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APPLICATION OF RESPONSE SURFACE METHODOLOGY FOR OPTIMIZATION OF Pb AND Cr ADSORPTION ON IRON-COATED LIMESTONE

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ABSTRACT
Daily discharging of excessive wastewater containing heavy metals into receiving water causes environmental problems such as eutrophication, corrosion and fouling. This paper presents the results of research carried out for Lead and Chromium adsorption on iron-coated limestone (ICL) as low cost adsorbent using response surface methodology (RSM) for optimization. Characteristics of the adsorbent studied were including pH, adsorbent particle size, bulk density, iodine value and surface area of 8.40, ≤63 µm Ø, 1.623 g/cm^3, 27.3 mg/g, 1031 m^2/g respectively. Scanning electron microscopy (SEM) of the adsorbent at 500 X magnification revealed a more porous nature on the surface and an irregular texture. X-ray fluorescence (XRF) analysis also showed appreciable increase in % weight of Fe_2O_3, Cl, MgO, SiO_2 and SO_3 due to the addition of $FeCl_3.6H_2O$ for coating. The factors considered for optimization were initial concentration (mg/L), adsorbent mass (g), contact time (mins), and the response obtained was the removal efficiency (%). The analysis of variance (ANOVA) was used to develop the model equations for both Pb and Cr removal efficiency. The result revealed that optimum conditions for the adsorption of Pb on iron-coated limestone are; initial concentration of 6.02 mg/L, adsorbent mass of 0.37 g and contact time of 33.84 minutes, this produced a removal efficiency of 95.38%, Cr has optimal conditions of initial concentration at 56.14 mg/L, adsorbent mass of 0.73 g and contact time of 157.14 minutes with a removal efficiency of 91.03%. The optimum adsorbent doses for both Pb and Cr showed that the adsorbent had more adsorption site and was more utilized at lower adsorbent dose.
Keywords: *Response Surface Methodology (RSM), Adsorption, Iron-Coated Limestone (ICL), Surface Area, Removal Efficiency.*

INTRODUCTION
In today's world, developing countries face alarming challenges in the rising demand for potable drinking water, and conditions are particularly bad with the rapid growth of industrialization and population towards a developed society. The waste products generated from major laboratories and industries such as textiles, chemicals manufacturing, mining, electroplating, tanneries, metallurgical and metal finishing industries are some of the major sources responsible for water contamination (Matheickal *et al.,* 1997). This contaminated water contains non-biodegradable effluents such as heavy metal ions which are persistent and toxic to the environment and human health even at low concentration because of their bioaccumulation. The metal ions subsequently enter the human food web through plants and can be transferred from one food chain to another (Hasan *et al.,* 2013). This implies that in order to have a healthy and safe environment, these toxic metal ions need to be removed from wastewater before disposal (Jepchirchirchebor, 2015).

Some of these heavy metals have main roles in biological systems; especially trace metals that are essential for living organisms. These elements can easily lead to poisoning when their concentration rises to supra-optimal values. They may cause alterations in numerous physiological processes at cellular/molecular level by inactivating enzymes, blocking functional groups of metabolically important molecules, displacing or substituting for essential elements and disrupting membrane integrity. A rather common consequence of heavy metal poisoning is the enhanced production of reactive oxygen species (ROS) due to interference with electron transport activities (Mohammed *et al.*, 2013). Lead accumulates mainly in bones, brain, kidney and muscles and may cause serious disorders like kidney disease, anemia, nervous disorder and even cancer (Gunatilake, 2015). Chromium (VI) has been reported to be a powerful carcinogen capable of modifying the deoxyribonucleic acid (DNA) transcription process in both animals and humans and resulting in important chromosome aberrations (Pandey *et al*., 2010). Excess level of Chromium is also associated with an increased risk for cancer, heart disease and other illness such as endocrine problem, arthritis, diabetes and liver disease (Niederau *et al.,* 1996).

In an effort to reduce the environmental effects of heavy metals, various techniques have been employed; some of these processes have been proven to be very expensive (Robert *et al.,* 1993). One of the critical reviews on current treatment methods for heavy metals removal by Barakat, (2011) reported that adsorption was an effective method, and was neither costly nor required special tools. In most cases, it can also be found in the environment naturally plentiful or produced as a by-product or waste from an industry or agricultural process (Pollard *et al.*, 1992).

Limestone is a naturally occurring low cost adsorbent which has been proven to significantly remove heavy metals such as Cd, Pb, Zn, Ni, Cu and Cr (III) by up to a 90%. This was higher than the 80% and 65% removal rates achieved using crushed bricks and gravel respectively (Mandadi, 2012). Various types of limestone such as pure, carbonaceous and brecciated limestones were found to have varying degrees of heavy metal removal abilities (Zhigang, 2009). Further studies on the removal behavior of these metals indicated that rough solid media with the presence of carbonate were more beneficial for the removal process (Swarna, 2012). This paper presents the use of ICL as an improved low cost adsorbent for the adsorption of Pb and Cr from wastewater. Response Surface Methodology (RSM) in Minitab v.18.1 was used for optimization to obtain an optimum condition for the variables considered.

MATERIALS AND METHOD

Preparation of Simulated Wastewater

Simulated 1000 ppm standard solution of wastewater containing Pb was prepared by dissolving 1.5695 g of lead acetate (Pb $(C_2H_3O_2)_2$) in 10 mL of distilled water which was then transferred to a 1000 mL flask and the volume was made up to 1000 mL with distilled water. Similarly, 1000 ppm standard solution of wastewater containing Cr was prepared by using 2.8289 g of potassium dichromate ($K_2Cr_2O_7$) which was dissolved in 10 mL of distilled water and then transferred to a 1000 mL volumetric flask after which the volume was made to 1000 mL with distilled water.

Preparation of Adsorbent

The solid limestone sample was pulverized into smaller particles using chisel and hammer. It was then sieved to an obtainable 63 μm Ø mesh size. 100 g of the purely pulverized limestone was poured into a round bottom flask, a 100 mL solution of 0.1 M iron (III) chloride ($FeCl_3$) solution was prepared and poured into the container and sealed. It was then placed on a model 5900 mechanical shaker. After 24 hours few drops of sodium hydroxide solution was then added to the solution, the granules was then rinsed with distilled water and then air dried (Mandadi, 2012).

Bulk Density

The use of Archimedes principle was applied to determine the bulk density. This was done by first measuring the weight of an empty 10 cm^3 measuring cylinder. The air dried measuring cylinder was then fully packed with the limestone sample, leveled and weighed. The volume of the limestone was also measured, the bulk density was then determined using equation 1 (Toshiguki *et al*., 2003).

$$\text{Bulk density } (g/cm^3) = \frac{(W2 - W1)}{V} \quad (1)$$

where, W_1, W_2 = weight of empty and filled cylinder (g), V = volume of cylinder (cm^3).

Surface Area

One of the methods used to determine the surface area of adsorbents is Saer's method, this method has been found to be accurate in the determination of surface area of solid adsorbents, the surface area was computed using Equation 2.

$$S\ (m^2/g) = 32V - 25 \quad (2)$$

Iodine Value

The iodine value determination was carried out using a standard method adopted by the Association of Analytical Chemist (1975), the iodine value calculated using Equation 3;

$$\text{Iodine Value, (I.V)} = (B - S) \times 126.5 \times \frac{N}{WEIGHT\ OF\ SAMPLE} \quad (3)$$

where, B = blank titre, S = sample titre, N = normality of $Na_2S_2O_3$, W = weight of sample (g).

Use of Minitab RSM for Optimization

RSM of a 3 factor CCD (Central Composite Design) was used for optimization in the adsorption process resulting to a set of 20 experimental hypothesis for Pb and Cr ion optimal removal. The three variables considered are Initial Concentration (X), Adsorbent Mass (Y) and Contact Time (Z). The minimum and maximum levels were selected for each variable to study the removal of Pb and Cr ion using iron-coated limestone for the conventional optimization method as shown in Tables 1 and 2. The hypothesis generated shows the interaction between the range of 3 variables considered, this represent actual experiments to be carried out for developing the model.

Figure 1: Air dried iron-coated limestone

Table 1: The range of independent variables used for lead adsorption experiment

Factors	**Variables**	**Range of actual and coded values**	
		Low actual (-1)	**High actual (+1)**
X	Initial Concentration (mg/L)	2	5
Y	Adsorbent Mass (g)	1	5
Z	Contact Time (minutes)	10	120

Table 2: The range of independent variables used for chromium adsorption experiment

Factors	**Variables**	**Range of actual and coded values**	
		Low actual (-1)	**High actual (+1)**
X	Initial Concentration (mg/L)	30	50
Y	Adsorbent Mass (g)	2	10
Z	Contact Time (minutes)	10	120

After running the variables in the software using the 3 factors CCD, 20 base and total runs was obtained consisting of 8 factorial runs, 6 axial runs and 6 center runs. The response variable to be considered after running the 20 experimental hypothesis in the laboratory is removal efficiency.

Batch Experiment Procedures for Adsorption of PB and CR on Iron-Coated Limestone

The various adsorbent masses of the iron-coated limestone was placed into 20 different 120 ml round bottom flasks each and 100 ml of the wastewater was added to each of the flask at 25^{o}C room temperature. The wastewater pH value was measured before the experiments. The flasks was placed on a mechanical shaker for the respective time intervals, the speed of the shaker was set to 1-2 cycles per sec. The solution was micro filtered using a whatman cellulose filter paper and collected into small vials. The pH was also measured after the test (Mandadi, 2012). The heavy metal concentration of the wastewater used was analyzed as specified by APHA (1998) at National Research Institute of Chemical Technology (NARICT) using the Atomic Adsorption Spectrophotometer (AAS) (model AA-6800 SHIMADZU, Japan) to obtain the remaining concentration after treatment.

Scanning Electron Microscopy and X-Ray Fluorescence Studies

SEM studies was done to study the surface behavior of the iron-coated limestone by showing how porous and irregular the adsorbent is, the procedure was performed using the Hitachi 2300 SEM. XRF spectroscopy was used to study for the qualitative and quantitative analysis of the material elemental composition in percentage using the X-supreme 8000 oxford instrument.

Statistical and Modeling Analysis

Analysis of Variance (ANOVA) was done to develop model equations for both Pb and Cr removal efficiency using Minitab version 18.1 software. This result was used to determine the significance of the model equations, and this was evaluated using statistical tools such as Fisher value (F-value), Probability value (P-value) and Error responses (Lima *et al.*, 2011; Roy *et al.*, 2013). Using the design of experiment (DOE) tool in the software, the response surface methodology was used to obtain a predicted removal responses of the three variables for Pb and Cr respectively. Actual and Predicted responses for Pb and Cr were plotted to check if the model equation developed can be used to represent the interaction of the three variables by checking for level of divergence in the plot.

RESULTS AND DISCUSSION

Characteristics of Adsorbent

Various characteristics of the iron coated limestone and uncoated limestones were studied, these studies include pH, adsorbent particle size, bulk density, iodine value and surface area.

Table 3: Physicochemical characteristics of adsorbent

Parameters	Uncoated limestone	Iron coated limestone
pH	8.90	8.40
Particle Size (µm Ø)	≤63	≤63
Bulk Density (g/cm^3)	1.571	1.623
Iodine Value (mg/g)	24.11	27.30
Surface Area (m^2/g)	935	1031

After iron-coating the raw uncoated limestone with iron chloride, the adsorbent was found to have about 10% increase in both surface area and iodine value respectively, Mandadi (2012) stated that this is attributed to the deposition of iron chloride on raw uncoated limestone. Iron-coated limestone was used for this study since the adsorbent was found to have a higher adsorptive characteristics than pure uncoated limestone.

X-Ray Fluorescence (XRF)

The iron-coated adsorbent was found to have an increased % weight of Fe_2O_3, Al_2O_3, Cl, MgO, SiO_2 and SO_3 due to the addition of $FeCl_3.6H_2O$ for coating as can be seen from the elemental composition peak in Figure 2. Some of these elements such as Al_2O_3, Fe_2O_3 and Al_2O_3.CaO have been found to be good adsorption catalysts as reported by Kim *et al.* (2017) and Ayesha *et al.* (2013). Silica (SiO_2) nano-particles have also been shown to have high surface area particles and good adsorption characteristics (Min *et al.*, 2003).

SEM Analysis

The SEM image was used to study the surface morphology of thee iron-coated limestone as shown in Plate 1 at x500 magnification, the image revealed a more irregular texture and porous nature of the adsorbent surface as compared to that of the uncoated limestone. Gnanasundaram *et al.* (2017) stated that this rough surface and increased number of pores indicate higher or increased surface area, this can be attributed to the precipitation of iron hydroxide on limestone from iron chloride solution (Swarna, 2012).

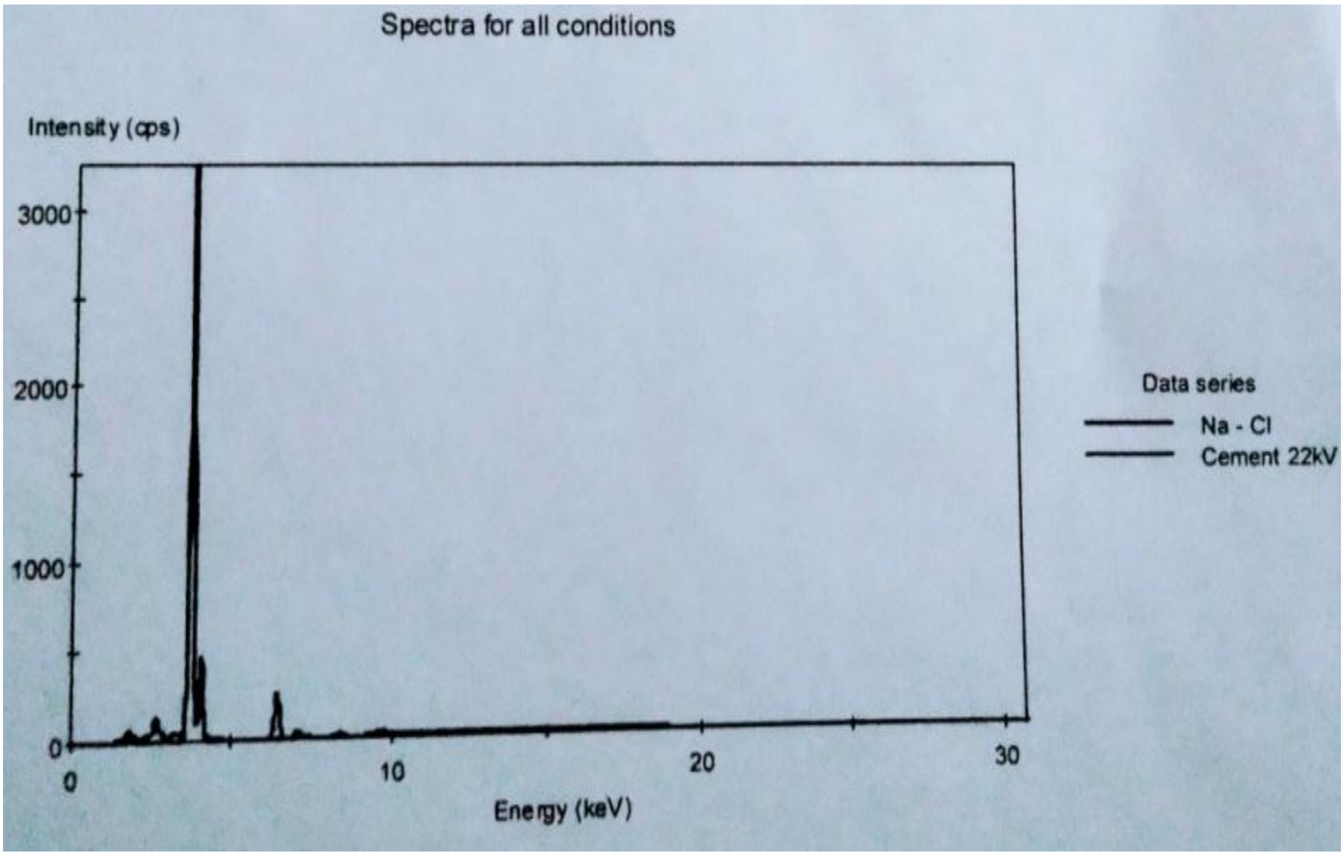

Figure 2: XRF graph of iron-coated limestone

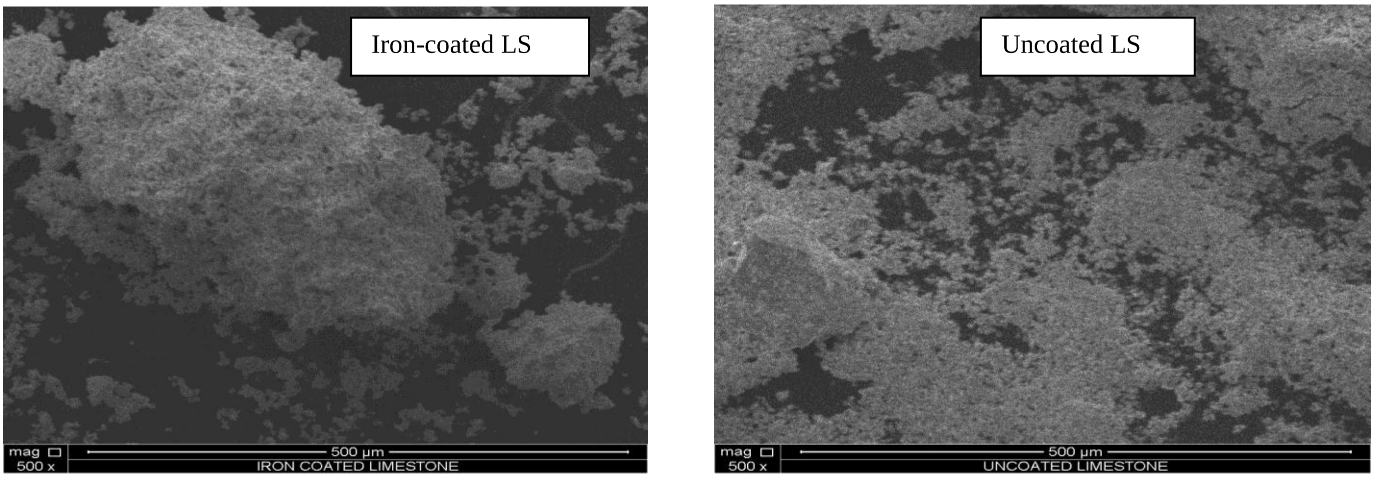

Plate 1: SEM image of iron-coated and uncoated limestone at x500 magnification

Responses Obtained from the Batch Adsorption Experiment of PB and CR

After obtaining the DOE for batch adsorption study of Pb and Cr on iron-coated limestone, the various percentage removal responses for both Pb and Cr were calculated after running the laboratory experiment as shown in Tables 4 and 5 respectively.

From the results of experiments in Table 4, it was deduced that the maximum removal efficiency for Pb was 98.99% (at X=3.50 mg/L, Y=3.00 g and Z=65.00 minutes), and the minimum efficiency achieved was 69.57% (at X=2.00 mg/L, Y=1.00 g and Z=10.00 minutes), this showed that the initial concentration had more effect on removal of Pb even at lower adsorbent dose as compared to the lesser effects of contact time.

Table 4: DOE Layout with response surface experiment for lead (Pb)

Std	**Run**	**Blocks**	**X: Initial Conc.(mg/L)**	**Y:Adsorbent mass (g)**	**Z: Contact time (min)**	**Removal effici. (%)**
18	1	Factorial	3.50	3.00	65.00	87.55
10	2	Factorial	6.02	3.00	65.00	86.06
3	3	Factorial	2.00	5.00	65.00	76.86
5	4	Factorial	2.00	1.00	10.00	69.57
19	5	Factorial	3.50	3.00	120.00	83.38
16	6	Factorial	3.50	3.00	65.00	86.18
11	7	Factorial	3.50	0.37	65.00	93.63
13	8	Factorial	3.50	3.00	27.50	96.25
14	9	Axial	3.50	3.00	157.50	84.45
2	10	Axial	5.00	1.00	10.00	95.25
8	11	Axial	5.00	5.00	120.00	93.29
1	12	Axial	2.00	1.00	10.00	86.82
6	13	Axial	5.00	1.00	120.00	94.06
17	14	Axial	3.50	3.00	65.00	92.85
15	15	Center	3.50	3.00	65.00	98.99
12	16	Center	3.50	6.37	65.00	92.85
4	17	Center	5.00	5.00	10.00	95.12
20	18	Center	3.50	3.00	65.00	95.86
7	19	Center	2.00	5.00	120.00	94.11
9	20	Center	0.98	3.00	65.00	84.05

Table 5: DOE Layout with response surface experiment for chromium (Cr)

Std	Run	Blocks	X: Initial conc.(mg/L)	Y: Adsorbent mass (g)	Z: Contact time (min)	Removal effici. (%)
6	1	Factorial	50.00	2.00	120.00	76.25
5	2	Factorial	30.00	2.00	120.00	54.29
11	3	Factorial	40.00	0.73	65.00	65.90
2	4	Factorial	50.00	2.00	10.00	73.85
4	5	Factorial	50.00	10.00	10.00	74.80
10	6	Factorial	56.82	6.00	65.00	76.54
16	7	Factorial	40.00	6.00	65.00	67.69
17	8	Factorial	40.00	6.00	65.00	99.63
15	9	Axial	40.00	6.00	65.00	83.60
1	10	Axial	30.00	2.00	10.00	54.11
19	11	Axial	40.00	6.00	65.00	65.48
7	12	Axial	30.00	10.00	120.00	54.89
18	13	Axial	40.00	6.00	65.00	68.09
3	14	Axial	30.00	10.00	10.00	64.14
9	15	Center	23.18	6.00	65.00	44.10
20	16	Center	40.00	6.00	65.00	66.40
14	17	Center	40.00	6.00	157.50	99.49
13	18	Center	40.00	6.00	27.50	67.62
8	19	Center	50.00	10.00	120.00	99.77
12	20	Center	40.00	12.73	65.00	98.87

Similarly, from the results of experiments obtained in Table 5, it was observed that the maximum removal efficiency for Cr was 99.77% (at X=50.00 mg/L, Y=10.00 g and Z=120 minutes), and the minimum efficiency achieved was 44.10% (at X=23.14 mg/L, Y=6.00 g, and Z=65.00 minutes), this shows that the removal response is more dependent on initial concentration as compared to the contact time and adsorbent mass. Studies by Pandey *et al.* (2010) suggested that this may be due to the availability of more number of Cr ions in solution for adsorption.

Analysis of Variance (ANOVA)

The model was evaluated using Analysis of Variance in Minitab18.1 as shown in Tables 6 and 7 to obtain the model equations for Pb and Cr removal response. The 3 variables considered in this study are X: (initial concentration), Y:(adsorbent mass) and Z:(contact time) and their reaction to the removal responses for both Pb and Cr in the development of the linear model was studied at 95% confidence interval. The model term having the largest F-value is identified as the term having the most significant effect on the response (Kalavathy *et al.*, 2009). The ANOVA analysis shows that the linear models developed for Pb and Cr removal responses were the most fitted models as compared to other models (such as 2FI, cubic and quadratic models) considered.

Table 6 shows that the response design linear model for Pb removal efficiency has an F-value of 1.72 and there is a 20% chance that a model with such F-value could occur. The X variable is the most significant model term having the most effect in the equation with F-value of 4.38, followed by the less significant Z and Y variables with F-values of 0.47 and 0.32 respectively. The model equation obtained for Pb removal is:

$$\text{Removal response} = 80.27 + 2.62\,X + 0.553\,Y - 0.0258\,Z \qquad (4)$$

Removing the insignificant model variables Z and Y, the model becomes;

$$\text{Removal response} = 80.27 + 2.62\,X \qquad (5)$$

Table 6: ANOVA analysis for removal efficiency of Pb response model

Source	DF	Sum of squares	Mean squares	F-Value	P-Value	Remarks
Model	3	248.75	82.92	1.72	0.20	
X	1	210.68	210.68	4.38	0.05	Significant
Y	1	15.37	15.37	0.32	0.58	
Z	1	22.65	22.65	0.47	0.50	
Error	16	770.32	48.15			
Total	19	1019.07				

Also, Table 7 showed that the response design linear model for Cr removal efficiency has an F-value of 5.97 which implies that the model is significant having a P-value of 0.006 implying that there is a 0.6% chance that a model with such F-value could occur. The X variable is the most significant model term having the most significant effect in the equation with F-value of 11.19, followed by the less significant Y and Z variables with F-values of 4.10 and 2.64 respectively. The model equation obtained for Cr removal is expressed as:

$$\text{Removal response} = 10.3 + 1.112\,X + 1.755\,Y + 0.1081\,Z \quad (6)$$

removing the insignificant model variables Y and Z, the model becomes;

$$\text{Removal response} = 10.3 + 1.112\,X \quad (7)$$

Table 7: ANOVA analysis for removal efficiency of Cr response model

Source	DF	Sum of squares	Mean squares	F-Value	P-Value	Remarks
Model	3	2702.2	900.7	5.97	0.006	Significant
X	1	1687.2	1687.2	11.19	0.004	Significant
Y	1	618.8	618.8	4.10	0.060	
Z	1	397.7	397.7	2.64	0.124	
Error	16	2413.3	150.8			
Total	19	5115.5				

Actual, Predicted and Error Response Analysis for PB and CR Adsorption on ICL

Graphical illustration was used to show the level of divergence of points from the diagonals between the actual and predicted responses and its R^2 values were used to further validate if the model equation for Pb and Cr can be used to represent the interaction of the 3 variables considered. Figure 4 shows the actual values of results obtained from the laboratory and the predicted values that were obtained from the software showing the divergence of points for Pb adsorption. The range of error for the removal efficiency was 2.68-6.14%. This is used to also check for the quality of the model in terms of predicting the responses (Mohammad *et al.*, 2014).

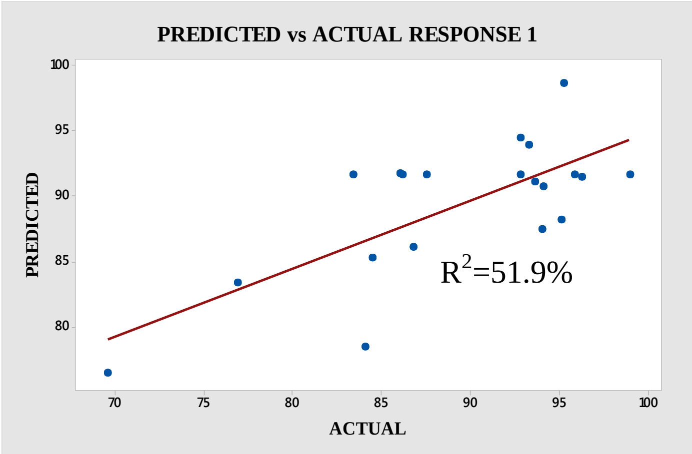

Figure 3: predicted versus actual plot for removal efficiency of Pb

Figure 3, showed that the response surface plots of the predicted versus actual values of removal response had R^2 value of 51.9% for Pb and it showed an average divergence of points from the diagonal, this implies that the model equation developed can be used to represent the interaction of the three (X,Y,Z) variables considered.

Figure 4 shows the actual, predicted and error of the response surface design for Cr adsorption. The highest-lowest range of error for the removal efficiency was obtained as 4.70-10.74%.

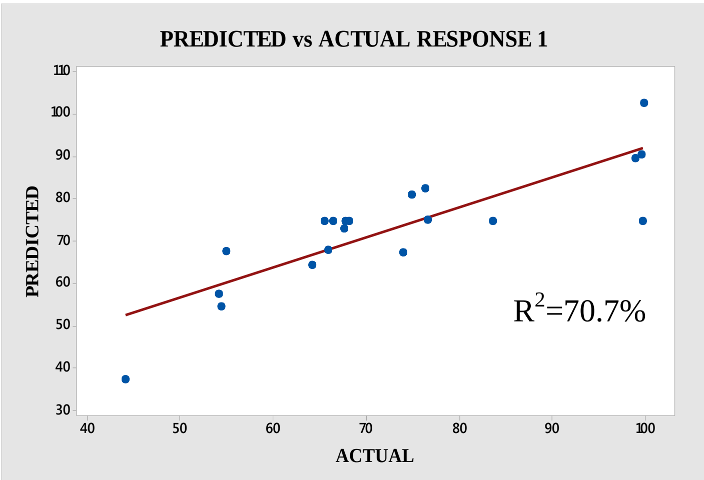

Figure 4: Predicted vs actual plot of removal efficiency for Cr.

From the plot in Figures 4, it was deduced that the response surface plots of the predicted versus actual values of the removal response had R^2 value of 70.7% for Cr, showing little or minimal divergence of points from the diagonal, this implies that the model equation developed can also be used to represent the interaction of the three (X,Y,Z) variables considered. Studies by Daniel. (2016) suggested that this can be used to represent the model developed.

Optimal Conditions for PB and CR Adsorption

The response surface methodology component of the software was used to optimize for removal efficiency, by selecting the most suitable optimum operating conditions for batch adsorption of Pb and Cr ion using iron-coated limestone as shown in Table 8.

Table 8: Optimal conditions for adsorption of Pb and Cr

S/No.	Parameters	Lead (Pb)	Chromium (Cr)
1	Initial Concentration: X (mg/L)	6.0227	56.1384
2	Adsorbent Mass: Y (g)	0.3636	0.7272
3	Contact Time: Z (mins)	33.8382	157.4986
4	Response Removal Efficiency (%)	95.38	91.03
5	Experimental Removal Efficiency (%)	96.97	99.43

Removal efficiency at optimal conditions obtained by the software for Pb and Cr using iron-coated adsorbent were given as 95.38% and 91.03% respectively, the lower response for Cr could be attributed to the high initial concentration as compared to that of Pb. The optimum adsorbent doses for both Pb and Cr showed that the adsorbent had more adsorption site and was more utilized at smaller adsorbent dose. Experimentally, applying these optimal conditions in the laboratory, removal efficiencies of 96.97% and 99.43% were obtained for Pb and Cr respectively.

CONCLUSIONS

This experimental study showed that the iron-coated limestone is an effective adsorbent for the adsorption of Pb and Cr ions from aqueous solution as an inexpensive and eco-friendly material. The optimum conditions obtained produced an optimal removal efficiency of 96.97% and 99.43% for Pb and Cr respectively, this showed a better and improved removal efficiency as compared to the 90% achieved by (Mandadi, 2012) using uncoated limestone. The statistical analysis showed that the removal response model had F-values of 1.72 and 5.97 for Pb and Cr respectively, whose most significant variables had F-values of 4.38 and 11.19 respectively, which indicates that the model equations developed are significant and can be used to represent the interaction between variables. The actual versus predicted removal response analysis also indicates that the model equations developed can be used to represent the interaction of the three (X,Y,Z) variables considered. The adsorbent could be recycled for its re-use in building material.

REFERENCES

APHA, (1998). "Standard method for the examination of water and wastewater, 20th edition". America Water Works Association and Water Pollution Control Federation, Washington DC.

Ayesha, I., Muhammad, A. F., Muhammad, K. and Rohan, A. (2013). "Michelle-Assisted Synthesis of Al_2O_3.CaO Nano-catalyst: Optical properties and their applications in photo-degradation of 2,4,6-trinitrophenol". *Scientific World Journal*.

Barakat, M. A. (2011). "New Trends in Removing Heavy Metals from Industrial Wastewater". *Arabian Journal of Chemistry*, (4), 361-377.

Collin, G. J., Fauziah, A. A., Hasnul, F. M. Z., Siti, F. D. (2006). "Treatment of landfill leachate in Kaya Madang, Sabah: Porosity and asdorption studies (part 2)". *Asian Chemistry Letters*, 10(3-4), 89-94.

Daniel, A. M. (2016). "Optimization of the process of activation of raw melon husk (citrullus lanatus) and adsorption of lead using response surface methodology". Ahmadu Bello University, Zaria.

Gunatilake, S. K. (2015). "Methods of Removing Heavy Metals from Industrial Wastewater".b*Journal of Multidisciplinary Engineering Science Studies (JMESS)*. vol. 1: (1) Nov. ISSN: 2912-1309.

Hassan, A. A. and Karzan A. H. (2013). "Evaluation of Trace Elements in Drinking Water of Duhok province/Kurdistan region of Iraq". *International Journal of Engineering Science Invention.* vol. 2: pp. 47-56. ISSN (Online): 2319-6734, ISSN (Print): 2319-6726.

Jepchirchirchebor, L. (2015). "Synthesis, characterization of ZnO nano photo-catalysts and their application in photo-remediation of wastewater". University of Eldoret Kenya.

Kalavathy, M. H., Regupathi, I., Phillai, M. G., and Miranda, L. R. (2009). "Modelling, analysis and optimization of adsorption parameters for H3PO4 activated rubber wood sawdust using response surface methodology (RSM)". *Colloids and Surfaces B: Biointer faces*, Vol. 70, No. 1, p. 35-45.

Kim, I. H., Seo, H. O., Park, E. J., Haan, S. W. and Kim, Y. D. (2017). "Low temperature CO oxidation over iron oxide nano-particles decorating internal structures of a mesoporous Alumina". *Sci Rep* 7, 40497.

Lima, L. S., Araujo, M. D. M., Quinaia, S. P., Migliorine, D. W. and Garcia, J. R. (2011). "Adsorption modelling of Cr, Cd and Cu on activated carbon of different origins by using fractional factorial design". *Chemical Engineering Journal*, vol. 166, p. 881-889.

Mandadi, K. (2012). "Removal of heavy metals using modified limestone media: Zinc and Cadmium". Western Kentucky university. Paper 1170.

Matheickal, J. T., Yu, Q. (1997). "Bio-sorption of lead (II) from aqueous solutions by phellinus badius". *Miner. Eng.* 10(9): 947-957.

Min, B. K., Santra, A. K. and Goodman, D. W. (2003). "Understanding silica-supported metal catalysts: Pd/silica as a case study". Elsevier B. V.

Mohammad, Y. S., Shaibu-Imodagbe, E. M., Igboro, S. B., Giwa, A., and Okuofu, C. A. (2014). "Modelling and optimization for production of rice husk activated carbon and adsorption of phenol". *Journal of Engineering Volume*, Article ID: 278075, 10 pages.

Mohammed, A. H., Abd E. E., Mohamed, E., Mahmoud, M. E., Wael, M. K., Yasser, H. M. and Noha, E. I. (2013). "Effect of different disinfecting agents on heavy metals during water treatment". *International Journal of Pharmaceutical Science,* 3(4): 270-276.

Niederau, R. F., Purschel, A., Stremmel, W. and Haussinger, D. (1996). "Long-term survival in patients with hereditary hemochromatosis Gastroenterology". 110: 1107–1119.

Pandey, P. K., Sharma, S. K., Sambi, S. S. (2010). "Kinetics and equilibrium study of chromium adsorption on zeolite NaX". *Int. J. Environmental science technology*, 7 (2), 395-404.

Pollard, S. J. T., Fowler, G. D., Sollars, C. J. and Perry, R. (1992). "Low-Cost Adsorbents for Waste and Waste-Water Treatment". a Review. *Science of the Total Environment*. 116: 31-52.

Robert, W. P. and Linda, S. (1993). "Separation of heavy metals: Removal from industrial wastewater and contaminated soil". U.S. Government, contract No. W-31-109-ENG-38.

Roy, P., Mondal, N. K. and Das, K. (2013). "Modelling of the adsorptive removal of arsenic: A statistical approach". *Journal of Environmental Chemical Engineering.* http://dx.doi.org/10.1016/j.jece.2013.10.014.

Swarna, L. S. (2012). Removal of heavy metals from drinking water by adsorption onto limestone with a focus on Copper and Aluminum. Western Kentucky University. Paper 1204: p. 56.

Toshiguki, S. and Yukata, K. (2003). "Pyrolysis of plant, animal and human wastes: physical and chemical characterization of the pyrolytic product". *Journal Bioresource Technolgy*, Vol. 90, No. 3. pp. 241-247.

Zhigang, Y., Lifa, Z., Zhengyu, B., Pu, Gao. and Xingwang (2009). Science journal geochemistry**,** 28, 293-298.