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Modification of granular activated carbon by aluminum and iron oxides for decontamination of poultry slaughterhouse wastewater using central composite design

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ABSTRACT

The effectiveness of commercial granular activated carbon (GAC) induced Fe_2O_3 and Al_2O_3 for the adsorption of contaminants from slaughterhouse wastewater (SWW) was investigated. Batch adsorption experiments were designed using the central composite design to ascertain the effects of contact time, adsorbent dosage, and pH on chemical oxygen demand (COD) removal efficiency. In comparison, activated carbon impregnated with Fe_2O_3 followed by Al_2O_3 was observed to have a higher pollutant removal. Under the optimized operating conditions; 70.73%, 56.40%, and 27.63% COD were removed by Fe_2O_3-GAC, Al_2O_3-GAC, and GAC, respectively. This study showed that modification of activated carbon using Fe_2O_3 has higher efficiency and performance than Al_2O_3 followed by GAC alone. The statistical model was found significant in all three cases and error was less than 5% in terms of predicted and validation results. Adsorbent showed promising features in terms of reuse for up to four times. The method adopted in this study is effective for the pretreatment of SWW.

Keywords: Iron oxide (Fe_2O_3); Aluminum oxide (Al_2O_3); Commercial activated carbon (AC); Slaughterhouse wastewater

1. Introduction

Slaughtering of animals for meat purpose produces large wastewater concentration. This emanates from cleaning the facilities, washing out used items and buckets. In addition to these contaminants, surfactants that are used during the process of cleaning contribute to the wastewater. Pollutants from slaughterhouse wastewater (SWW) affect the aquatic matrix negatively when discharge to surface water is done without prior treatment [1,2]. SWW has proteins, fats, and loose strands which are products of butchering. One of the main problems of SWW is the deoxygenation of rivers, lakes and/or available surface water when there are incomplete treatment and waste disposal and this would likely cause toxicity to aquatic life [3]. In addition, its presence would contribute to excess nutrients in any given surface water. This may cause explosive growth of plants and algae, and could lead to eutrophication, and could terminate aquatic life. The concentration of pollutants (organic and inorganic) in wastewater can be expressed by chemical oxygen demand (COD) concentration. When it is very high and discharged to surface water, it may deactivate bacteria culture in a biological plant during its operation and as such a pretreatment phase would be appropriate before proceeding to the biological treatment method. Thus, SWW may require pretreatment to improve its biodegradability which would make it amenable to biological treatment [4].

Some treatment methods have been reportedly applied for the remediation of SWW. As a need to protect freshwater sources, many treatment processes have been implemented to assist toxic pollutants removal from SWW before discharge to rivers, lakes or inland waterways. These include electrocoagulation [5], digestion through anaerobic means [6], and electrochemical advanced oxidation methods [7]. Amongst all of these treatment methods, adsorption has been preferred due to its advantages, including ease of operation, lower operating cost and high removal efficiency in comparison to other methods [8]. The choice of the Fe_2O_3 and Al_2O_3 salts is due to their popular use for modification of adsorbents in several works. Importantly, both salts complement the characteristics of granular activated carbon (GAC). Activated carbon possesses a good number of properties that make it recommended for adsorption. These include large surface area and porosity, appropriate surface chemistry which supports the reaction of molecules with other functional groups. Since wastewater treatment is a continuous process, it is advisable to carry out the treatment at a low operating cost. This makes adsorption an alternative for the treatment of SWW containing a low concentration of waste. Notably, the large surface area and micropores of the commercial activated carbon are normally able to remove contaminants in wastewater. However, there are reported enhancements in the performance of modified activated carbon for the removal of pollutants [9,10]. These improvements help to enlarge the available sites on the GAC and provide more space for pollutant adsorption. GAC has several vital surface functional groups having a special distribution of phenol, carboxyl, quinone and hydroxyl groups on its surface. The surface chemical characteristics or difference enables it adsorption capability to be easily influenced for good or vice versa. Thus, when there is impregnation with iron and aluminum oxides, the GAC surface becomes more effective for pollutant removal unlike when GAC is used alone. In essence, when iron and aluminum are diffused by oxidation into the internal pores of GAC, because it does hydrolyze easily and do not precipitate instantaneously, it forms a stronger surface complexes and enhances the equilibrium quantity of iron or aluminum to be impregnated, which eventually increases the sites on the adsorbent for more pollutant removal [11]. Generally, GAC there are sparse reports related to the modification of GAC by Fe_2O_3 and Al_2O_3 for the decontamination of SWW. In addition, the use of one-variable-at-a-time method application in an experimental system can be both material and cost involving [12] Thus, response surface methodology (RSM) was adopted to investigate the optimal conditions that would maximize the modified adsorbent (Fe_2O_3-GAC and Al_2O_3-GAC dosage) removal capacity of pollutants (measured as COD) from SWW. In addition, to compare the performance of iron and aluminum salts when used in surface modification of GAC. RSM is widely used for experiment design and data analysis in wastewater treatment and has been reported in related works [13].

In this study, the experiment was designed so as to minimize the required operational input factors such as reaction time, adsorbent dosage and pH while orbital shaking speed was kept fixed. To monitor the performance of the process, COD was measured during treatment. The study attempted to minimize the materials and time required for the treatment of SWW before discharge.

2. Material and method

2.1. Materials

Commercial GAC used during this investigation were bought from shops and blended to further reduce the size to about 425 µm. The GAC brand used was Bendosen Company, (Hamburg, Germany) product. The aluminum oxide and iron oxide salts were purchased from R&M Marketing, UK.

2.2. Modification of GAC to obtain GAC- Fe_2O_3 and GAC-Al_2O_3

The modified activated carbon by iron-oxide and aluminum oxide process is described in Fig. 1. The schematic diagram of the set-up is shown in Fig. 2.

2.3. Adsorbent regeneration regime

In the desorption experiment, the spent adsorbent was initially rinsed at least twice with distilled and/or deionized water and acetone. Thereafter, it was subjected to another washing with acetone and then put to dry in an oven at 100°C for a period of 2 h. After cooling for another 30 min, the adsorbent was ready for use again.

2.4. Wastewater

SWW was collected from a poultry farm. Permission was granted for SWW collection from the initial flow equalization tank. The most significant pollutant measured from the SWW was COD. The SWW characteristics were 145 mg/L total suspended solids, 7.6 pH, 267 mg/L biological oxygen demand and COD was 899 mg/L.

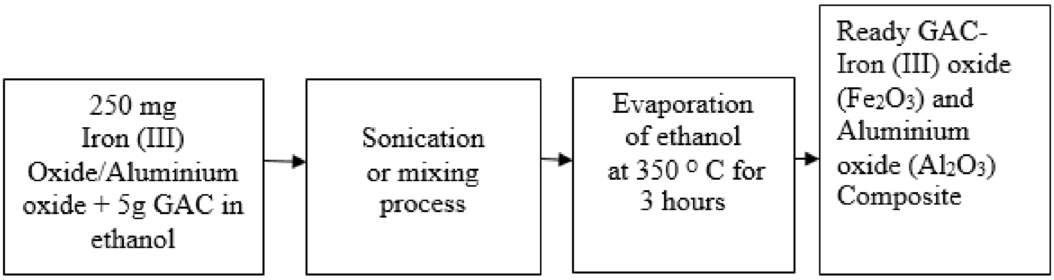

Fig. 1. Synthesis procedure for Fe_2O_3/GAC and Al_2O_3/GAC adsorbents.

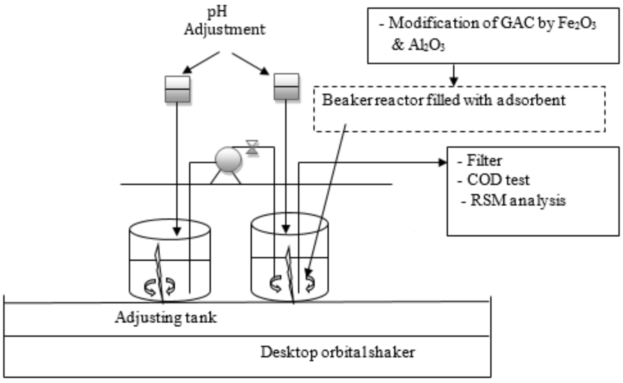

Fig. 2. Schematic diagram of the experimental set-up.

2.5. Batch adsorption studies

A 500 ml beaker containing 200 ml of the wastewater sample was used to experiment. The batch adsorption was conducted at room conditions. After the addition of the wastewater to the beaker, adjustment of the solution pH was made. Thereafter, the adsorbent was added and place on an orbital shaker and was removed when the time was due. The effects of the input factors, that is, reaction time, dosage and pH on the pollutant (COD) removal was monitored in Fe_2O_3/GAC, Al_2O_3/GAC, and GAC processes. After the desired time elapsed, sample aliquots were filtered and tested for the COD concentration.

2.6. Analytical methods

The determination of COD was according to Standard Methods 5220 D for wastewater examination (APHA 2005) [14]. The colorimetric method was used to determine the COD. After heating the sample for 2 h and allowing it to cool down for another 30 min. Thereafter the sample was filtered using a 45 µm diameter size filter and immediately, the COD concentration was measured at 620 nm of the Hach spectrophotometer DR 6000, (USA).

2.7. Experimental design matrix and range of input parameters

The central composite design (CCD) is very widely employed in experimental design to ensure sequential testing of lack-of-fit by applying a considerable number of design points. In addition, it helps to ensure the statistical analysis of the effect of the input variables on the chosen response. The appropriate ranges variable ranges were obtained from a preliminary experiment and regarding prior studies [22]. Table 1 shows the input range for variables in the CCD of the RSM). This was conducted for the Fe_2O_3/GAC and Al_2O_3/GAC and GAC processes.

During the study, a maximum number of 20 experiments were designed according to the CCD and that consisted of 10 factorial experiments, 6 axial experiments and 4 replicas at the center points for assessment of the random error [15]. The optimum operating variables were identified from the response surface plots and the response equation simultaneously. The following response equation was used (Eq. (1)).

Table 1
Range of input variables for the CCD

Variable	Low level (–1)	High level (+1)
pH	3	7
Adsorbent dosage, g	2	5
Time, min	30	90

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2 + \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC \quad (1)$$

This was used to assess the predicted result (Y) as a function of the variables Adsorbent dosage (A), reaction time (C) and pH (C), and estimated as the sum of a constant (β_0), three first-order effects (A, B and C), three second-order effects (A^2, B^2 and C^2) and three interaction effect (AB, AC, and BC).

3. Results and discussion

3.1. Central composite design

The removal efficiency measured in terms of COD removal was recorded in duplicates after each study. The response obtained was statistically evaluated to determine the model's significance. The experimental design of the variables and responses are shown in Tables 2–4. For Fe_2O_3/GAC, Al_2O_3/GAC and GAC processes, respectively.

3.2. Effect of contact time and dosage of adsorbent

The COD concentration removed in the 20 experiments were progressive as the contact time varied from 30 to 90 min according to the designed experiment (Tables 1–3). In the case of GAC/iron oxide, GAC/aluminum oxide, and GAC processes, as shown in Figs. 3a–c. Increasing contact time and adsorbent dosage from 2 to 5 g, increased the COD removal. This was due to an increase in available adsorption sites on the surface of the modified adsorbent. However, the increase was marginal above 3.5 g of adsorbent was added. Thus, it would be wasteful to increase of adsorbent more than the said amount. A similar study reported an increase in adsorption capacity of prepared adsorbent from aged refuse from landfill which was used to remove pollutants from slaughterhouse via fish farm [16]. When the dosage was increased from 2 to 10 g, the highest removal was obtained at 6 g of the adsorbent and it removed about 91% COD. At 6 g, the adsorbent active sites available were sufficient to remove the pollutants and beyond that, it was not significant.

3.3. Process analysis

The process was analyzed by several means including analysis of variance (ANOVA) to confirm "goodness of fit" through the diagnostic tools of the RSM. In addition, the selected mode for COD removal (Y) was significant by the F-test at a 95% confidence level only if the prob. > $F < 0.05$. The second-order polynomial fitted regression equations (Eqs. (2)–(4)) were used to quantitatively ascertain the intrinsic effects of adsorbent dosage (A), reaction time (B), and

Table 2
Experimental design, variables and responses (GAC/iron oxide)

Run	Adsorbent dosage (g)	Time (min)	pH	COD removal (%)
1	3.50	60.00	5.00	80.02
2	5.00	30.00	5.00	84.1
3	2.00	30.00	5.00	67.1
4	5.00	90.00	3.81	82.86
5	2.00	90.00	5.00	70.05
6	3.50	9.55	3.00	68.68
7	3.50	60.00	5.00	71.63
8	3.50	60.00	3.81	70.88
9	3.50	60.00	7.00	71.34
10	3.50	60.00	5.00	71.76
11	6.02	60.00	3.81	82.86
12	3.50	60.00	5.00	71.66
13	0.98	60.00	6.19	57.23
14	3.50	60.00	5.00	70.82
15	3.50	110.45	5.00	73.22
16	2.00	30.00	6.19	57.12
17	5.00	30.00	3.81	69.14
18	5.00	90.00	6.19	71.75
19	2.00	90.00	6.19	59.84
20	3.50	60.00	5.00	71.77

Table 3
Experimental design, variables and responses (GAC/aluminum oxide)

Run	Adsorbent dosage (g)	Time (min)	pH	COD removal (%)
1	3.50	60.00	6.19	57.31
2	5.00	30.00	5.00	54.41
3	2.00	30.00	5.00	56.42
4	5.00	90.00	3.81	60.15
5	2.00	90.00	3.81	47.55
6	3.50	9.55	5.00	60.39
7	3.50	60.00	5.00	58.12
8	3.50	60.00	5.00	57.99
9	3.50	60.00	5.00	58.06
10	3.50	60.00	7.00	58.19
11	6.02	60.00	6.19	59.11
12	3.50	60.00	5.00	58.2
13	0.98	60.00	3.00	47.46
14	3.50	60.00	5.00	57.96
15	3.50	110.45	6.19	62.99
16	2.00	30.00	6.19	52.79
17	5.00	30.00	5.00	55.32
18	5.00	90.00	3.81	60.05
19	2.00	90.00	3.81	45.6
20	3.50	60.00	5.00	59.51

Table 4
Experimental design, variables and responses (GAC)

Run	Adsorbent dosage (g)	Time (min)	pH	COD removal (%)
1	3.50	60.00	6.19	40.02
2	5.00	30.00	5.00	44.10
3	2.00	30.00	5.00	27.10
4	5.00	90.00	3.81	42.86
5	2.00	90.00	3.81	30.05
6	3.50	9.55	5.00	28.68
7	3.50	60.00	5.00	31.63
8	3.50	60.00	5.00	30.88
9	3.50	60.00	5.00	31.34
10	3.50	60.00	7.00	31.76
11	6.02	60.00	6.19	42.86
12	3.50	60.00	5.00	31.66
13	0.98	60.00	3.00	17.23
14	3.50	60.00	5.00	30.82
15	3.50	110.45	6.19	33.22
16	2.00	30.00	6.19	17.12
17	5.00	30.00	5.00	29.14
18	5.00	90.00	3.81	31.75
19	2.00	90.00	3.81	19.84
20	3.50	60.00	5.00	21.77

pH (C), therefore predicting the COD percent removal and expressed in terms of the coded factors.

For COD removal in Fe_2O_3/GAC process,

$$Y_1 = 72.13 + 3.3A + 0.35B - 3.12C - 0.87AB + 2.93AC - 2.56BC + 0.52A^2 - 9.842E - 003B^2 - 0.7C^2 \quad (2)$$

For COD removal in Al_2O_3/GAC process,

$$Y_2 = 58.20 + 2.37A - 0.088B + 0.083C + 1.71AB + 1.22AC + 1.11BC - 1.16A^2 + 0.24B^2 - 0.14C^2 \quad (3)$$

For COD removal in GAC process,

$$Y_3 = 28.15 + 1.16A + 1.87B + 3.25C - 1.96AB + 0.86AC - 3.09BC + 0.39A^2 + 1.05B^2 - 2.72C^2 \quad (4)$$

In Eqs. (2)–(4), the values of the sum of constant (β_0), 72.13, 58.20, and 28.15 represent COD removal (%) in Fe_2O_3/GAC, Al_2O_3/GAC, and GAC processes, respectively under the optimum condition of the process. It is indicative that the adsorbent dosage was the only significant and effective parameter from the experiments in this study. Thus, the equations above may be modified to show only the adsorbent parameter. A positive and negative sign indicates direct proportionality and inverse proportionality, respectively in terms of input factor contribution to the response factor.

Re-writing Eqs. (2)–(4) to become Eqs. (5)–(7) respectively would be preferable in order to show the effective contributions of the individual or main input parameters:

For COD removal in Fe_2O_3/GAC process,

$$Y_1 = 72.13 + 3.3A + 0.35B - 3.12C - 0.87AB + 2.93AC + 0.52A^2 \quad (5)$$

For COD removal in Al_2O_3/GAC process,

$$Y_2 = 58.20 + 2.37A - 0.088B + 0.083C + 1.71AB + 1.22AC + 1.11BC + 0.24B^2 \quad (6)$$

For COD removal in GAC process,

$$Y_3 = 28.15 + 1.16A + 1.87B + 3.25C + 0.86AC + 0.39A^2 + 1.05B^2 \quad (7)$$

Corresponding plots in Figs. 4–6 shows the 3D view of the COD removal in all cases. Fig. 4 shows the response surface plot for COD removal in the GAC/iron oxide process. Accordingly, optimum COD removal was 72.13% at GAC/iron oxide dose of 0.70 g/200 mL (3.5 g/L) and reaction of time 60 min. Fig. 6 shows COD removal in the GAC/aluminum oxide process. Optimum COD removal was 58.20% at GAC/aluminum oxide dose of 0.70 g/200 mL (3.5 g/L) and a reaction time of 60 min. Similarly, in the GAC process, COD removal was 28.15% at GAC dose of 0.70 g/200 mL (3.5 g/L) and the reaction time was 60 min. Generally in Figs. 7–9 an increase in adsorbent dose and time yielded an increase in the pollutant removal efficiency. This is owing to more available active sites on the surface of the adsorbent created by the salts used for modification of the GAC.

Table 4a
Analysis of variance (ANOVA) for GAC/iron oxide process

Source model	SS	*df*	MS	*F*-value	*p*-value Prob > *F*
Model	866.37	9	96.26	4.66	0.0123
A-adsorbent	253.37	1	253.37	12.26	0.0057
B-time	3.65	1	3.65	0.18	0.6833
C-pH	58.16	1	58.16	2.82	0.1243
AB	31.58	1	31.58	1.53	0.2446
AC	52.95	1	52.95	2.56	0.1405
BC	72.81	1	72.81	3.52	0.0899
A^2	11.33	1	11.33	0.55	0.4760
B^2	7.597E-003	1	7.597E-003	3.677E-004	0.9851
C^2	3.23	1	3.23	0.16	0.7009
Residual	206.61	10	20.66		
Lack of fit	145.87	5	29.17	2.40	0.1792 not significant
Pure error	60.74	5	12.15		
Corr. total	1,072.98	19			

Table 4b
Analysis of variance (ANOVA) for the GAC/aluminum oxide process

Source model	SS	*df*	MS	*F*-value	*p*-value Prob > *F*
Model	409.74	9	45.53	91.20	<0.0001
A-adsorbent	97.57	1	97.57	195.47	<0.0001
B-time	0.20	1	0.20	0.40	0.5436
C-pH	0.040	1	0.040	0.081	0.7819
AB	79.67	1	79.67	159.61	<0.0001
AC	7.66	1	7.66	15.34	0.0029
BC	8.55	1	8.55	17.12	0.0020
A^2	31.54	1	31.54	63.18	<0.0001
B^2	4.31	1	4.31	8.63	0.0148
C^2	0.13	1	0.13	0.26	0.6225
Residual	4.99	10	0.50		
Lack of fit	0.90	2	0.45	0.87	0.4533 not significant
Pure error	4.10	8	0.51		
Corr. total	414.73	19			

Table 4c
Analysis of variance (ANOVA) for the GAC process

Source model	SS	*df*	MS	*F*-value	*p*-value Prob > *F*
Model	857.63	9	95.29	3.19	0.0425
A-adsorbent	242.29	1	242.29	8.11	0.0173
B-time	3.76	1	3.76	0.13	0.7302
C-pH	64.06	1	64.06	2.14	0.1739
AB	41.71	1	41.71	1.40	0.2647
AC	67.71	1	67.71	2.27	0.1631
BC	94.55	1	94.55	3.16	0.1056
A^2	26.18	1	26.18	0.88	0.3713
B^2	2.51	1	2.51	0.084	0.7777
C^2	12.03	1	12.03	0.40	0.5400
Residual	298.78	10	29.88		
Lack of fit	131.24	5	26.25	0.78	0.6024 not significant
Pure error	167.54	5	33.51		
Corr. total	1,156.41	19			

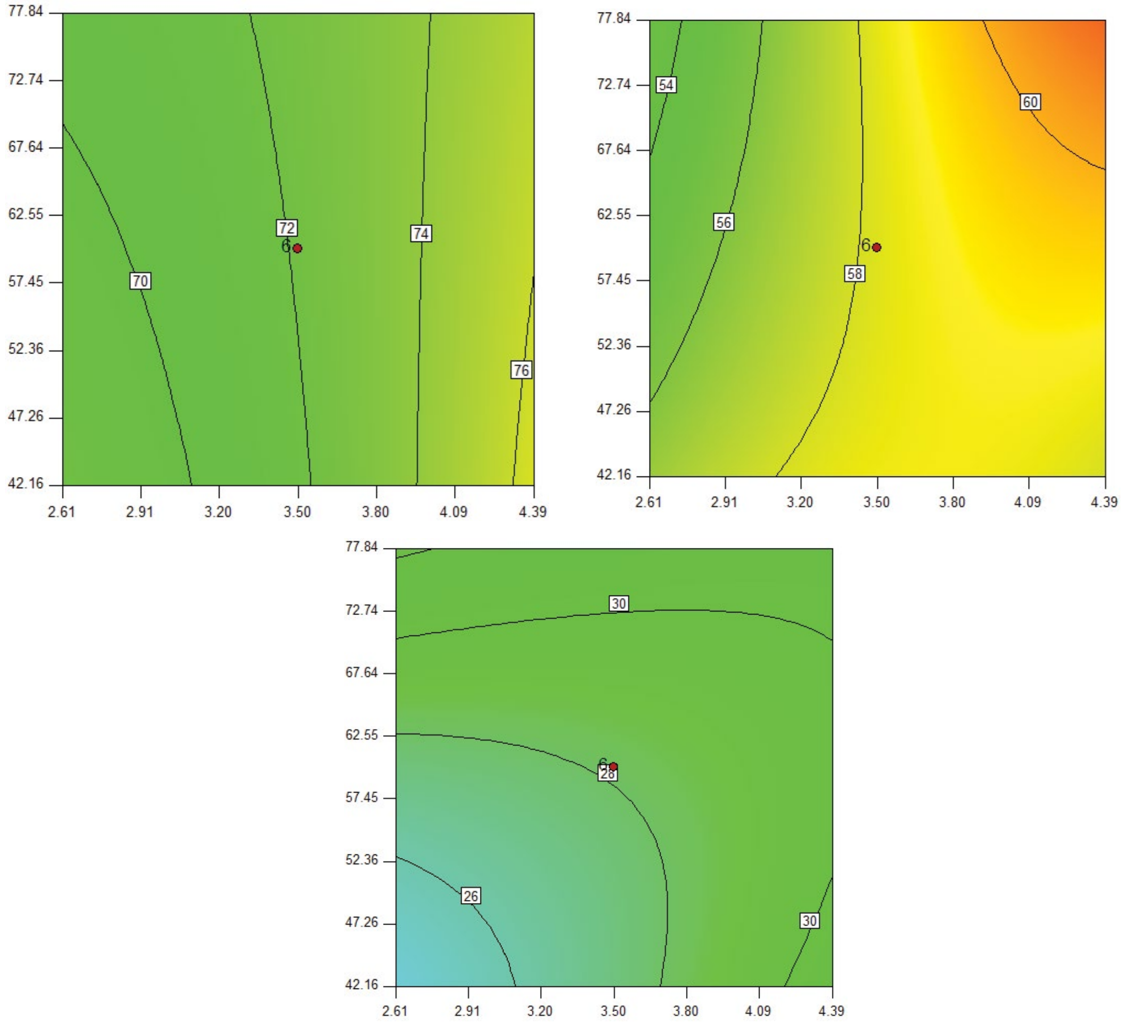

Fig. 3. Effect of contact time and adsorbent dosage on the (a) GAC/iron oxide (b) GAC/aluminum oxide, and (c) GAC process (COD removal (%)).

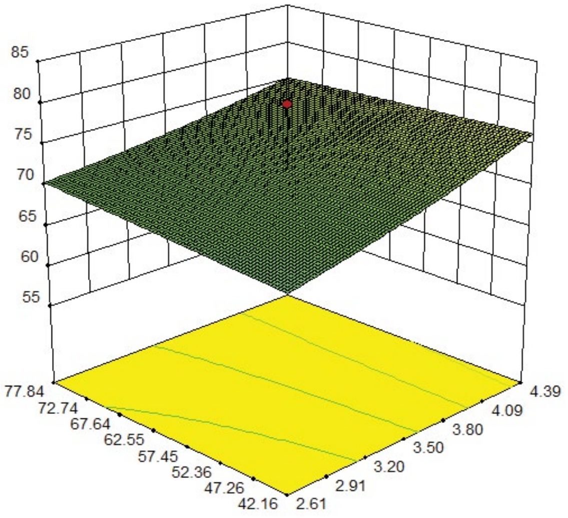

Fig. 4. 3D Plot of COD removal in the GAC/iron oxide process.

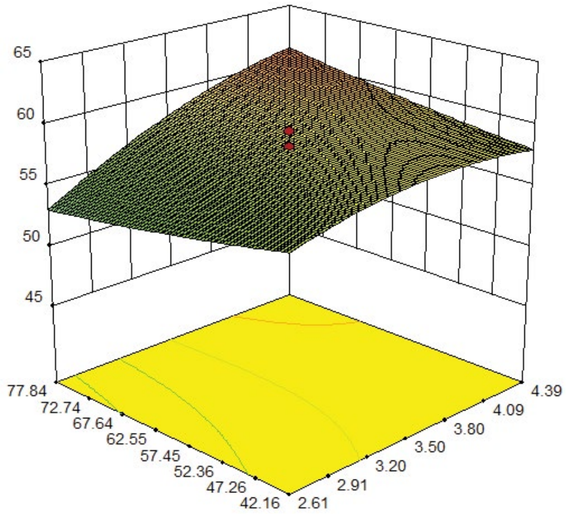

Fig. 5. 3D Plot of COD removal in the GAC/aluminum oxide process.

To ascertain the constant variance, a plot of the studentized residuals and predicted values (figures not shown) showed a random scattering of the points between the boundaries and this confirms prediction is satisfactory as all points lie within region described by quadratic Eqs. (1)–(3). In another diagnostic, it shows that data obtained were not normally distributed as shown in the plot of normal % probability vs. internally studentized residuals (Figs. 7–9).

In addition, the study indicated that all input variables were significant from the perturbation diagnostics plot shown in Fig. 10. When there is a curvature in the line representing the input parameter, it means a significant contributor to the process. The higher curvature indicates a better correlation between one factor and another. As seen in Fig. 10, all the input factors whereof importance during the experimental phase however, the adsorbent dosage was the only significant input parameter in all cases.

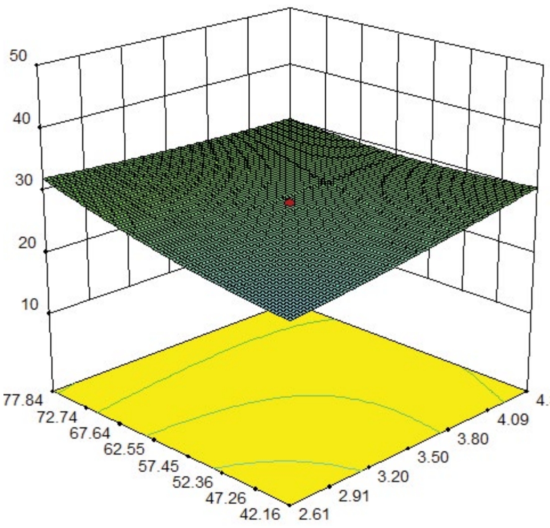

Fig. 6. 3D Plot of COD removal in the GAC process.

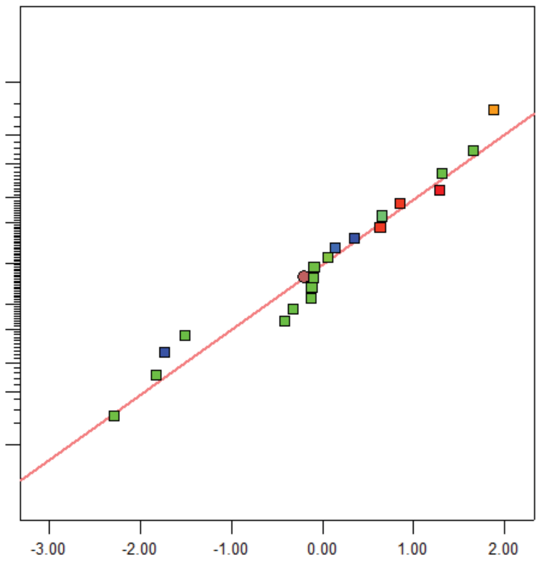

Fig. 7. Plot of normal % probability vs. studentized residuals in the GAC/iron oxide process.

3.4. Analysis of variance

To further ascertain the model accuracy, data obtained from the experiment were subjected to ANOVA to statistically test the model (Tables 4a–c). The assessment of the *p*-value, *F*-value, mean squares (MS), the sum of squares (SS) and degree of freedom were using the ANOVA [17]. In the case of the GAC/iron oxide, GAC/aluminum oxide and GAC alone, the model had an *F*-value of 4.46%, 45.53%, and 3.19%, respectively. Thus implying the models were significant. The *p*-value in all three cases was 0.0123, <0.0001, and 0.0173. A statistically significant model is required to have a p-value of not more than 0.05 at 95% confidence level. The data which was fitted to the model had a minimal variation with the residual error and pure error. The model indicated a lack of fit value was greater than 0.05 and which

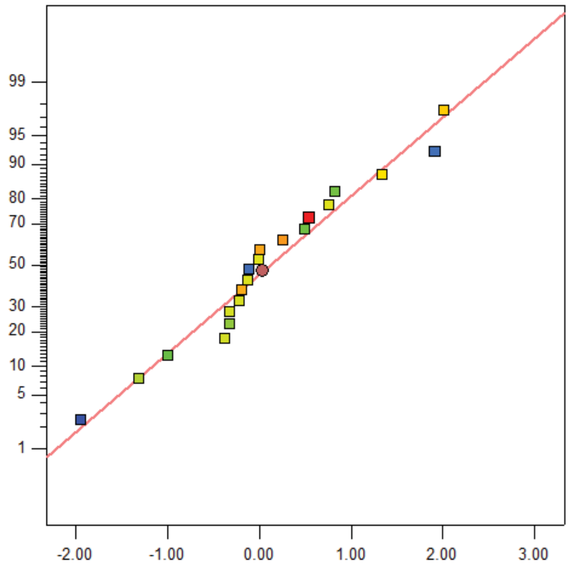

Fig. 8. Plot of normal % probability vs. studentized residuals in the GAC/aluminum oxide process.

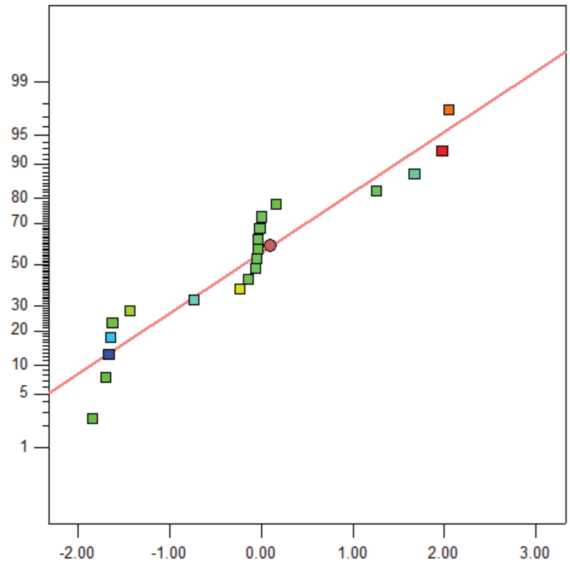

Fig. 9. Plot of normal % probability vs. studentized residuals in the GAC process.

means that the model fits well. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is acceptable. In GAC/iron oxide, GAC/aluminum and GAC processes, adequate precision was 7.735%, 32.767%, and 6.4% which indicated that all three models were adequate. The R^2 value was 0.80, 0.98, and 0.79, for GAC/iron oxide, GAC/aluminum oxide, and GAC processes, respectively. A usually high R^2 value indicates a good process efficiency when predicted in a known experimental range and also shows data were properly aligned [18,19]. The coefficient of variation (C.V.) indicates the reproducibility of the treatment process. In the three processes, C.V. was 6.38%, 1.25%, and 3.08%, respectively. In other to have an assured reproducibility, C.V. should not be more than 10% [19].

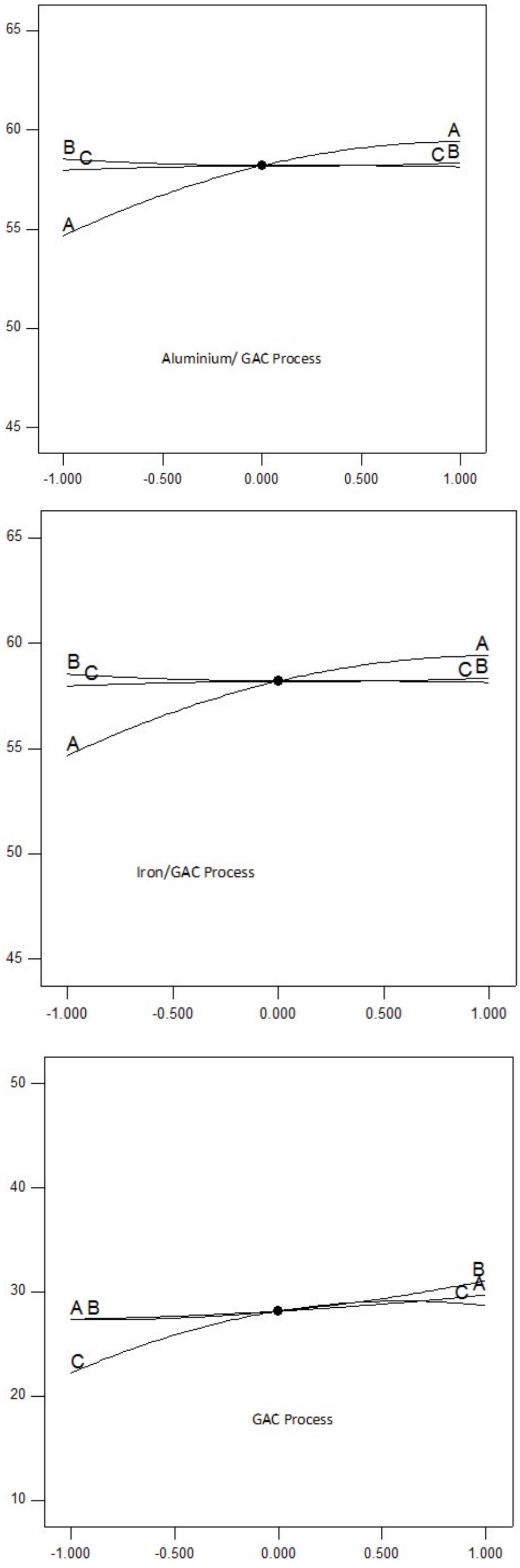

Fig. 10. Perturbation plot of GAC/iron oxide, GAC/aluminum oxide, and GAC processes.

3.5. Optimization and validation of model

To validate the three model responses, two confirmatory experiments were conducted under optimum conditions obtained. The model predictions COD removal for Fe_2O_3/GAC, Al_2O_3/GAC and GAC processes were 72.13, 58.20% and 28.15%, respectively. Whereas after duplicate sampling and testing, the confirmatory experimental removal was 70.73%, 56.40%, and 27.63%, respectively (Table 5). The experimental removal efficiency (observed) and model prediction data were in very close agreement of <5.0% error.

3.6. Process kinetics

To know the true mechanism of SWW degradation, the investigation of the process kinetics was done. After obtaining the optimal conditions from the treatment process, the same values were applied in a 'one factor at a time' condition to get the kinetic model which describes both processes. The pseudo-first-order [Eq. (8)] and pseudo-second-order (Eq. (9)) were applied to the available data from the experiments.

$$\ln\left(\frac{C_0}{C_t}\right)K_t \tag{8}$$

$$\left(\frac{1}{C_t}\right)=K_t \tag{9}$$

These models were used to describe the relationship between the number of pollutants adsorbed or rather the uptake rate and its equilibrium concentration in solution [20,21]. Where C_0, C_t, K expresses pollutant initial concentration, pollutant concentration at time t and the pseudo-first-order rate constant of pollutant degradation, respectively. The finding shown in Figs. 11–13, indicates that the pollutant removal process was according to the pseudo-first-order model in all three cases since they fitted better to the first order. The R^2 values obtained where, GAC/iron oxide, $R^2 = 0.85$, GAC/aluminum, $R^2 = 0.79$ and, GAC, $R^2 = 0.79$. In a similar study, kinetics was found to follow the pseudo-second-order model [16]. However, in our case, it shows the process was limited by physio-sorption and not chemisorption process. This may have been enhanced by the method of preparation of the adsorbent by using less salt.

3.7. Synthesized GAC using iron and aluminum oxides capability in adsorption

Table 5
Validation of model prediction

Process	Model prediction (%)	Experimental removal (%)	Error
Fe_2O_3/GAC	72.13	70.73	1.4
Al_2O_3/GAC	58.20	56.40	1.8
GAC	28.15	27.63	0.52

Normally adsorption capacity improves when there is a large number of available sites on an adsorbent such as activated carbon. Performance is higher when the concentration of wastewater pollutants is low. To increase the capacity of activated carbon, alternative methods such as modification of the surface area has been sought [22]. Treatment of activated carbon using acids has been known to be effective [23]. Other modifications such as the use of salts including Al_2O_3 [24] and Fe_2O_3 [25] has been reported to improve the surface area. Specifically, Al_2O_3 is reported to have good mechanical strength and thermal stability, possess acceptable isoelectric point, regulates physical and chemical properties when in solution, and could adjust its surface area when in acid and alkaline phase [26]. In addition, Al_2O_3 comprises of oxygen has a stable oxidation state in all its compounds due to the +3 and also its six-coordinate and tetra-coordinate nature [27]. Thus, makes it a veritable modifier for high efficiency activated carbon, stable performance and low operating cost. In the case of Fe_2O_3, when used to modify activated carbon, it provides a very large area-to-volume ratio, good magnetic property, excellent biocompatibility, easy to separate if the external magnetic field is available, reusable and as well as comparatively very low cost [28,29]. Additionally, It can easily coordinate with any other elements owing to the intrinsic variable oxidation state it possesses [30,31]. Thus, it was effective for this study and highly recommended in other works.

3.8. Reuse of adsorbent

The possibility of reusing a spent adsorbent adds value to it and thus economically it would be recommended for large scale applications [26]. Hence, the reusability of adsorbent depends on the successful sorption-desorption series. The adsorbent was recycled three times and including its initial use making it a total of four cycles (Fig. 14). In each phase, only a slight decrease was observed when it was reused. This shows that the adsorbent could be economical in terms of cost-saving. However, other sources of adsorbent may be used to eliminate this cost. If economic viability is expected to be considered, Table 6 shows the associated cost with this process while Table 7 shows the cost for regeneration of the adsorbent. The assumption of cost for water deionization and oven heating has been taken from a study [32]. Using the developed modified adsorbent (adsorbent and regeneration costs), material and operational cost would be 49.1 and 49.8 cents (rated in Malaysian Ringgit (MYR)) for Fe_2O_3-GAC and Al_2O_3-GAC treatments, respectively. In addition, regeneration costs (43.5 cents) will become the operating cost after the initial usage of the OPKS. The analysis shows that it would cost less 0.10 US$ per L to treat SWW as well as regenerate the adsorbent. Where a typical wastewater treatment plant is used for the treatment of SWW, the most important consideration would be electricity cost for operation of the entire plant including aerators, clarifiers, pumps, etc. The cost would include electricity charge per KWh which is currently 39.45 cent KWh (rated in MYR). For operational purpose excluding other costs such as personnel, maintenance, fuel, etc. and it may require that the treatment plant be operated for at least 3 h or more will cost from 118.4 cents (rated in MYR) including electricity cost for use of other equipment with heavy electrical ratings and as such an obvious increase in the overall operating cost.

Table 6
Cost implication during SWW treatment

Adsorbent/ Process	Optimum dosage (g)	Volume (L)	Unit price ($ per kg)	Total cost ($)	Wastewater treatment plant cost ($)
Fe_2O_3/GAC process					Total cost ($)
Fe_2O_3	3.5	1	16	0.056	Total cost ($)
GAC	3.5	1	10	0.00035	Total cost ($)
			Total ($)	0.056	Total cost ($)
Al_2O_3/GAC process					Total cost ($)
Al_2O_3	3.5	1	18	0.063	Total cost ($)
GAC	3.5	1	10	0.00035	Total cost ($)
			Total ($)	0.063	Total cost ($)

Table 7
Adsorbent regeneration cost

Adsorbent	Optimum dosage (g)	Unit price ($ per L or kg)	Total cost ($)
Water deionization	3.5	0.2	0.2
Oven heating	3.5	0.2	0.2
Acetone	3.5	10	0.035
		Total ($)	0.435

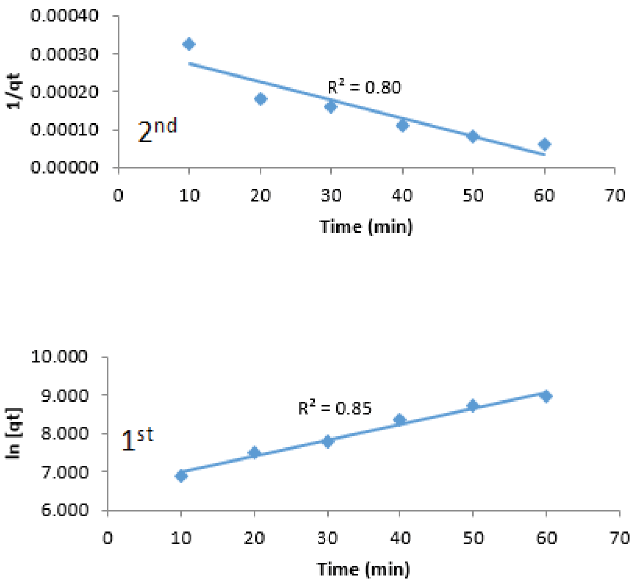

Fig. 11. First and second pseudo-order plots for GAC/iron oxide.

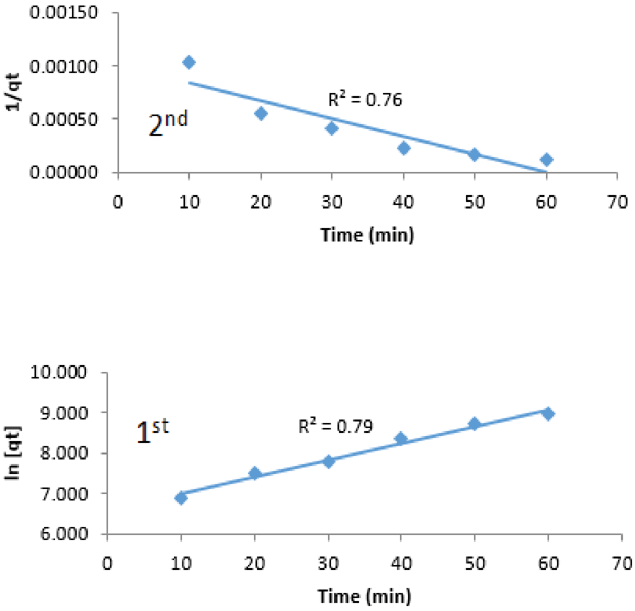

Fig. 12. First and second pseudo-order plots for GAC/aluminum oxide.

In comparison, a simple stand-alone adsorption unit would be cheaper to operate with less and mobile equipment, maintenance and personnel cost implications.

4. Conclusion

This study indicates that iron oxide holds a better potential than aluminum oxide in GAC modification to the results obtained. Under the optimized operating conditions; 70.73%, 56.40%, and 27.63% COD were removed by Fe_2O_3-GAC, Al_2O_3-GAC, and GAC, respectively. This study showed that modification of activated carbon using Fe_2O_3 has higher efficiency and performance than Al_2O_3 followed by GAC alone. The performance sequence for all three treatments was GAC/Fe_2O_3 > GAC/Al_2O_3 > GAC. While the ANOVA analysis showed that all three models were statistically significant, in terms of $p < 0.05$, their COD removal efficiencies were not the same. The correlation of input parameters was according to quadratic equations which were developed for the removal of COD from the SWW and validated by the model statistical analysis. An economic angle to the adsorbent was that it can be reused up to four times and this would save huge costs for large applications. The SWW biodegradability could be enhanced by Al_2O_3 and Fe_2O_3 modification of the surface area of GAC. In our next study, we shall extend this to biochar modification to see the performance for the same model pollutant.

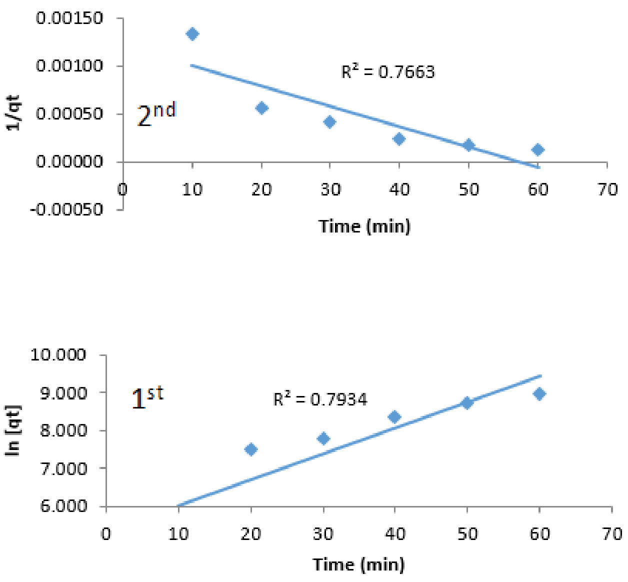

Fig. 13. First and second pseudo-order plots for GAC.

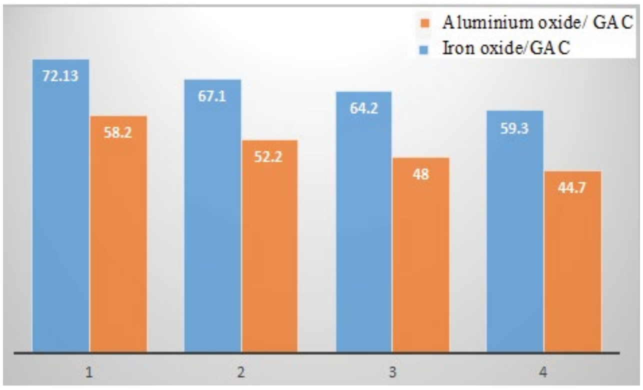

Fig. 14. Reuse of adsorbent over 4 cycles.

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