Development of Activated Local Clay for Removal of Heavy Metals from Breweries Wastewater

By

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ABSTRACT

Clay obtained from Kankara clay, Katsina State was modified to study its adsorptive potential of heavy metals in brewery effluent streams. The Optimum operating parameters for the activation of Kankara clay activation with HCl acid were: acid concentration, 3M; activation temperature, 100 °C and activation time, 75 min which gave adsorption uptake of 99.42 % on Fe^{2+} removal. The activated Kankara clay at optimum conditions were subjected to batch adsorption for removal of Pb^{2+}, Cr^{2+} and Fe^{2+} which gave an adsorption capacity of 1.156 mg/g.

INTRODUCTION

Pollution to the environment, most especially water with toxic substances is a major problem to humans, plants and aquatic health as well as environmental quality (Erdem *et al*., 2004).The major challenge with industries is how dyes are indiscriminately released into the environment causing pollution to man and his environment due to their slow biodegradability. Among several toxic substances released into the environment, heavy metals are known to be one of the most dangerous to the ecosystem (Auta and Hameed, 2011). This is because they are very toxic at low concentrations in water, not susceptible to biological degradation and do not degrade into harmless end products (Akpomie *et al*., 2013).In order to regulate the uncontrollable discharge of these hazardous pollutants in wastewater, novel and recent water treatment technologies are proposed globally. Several techniques like chemical precipitation, evaporation, solvent extraction, ion exchange, electrochemical treatment, and membrane filtration technologies have been used severally to remove these hazardous pollutants from wastewater (Khan *et al*., 2014, Liu *et al*., 2010).

Adsorption process is a suitable technique for inorganic and organic pollutants removal from wastewater, because of the significant advantages like low-cost, availability, profitability, ease of operation, efficiency, and effectiveness than other techniques (Rao *et al*., 2014; Gupta *et al*., 2013). Adsorption process involves separation of a substance from one phase and its accumulation at another surface. This technique is easy to operate and equally effective in the removal of toxic pollutants, even at low concentrations. Researchers have reported the use of different adsorbents for waste treatment which include biomass materials, Zeolites, Silica gel, activated carbon and ash. Among these adsorbents studied, attention has become drawn to natural materials capable of removing pollutants from contaminated wastewaters yet at the same time low in cost and available.

Clay minerals are indicated as an amply suitable alternative and very good substitute for expensive commercial activated carbon used in adsorption processes. They have many advantages over other low cost adsorbents such as availability, affordability, ion exchange capability, high adsorption capacity and surface area, mechanical and chemical stability, and different structural and surface characteristics. Clay, a fine-grained natural raw material which has now generated much attention due to its use as an effective adsorbent to trace heavy metal ions present in aqueous solution for more than a decade now, is composed mainly of silica, alumina, water and weathered rock. Variety of clays and clay minerals play an important role in the environment and are used as an effective adsorbent material for the removal of toxic metal ions from wastewater solution. The use of clays as adsorbent have advantages upon many other commercially available adsorbents in terms of low-cost, an abundant availability, high specific surface area, excellent adsorption properties, non-toxic nature, and large potential for ion exchange (Crini and Badot, 2010). Clays also contain exchangeable cations and anions held to the surface and for these reasons; the attention of scientists worldwide has been focused on using natural or modified clay materials as adsorbent for water treatment (Srinivasan, 2011). The most of the clay minerals are negatively charged and very effective and extensively used to adsorb metal cations from the solution and this can be attributed to their high cation exchange capacity, high surface area, and pore volume. The uptake of heavy metals by clay minerals involves a series of complex adsorption mechanisms; such as direct bonding between metal cations with the surface of clay minerals, surface complexation, and ion exchange. In many studies, pre-treatment is required to enhance the adsorption capacity of clays and hence modified to increase metal uptake. This pre-treatment enhances the surface area, pore volume, and number of present acid sites on the surface. Through this treatment or modification, the clay minerals become hydrophobic, organophilic, and it thus enhances the uptake of small non-ionic organic compounds (O'Connell, 2008). The industrial utilization of clay is closely related to its reactivity and surface properties, which depend strongly on surface modification. Several methods have been suggested in literature to improve the properties of these clay materials which includes physical modification (thermal or microwave treatment) which involves alteration of chemical composition and crystalline structure by the effect of high temperature and chemical modification (by acids, bases, organic compounds) which is usually by the alteration of structure, surface functional groups and surface area. Acid treatment is one of the most common chemical treatments for clay minerals and has been used to increase the specific surface area and the number of acidic centers, modify the surface functional group and to obtain solids with high porosity.

The various types of acids used for acid treatment including inorganic acids such as hydrochloric, sulphuric, nitric and organic acids such as acetic, citric, oxalic and lactic. Among all of these, hydrochloric acid and sulphuric acid are probably the most widely used in acid activation, because it shows strong affection by the process parameters and superior results in specific surface area, porosity and adsorption capacity (Kumar *et al*., 2013).

Currently many industries commonly use several techniques like chemical precipitation, evaporation, solvent extraction, ion exchange, electrochemical treatment, membrane filtration and adsorption to remove the hazardous pollutants from wastewater. But all these have limitations. Adsorption process is outstanding due to its simplicity and efficiency but its major challenge is the cost and problems associated with regeneration of adsorbents usedwhich led researchers to find alternate low cost adsorbent. There are numerous commercially available adsorbents which have been used for metal ion removal. Moreover, as the adsorption capacities of various adsorbents are not very large, new modified adsorbents which are more economically available and highly effective are needed, for which extensive work is being conducted. The added advantage of Kankara clay is to obtain a cost effective and efficient adsorbent.

METHODOLOGY

Preparation of activated Kankara clay using response surface methodology

The raw clay was collected around longitude 7°26 E and 7°28 E and latitude 11°53 N located in Kankara local government area of Kastina State, Nigeria. The Kankara clay was treated by hand picking to remove dirt and other foreign bodies and after which it was sieved with a 125 μm mesh sieve. Kankara clay was activated with HCl acid as activating agents under the consideration of the following factors: acid concentration, of (1.0– 5.0 M), temperature of activation (50– 100 °C) and time of activation (30–120 min). 10 g of dried raw clay of particle sizes 125 μm were measured and mixed with 100 mL of different concentration of HCl acid on 250 mL beakers at different activation temperature and time on a magnetic stirrer as were determined by the design of experiment (DOE) in Table 3.4. At the end of the experimental duration, the prepared adsorbents were poured into a Buchner funnel to separate the acid and clay. The residual clay was washed severally with distilled water until neutral points (pH 7.0) were achieved with pH indicator. The clay residue was dried in an oven at 120 °C for 4 h and then stored in airtight container for further use.

Design of experiments using response surface methodology

Central composite design (CCD) amongst other designs under RSM was used to study the individual and synergetic effect of the three factors (acid concentration, temperature and time) towards the responses. It is a method that helps to prune unnecessary experiments and checkmate whether or not there is synergy amongst the factors. CCD is characterized by three operations namely: 2n axial runs, 2^n factorial runs and six center runs. For this case, it translated to 6 axial points, 8 factorial points and 6 replicates at the center which gives a total of 20 experiments.

Total number of experiments = $2^n + 2n + n_c$ (1)

where n is the number of factors, n_c is the number of center points(six replicates).The usual code of ±1 was used to represent the eight factorial points, the six axial points located at (±, 0, 0), (0, $\pm_{\alpha}$ 0), (0, 0, $\pm_{\alpha}$), and the six replicates located at the center (0, 0, 0) were run. The coded points and their corresponding values are presented in Table 1. This value of rotatability α which depends on the number of points in the design of the factorial portion was obtained from the following equation (Ahmad and Alrozi, 2010).

Table 1: Independent Variables and their Coded Levels for Central Composite Design

Variables (Factors)	Code	Unit	Coded variable levels		
			-1	0	+1
Acid Concentration	x_1	M	1	2.5	4
Activation temperature	x_2	°C	50	75	100
Activation time	x_3	min	30	75	120

$\alpha = N_p^{1/4}$ (2)

Where $N_p = 2k$ is the number of points in the cube portion of the design, k is the number of factors.

The optimal conditions for the responses yield and percentage removal of both HCl and H_2SO_4 activated clay were determined using the optimal model predictor equation given as:

$$Y = b_0 + \sum_{i=1}^{n} b_{ii}x_i + \left(\sum_{i=1}^{n} b_{ii}x_i\right)^2 + \sum_{i=1}^{n-1}\sum_{j=i+1}^{n} b_{ij}x_ix_j \quad (3)$$

Where Y is the predicted response, b_o is the constant coefficients, b_{ii} is the quadratic coefficients, b_{ij} is the interaction coefficients and x_i, x_j are the coded values of the variables considered. The regression analysis to fit the equations for both responses developed and for the evaluation of the statistical significance of the equation obtained with the aid of the experimental data were analyzed using Design Expert software (statistical) version 7.0.0 (STAT-EASE Inc., Minneapolis, USA). The characteristics of the reliability of the analysis carried out was measured by the variability in the observed responses values expressed by coefficient of determination R^2, the probability P-value (95% confidence level) and Fisher's test. Table 2 shows the experimental design matrix for the Kankara clay activation preparation for HCl acid.

Table 2: Experimental design matrix for Kankara clay activation using HCl

Run	Activated preparation parameters			Percentage removal
	X_1 (M)	X_2 (°c)	X_3 (min)	
1	-1	-1	-1	R_1
2	+1	-1	-1	R_2
3	-1	+1	-1	R_3
4	+1	+1	-1	R_4
5	-1	-1	+1	R_5
6	+1	-1	+1	R_6
7	-1	+1	+1	R_7
8	+1	+1	+1	R_8
9	-1	0	0	R_9
10	+1	0	0	R_{10}
11	0	-1	0	R_{11}
12	0	+1	0	R_{12}

13	0	0	-1	R_{13}
14	0	0	+1	R_{14}
15	0	0	0	R_{15}
16	0	0	0	R_{16}
17	0	0	0	R_{17}
18	0	0	0	R_{18}
19	0	0	0	R_{19}
20	0	0	0	R_{20}

RESULTS AND DISCUSSION

Experimental results obtained from the experiment

Central composite design (CCD), a segment of response surface methodology was used to optimize the selected preparation parameters (activation temperature, activation concentration and activation time) on Kankara clay acid activation. The response for this optimization was percentage adsorption as shown on Table 3. This result can be found on the total experimental design matrix and the values of the response obtained as presented. Quadratic model was used as selected by the software for the response. The models were selected based on the highest order polynomials where the additional terms were significant and the models were not aliased according to the sequential model sum of squares. The six replicate variables at the centre points run 15- 20 were conducted to determine the experimental error and the reproducibility of the data.

Table 3: Result of Experimental Design Matrix for Kankara clay Activation on HCl

Runs	X_1(M)	X_2 (°C)	X_3(Min)	Fe^{2+} Removal (%)
1	1.00	50.00	30.00	80.78
2	5.00	50.00	30.00	77.11
3	1.00	100.00	30.00	86.75
4	5.00	100.00	30.00	76.42
5	1.00	50.00	120.00	78.90
6	5.00	50.00	120.00	88.78
7	1.00	100.00	120.00	87.97
8	5.00	100.00	120.00	88.98
9	1.00	75.00	75.00	87.84
10	5.00	75.00	75.00	89.48
11	3.00	50.00	75.00	94.77
12	3.00	100.00	75.00	99.42
13	3.00	75.00	30.00	89.51
14	3.00	75.00	120.00	96.57
15	3.00	75.00	75.00	95.51
16	3.00	75.00	75.00	96.14
17	3.00	75.00	75.00	95.51
18	3.00	75.00	75.00	97.02

Runs	X_1(M)	X_2 (°C)	X_3(Min)	Fe^{2+} Removal (%)
19	3.00	75.00	75.00	96.56
20	3.00	75.00	75.00	95.02

A= Acid concentration B = Activation temperature C = Activation time

The result shows that the percentage removal for Fe^{2+} ions on the Kankara activated clay was in the ranges of 79.42– 99.42 %. In comparison, recent studies by Mohammad *et al*. (2010) on adsorption of Fe^{2+} onto polyphosphate modified kaolinite clay using H_2So_4 as an activating agent shows that the removal efficiency of 92.10 % was obtained. Olgun and Atar (2012) also reported the percentage removal of Fe^{2+} to be 82.10 % using clay mixture containing boron impurity as an adsorbent.

Development of regression model equation

The development of a polynomial regression equation for analysis of correlation for Kankara clay acid activation and its ability to remove Fe^{2+} from industrial effluent was done. Correlation between the response surface and factors were developed using central composite design (CCD) of the design expert software as shown on Table 2.

The accuracy of the model developed can be understood by the value of R^2, adjusted R^2 and standard deviation. R^2 indicates the ratio between sum of the squares (SSR) with total sum of the square (SST) and it describes up to what extent perfectly the model estimated experimental data points. Correlation coefficient and standard deviation were used to evaluate the fitness of the model developed. The closer the R^2 value to unity and the smaller the standard deviation, the better the model in predicting the response (Alam *et al.,* 2009). Table 5 shows that the quadratic model percentage removal for Fe^{2+}. The result shows a relatively small standard deviation of 1.12 and relatively R^2 value of 0.9868 in reasonable agreement with adjusted R^2 (0.9749). The result implies that the quadratic model for Fe^{2+} removal on acid activated Kankara clay was not aliased and can be used to describe excellently the relationship between response on removal efficiency and the interacting variables. Determination of CV value is essential as it indicates the ratio between standard error of estimate with the mean value of the observed response as percentage. It measures the reproducibility of the model. If the value is less than 10% the model used can be considered reproducible. It was found that the CV values obtained for the percentages removal of Fe^{2+} was 1.25 % showing reproducibility of the model (Sarra *et al*., 2016). The R^2 values can be attributed to the four factors (A- Acid concentration, B- Activation temperature and C- Activation time) considered. Therefore, the development of a polynomial regression equation for analysis of correlation on Fe^{2+} percentage removal was done using the quadratic model as suggested by the central composite design (CCD). Final coded factors empirical model with inclusion of insignificant terms for percentage removal on Fe^{2+} is given as

$$Fe^{2+} \text{ Removal (\%)} =+ 96.49 - 0.15 * A + 1.92 * B + 3.06 * C - 1.94 * A * B + 3.11 * A * C + 0.50 * B * C - 8.63 * A^2 - 0.20 * B^2 - 4.25 * C^2 \quad (1)$$

The above equation describes how Fe^{2+} removals on HCl activated Kankara clay was affected by the individual (linear and quadratic) or double interaction. Negative coefficient values indicate that individual or double interaction factors negatively affects the metal removal percentage while positive coefficient values shows that factors increase the Fe^{2+} removal percentage. Positive effect increases the percentage removal while negative effect decreases the percentage removal on Fe^{2+} (Aravind *et al*., 2015).

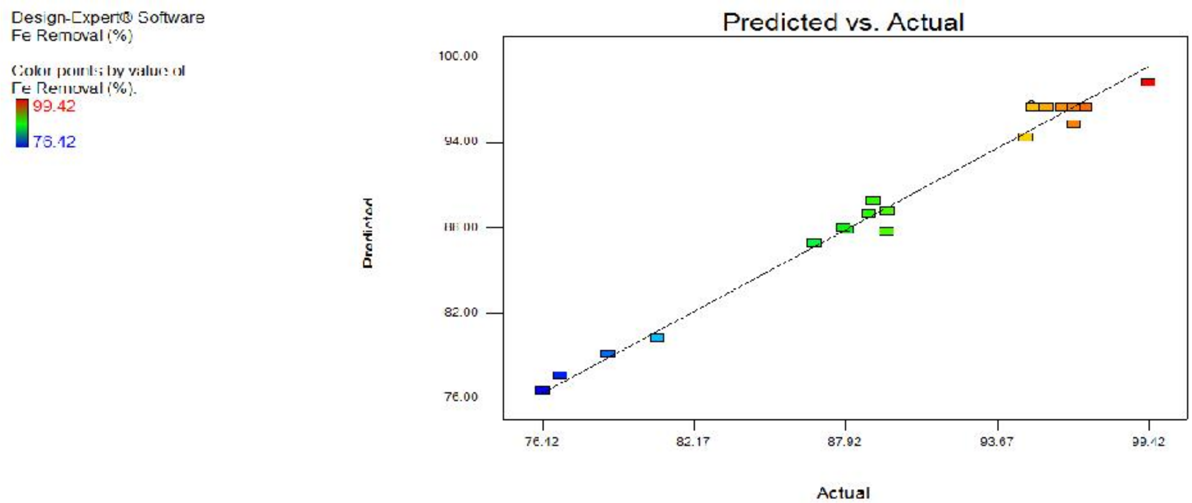
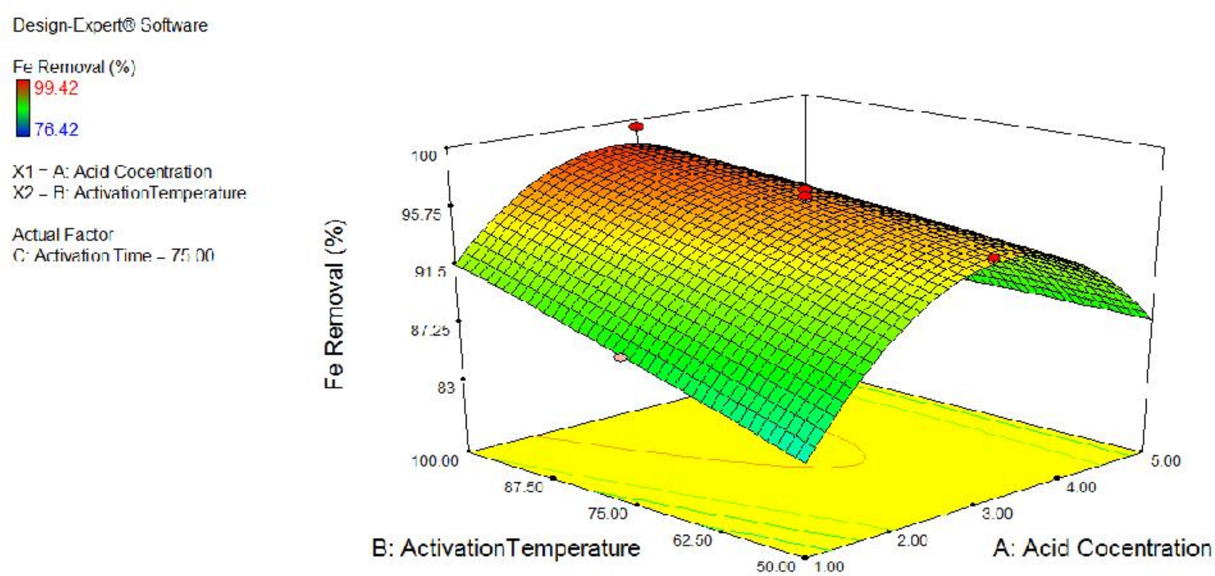


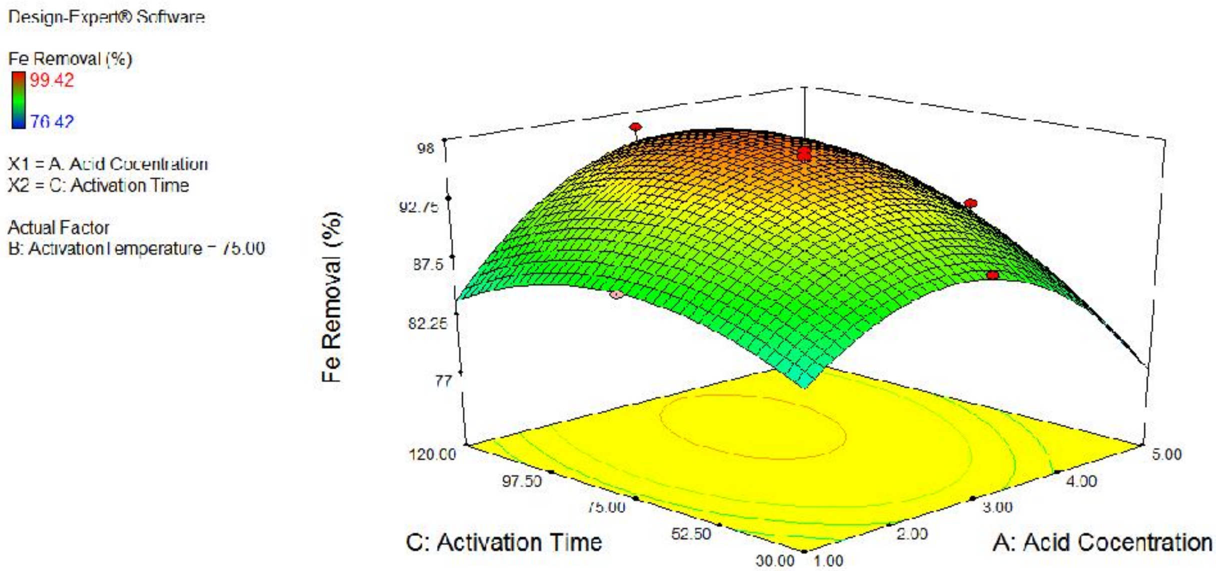
Figure 1: Actual – predicted value plot on percentage removal of Fe^{2+} on Kankara activated Clay

Response surface plots for Fe^{2+} removal on activated Kankara clay

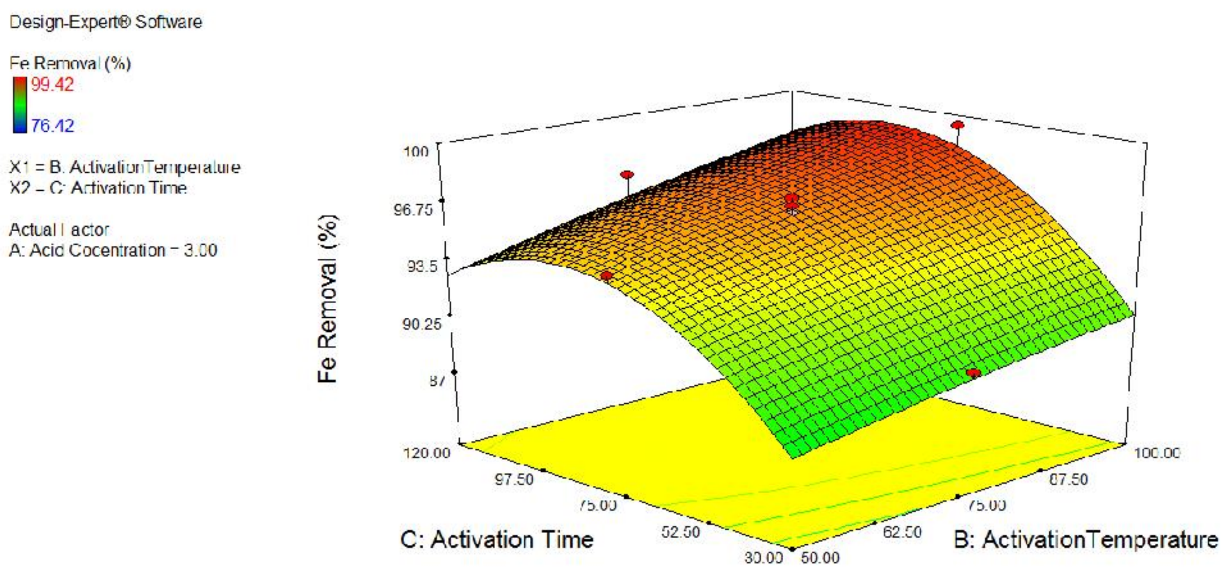
The interaction effects of acid concentration, activation temperature and activation time parameters for Fe^{2+} removal on Kankara activated clay as shown in Figure 2 (a-c)



(a)



(b)



(C)

Figure 2: 3D Surface plots for effects of (a) acid concentration and activation temperature (b) acid concentration and activation time and (c) activation temperature and time on Kankara activated for Fe^{2+} removal

The interactive effects of the process variables on the percentage removal efficiency were studied by plotting three dimensional surface curves against any 2 independent variables, while keeping other variables at their central (0) level. The 3D curves of the response (Fe^{2+} removal efficiency) and contour plots from the interactions between the variables are shown in Figure 2 (a-c). Figure 2 (a) shows the interactive effects of acid concentration (A) and activation temperature (B) on the removal efficiency is significant as shown on Table 3. The plot indicates that both parameters have significant effect on Fe^{2+} removal with the linear (A, B) and interaction AB terms having a marked effect (p-<0.05) as seen on Table 3. The resultant effect of both parameters on Fe^{2+} removal may be attributed to the enhanced surface area and the availability of more active binding sites in adsorbing the solute. The Fe^{2+} concentration ensued increasing of the mass transfer driving force and the rate of metal passing the bulk solution to the particle surface. At acid concentration of 3 M and activation temperature of 100 °C, the maximum percentage removal of copper was 99. 42 % and thereafter decreased with the increase in acid concentration and activation temperature which may causes destruction of the active site due to higher acid concentration. The sloppy nature of the 3D plot as a function of acid concentration (A) and activation time (C) depicted in Figure 2 (b), shows that the two terms have significant effect on Fe^{2+} removal with the linear (A, C) and interaction AC term having a marked effect ($p<0.05$) as seen on Table 6. The Fe^{2+} percentage removal increased from 76.42- 99.42 % as the acid concentration and activation time increased and further increased resulted to decrease in the percentage removal. This may be attributed to the damage of the clay surface as a result of the acid concentration being too high. Figure 2 (c) also depicted the interactive effect of activation temperature (B) and time (C). The linear interaction (B, C) has significant effect while double interaction (BC) has insignificant effect on the removal efficiency. The optimum conditions are: acid concentration 3 M; activation temperature 100 °C; activation time 75 min and the optimum removal efficiency at this optimum condition were predicted to be 98.22 %. Experiments were carried out at these optimum conditions to validate the predicted optimum values. Experimental value of 99. 42 % agreed closely with that obtained from the regression model.

CONCLUSION

Central composite design was used to optimize the activation of Kankara clay and its use for removal of Fe^{2+} using HCl at various parameters such as: activation temperature, acid concentration and activation time under study. The optimal conditions obtained for HCl activated Kankara clay were 100 °C, 3 M and 75 min which translated to 99.42 % Fe^{2+} removal.

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