice Husk", IOSR Journal of Applied Chemistry, Vol. 3, Issue 1, pp 38-45.
11. Dhermendra K. Tiwari et al., (2008) "Application of Nanoparticles in Waste Water Treatment", World Applied Sciences Journal, 3 (3), pp. 417-433.
12. Dr. Khalid FarhodChasib Al-Jiboury et al., (2013) "Adsorption of Phenol from Industrial Wastewater using Commercial Powdered Activated Carbon", ICOEST, pp21.
13. Evan H. Crook et al., (1975) "Removal and Recovery of Phenols from Industrial Waste Effluents with Amberlite XAD Polymeric Adsorbents", I&EC Product Research and Development, 14 (2), pp 113–118.
14. Ghaffarian et al., (2011) "Synthesis of ZnO Nanoparticles by Spray Pyrolysis Method", Iran. Journal Chemical Engineering, Vol. 30, No. 1.
15. Hou L et al., (2013) "Removal of ZnO nanoparticles in simulated wastewater treatment processes and its effects on COD and NH(4)(+)-N reduction", Water Sci Technol., vol. 67(2), pp. 254-60.
16. JussiHakanen et al., (2008) "Simulation-Based Interactive Multi objective Optimization in Wastewater Treatment", International Conference on Engineering Optimization.
17. K. Prasad et al.,(2009) "ZnO Nanoparticles: Synthesis and Adsorption Study", Natural Science ., Vol.1, No.2, pp 129-135.
18. KamelliaNejati et al., (2011) "Synthesis of ZnO Nanoparticles and Investigation of the Ionic Template Effect on Their Size and Shape", International Nano Letter.
19. Kulkarni SunilDatta et al., (2013) "Adsorption for Phenol Removal-A Review", International Journal of Scientific Engineering and Research, Volume 1, issue 2.
20. Mehdi Vadi et al., (2010) "Application of the Freundlich , Langmuir, Temkin and Harkins-Jura Adsorption Isotherms for Some Amino Acids and Amino Acids Complexation with Manganese Ion(II) on Carbon Nanotube", 2010 International Conference on Nanotechnology and BiosensorsIPCBEE ,vol.2.