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## Removal of natural organic matter from water using chemically activated coffee husk

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### ABSTRACT

The presence of natural organic matter (NOM) in source water has posed many challenges for conventional water treatment facilities. Small organic acids, such as humic acid, present in NOM, have a high potential to influence the performance of water treatment processes. Uncontrolled application of agricultural chemicals leads to the simultaneous presence of toxic substances. In this work, batch adsorption experiments were conducted to examine the biosorption of HA onto chemically activated coffee husk. The biosorption process was studied as a function of operating conditions, such as contact time, pH of the solution, HA concentration, adsorbent dose and agitation speed parameters. Experimental results showed that the adsorption has an equilibrium time of 60 min with a maximum adsorption of 93.7%. The optimum pH for maximum HA adsorption was found to be 5.5, with a maximum adsorption of 94.3%. As the dose of adsorbent increased from 1 to 25 g/L, the concentration of HA was observed to reduce from 10 to 1.67 mg/L which is below the WHO (World Health Organization) guideline value of 2 mg/L. The amount of HA adsorbed increased with increasing the initial adsorbent concentration from 0.5 to 20 mg/L. The adsorption kinetics well fitted the pseudo-second order model with the correlation coefficient  $R^2 = 0.997$  and  $K_s = 0.078$ . The experimental sorption equilibrium can be represented by the Langmuir isotherm ( $R^2 = 0.998$ ,  $SSE = 0.006$ ). An average desorption capacity of 87.3% was observed. The study shows that chemically activated coffee husk can be a potential candidate to be used as a biosorbent in the removal of NOM from aqueous solutions.

**Keywords:** Natural organic matter; Biosorbent; Adsorption isotherm; Adsorption kinetics

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## 1. Introduction

Natural organic matter (NOM) occurring in source water has poses a challenge for conventional water treatment facilities (Rao et al., 2011). The occurrence of NOM in raw water used for water supply noticeably affects many water treatment unit processes and operations such as oxidation, coagulation, disinfection and ultimately biological stability (Heijman et al., 2007 and Van der Helm et al., 2009).

Humic substances (HS) are among the major components of NOM and account for 30–80% of the dissolved organic matter in natural water; they are well known as precursors for potentially harmful disinfection by-products (Yang et al., 2004). The major fractions of HS are humic acid (HA), fulvic acid (FA), and humin (Matilainen et al., 2011). The presence of these species in raw water facilitates the reproduction of microorganisms in drinking water distribution systems. They also induce the utilization of a high chlorine dose and act as the precursor for the formation of harmful disinfection by-products (DBP), such as trihalomethanes (THMs), which are classified as potentially carcinogenic chlorine organic compounds (Lee et al., 2009). They can cause a reducing in the efficiency of water treatment facilities by interfering with various oxidants, increasing the solubility of heavy metals due to complexation with metals and adsorbed organic pollutants (Yang et al. 2007).

Particularly, small organic acids such as HA facilitate the regrowth of bacterial activities in the distribution system and biofilm formation in pipelines. Microbial regrowth can deteriorate the taste and odour of the drinking water and it can even lead to potential health hazards (Anke Grefte, 2013).

Many technologies have been introduced to remove NOM from drinking water sources. Among these coagulation, flocculation, granular activation carbon (GAC), reverse osmosis, ion exchange, electro-dialysis, electrolysis, advanced oxidation and adsorption processes

are highly recommended technologies in removal of NOM from the water (Matilainen et al., 2010 and Metsämuuronen et al., 2014). Nevertheless, most of these technologies are expensive, have a high chemical and energy consumption, need skilled work force and often generate chemical sludge, of which the disposal is challenging for water treatment facilities and hence not easily applicable in developing countries (Haftu G. et al., 2014).

However, adsorption is regarded as a promising method for the removal of HS from water due to its universal nature, ease of regeneration, inexpensiveness and ease of operation (Ali, 2011, Dabrowski, 1999).

A variety of adsorbents such as amino-functionalized magnetic mesoporous silica, cationic surfactant-modified bentonite and activated carbon have been reported as being effective for the removal of NOM from drinking water (Dabrowski, 1999). Yet it is important to explore low cost and locally available adsorbents with a high adsorption efficiency to remove NOM from water and wastewater.

Activated carbon (AC) is a widely used adsorbent in water and wastewater treatment processes. For years, many biosorbent materials made from agricultural byproducts have been utilized to remove pollutants from water and wastewater. These include coconut husk and shell, sea weeds (Amuda et al., 2007), maize leaf, coffee beans (Kaikake et al., 2006 and Haftu G. et al., 2014) and rice husk ash (Imyim and Prapalimrungsi., 2010). By optimizing the preparation conditions or/and adsorption process, it is possible to increase the removal efficiency of pollutants onto activated carbon. The maximum adsorption capacities, ease of regeneration and low-cost of adsorbents demonstrated that the adsorbents obtained from agricultural waste have a wide range of applications for organic pollutants removal (Zhou et al., 2015).

This study addresses the utilization of chemically activated coffee husk (CACH) for biosorption of HA from water.

## 2. Materials and Methods

### 2.1. Adsorbent Collection and Preparation

The adsorbent, coffee husk was obtained from a local coffee processing factory in Jimma, Ethiopia. It was washed with distilled water, dried at 110°C for 24 h in a laboratory oven to remove moisture, then crushed and sieved to obtain a particle size  $< 0.3$  mm. Then it was treated with  $H_3PO_4$ , 85% (w/w) solution in a 1:1 mass proportion, and activated at 550°C for 2 h in a muffle furnace (Nabertherm Muffle Furnace LT 15/11). After the activation, excess  $H_3PO_4$  was washed with hot distilled water until a pH  $\approx 6$  was reached (Oliveira et al., 2009 and Lamine et al., 2014). Chemical activation of the biosorbent could increase the anion adsorption efficiency by creating an external surface of the adsorbent to be positively charged (Wang et al., 2016).

### 2.2. Preparation of Adsorbate Solution

A stock solution of 1000 mg/L of HA was prepared by dissolving 1 g HA powder in distilled water. The pH of the stock solution was raised to pH  $\approx 11$  with 0.1 M NaOH and stirred in hot plate slowly up to 60°C in order to accelerate the dissolution. Then the super-saturated HA suspension was gradually cooled down to room temperature. Later the pH of the solution was adjusted back to pH  $\approx 6$  with 0.1 M or N HCl and filtered through a 0.45  $\mu$ m filter to remove the undissolved HA powder. The concentration of the HA in the clear solution was calculated by a gravimetric method. The stock solution was stored in refrigerator at 4 - 6°C for later use. Finally, the stock solution was further diluted to obtain working solutions of various known concentrations of HA in the concentration ranges that can exist in natural water (0.1 – 20 mg/l) (Alexandrina, et al., 2009).

### 2.3. Adsorption Experiments

Series of batch adsorption experiments were performed to investigate the HA adsorption process of CACH under various experimental conditions. The experiments were carried out by mixing 100 mL of adsorbate with a given

amount of adsorbent in 250 mL Erlenmeyer flask. The effects of different operating parameters such as adsorbate concentration, adsorbent dose, contact time, agitation speed and pH of the solution were investigated. The working solution was agitated on a horizontal shaker at 200 rpm for adsorption equilibrium to be achieved. Then each sample was filtered through 0.45  $\mu$ m filter paper and prepared for further analysis of dissolved organic matter. Finally, the concentration of HA in the solution was determined using a DR-5000 spectrophotometer at a wavelength of 254 nm (Joseph et al., 2012).

Beside the adsorption experiments, control experiments with HA using blanks with no adsorbent material were performed periodically and ensured that no HA losses occurred during the experiments.

The percentage and the amount of HA adsorbed per unit mass of adsorbent,  $q_t$  (mg/g), at any time  $t$  (min) were computed employing Eqs. (1) and (2) respectively.

$$HA_{removal}(\%) = \frac{(C_0 - C_t)}{C_0} * 100 \quad (1)$$

$$t = (C_0 - C_t) * \frac{V}{M} \quad (2)$$

where  $C_0$  = initial concentration of HA in aqueous phase (mg/L),  $C_t$  = mass concentration of HA in aqueous phase at time  $t$  (mg/L),  $q_t$  = the amount of HA adsorbed per unit mass of the adsorbent (mg/g),  $M$  = dry mass of the adsorbent (g),  $V$  = initial volume of the adsorption test (L).

### 2.6. Adsorption kinetics

To determine the kinetic adsorption parameters, the obtained kinetic adsorption data was evaluated by employing the linear Langergren pseudo-first order equation (eqn. 3), pseudo-second order equation (eqn.4) and intra-particle diffusion model (eqn.5) as shown below.

$$\log(q_e - q_t) = \log q_e - \frac{k_f t}{2.303} \quad (3)$$

Where  $k_f$  is the pseudo-first order rate constant of adsorption (1/min),  $q_t$  and  $q_e$  (both in mg/g) is

the amount of HA absorbed at time  $t$  and at equilibrium, respectively. The straight-line plot of  $\log(q_e - qt)$  vs  $t$  at different times were plotted to determine the rate constants.

$$\frac{t}{qt} = \frac{1}{K_s q_e^2} + \frac{t}{q_e} \quad (4)$$

Where  $k_s$  is the rate constant for sorption kinetics ( $\text{g mg}^{-1} \text{min}^{-1}$ ). The straight-line plot of  $t/qt$  vs  $t$  was used to calculate the rate constant,  $k_s$  (Hameed et al., 2007; Oliveira et al., 2007; Ahmad and Rahman, 2011).

$$qt = kpt^{0.5} + C \quad (5)$$

Where  $qt$  is the amount of HA absorbed ( $\text{mg/g}$ ) at a given time ( $\text{min}$ );  $kp$  ( $\text{mg}/(\text{g} \cdot \text{min}^{0.5})$ ) is the intra-particle diffusion rate constant;  $C$  ( $\text{mg/g}$ ) is the intercept of the intra-particle diffusion model. The plot of  $qt$  versus  $t^{0.5}$  was used to determine the adsorption mechanism.

## 2.7. Adsorption Isotherms

Adsorption isotherm models were used to evaluate the capacity of CACH to adsorb HA, the relationship between the amounts of HA adsorbed at equilibrium per unit mass of the adsorbent and the concentration of HA in the aqueous phase at equilibrium. In this study, Langmuir and Freundlich models were tested for equilibrium description.

### 2.7.1. Langmuir isotherm

Langmuir equation is based on a theoretical model, which assumes monolayer adsorption over an energetically homogeneous adsorbent surface containing a finite number of adsorption sites. It does not take into account interactions between adsorbed molecules. It can be expressed by the following non-linear equation (eq. 6):

$$\frac{C_e}{q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad (6)$$

where  $q_e$  corresponds to the amount of HA adsorbed per gram of adsorbent at equilibrium ( $\text{mg/g}$ ),  $C_e$  is the solute (HA) concentration ( $\text{mg/L}$ ) in the aqueous solution at equilibrium. The Langmuir constants  $Q_0$  ( $\text{mg/g}$ ) represent monolayer adsorption capacity and  $b$  ( $\text{L/mg}$ ) relates the heat of adsorption. In order to

evaluate the feasibility of the process, the Langmuir isotherm can be described in terms of the dimensionless constant; separation factor or equilibrium parameter (eqn. 7):

$$R_L = \frac{1}{1 + bC_0} \quad (7)$$

where  $b$  ( $\text{L/mg}$ ) is the Langmuir isotherm constant and  $C_0$  ( $\text{mg/L}$ ) is the initial concentration of HA. The shapes of the isotherm are expressed by  $R_L$ . There are four probabilities for the  $R_L$  values: For favorable adsorption ( $0 < R_L < 1$ ), for unfavorable adsorption ( $R_L > 1$ ), for linear adsorption ( $R_L = 1$ ) and irreversible adsorption ( $R_L = 0$ ) (Haftu et al., 2014).

## 2.9. Freundlich isotherm

Freundlich's equation is an empirical model based on heterogeneous adsorption over independent sites and is given by non-linear equation (Eq. 8):

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (8)$$

where  $K_f$  ( $\text{L/g}$ ) related with the total adsorption capacity and  $1/n$  is dimensionless number related to the intensity of adsorption incorporating all the factors affecting adsorption capacity and intensity.

## 2.10. Desorption

Desorption was investigated by eluting the HA using 0.1 – 0.3 M NaOH solution as eluent agent. The adsorbent was then separated from the solution by filtration through 0.45  $\mu\text{m}$  filter paper (MN 640 d, No. 42, Blauband, Germany) and washed gently with distilled water to remove unadsorbed HA on adsorbent surface. The HA loaded on CACH was dried in an oven at 105°C for 24 h and then soaked and shaken in (0.1 - 0.3M) NaOH solution.

Afterwards, the efficiency of the regenerated CACH was studied in the three cycles of adsorption, desorption and resorption for HA removal. Every setup was conducted at the optimal conditions. Then, the amount of desorbed HA was measured and desorption ratio of HA was calculated following equation (eq. 9) (Lin and Zhan, 2012).

$$\text{Desorption ratio(\%)} = \frac{\text{Amount desorbed}}{\text{Amount adsorbed}} \times (100) \quad (9)$$

### 3. Results and Discussion

#### 3.1. Effect of contact time

The effect of contact time on the adsorption process was investigated by taking 10 g/L adsorbent with 10 mg/L HA concentration in different volumetric flasks. Fig. 1 shows the effect of contact time on adsorption of HA. HA removal from 62.54 to 93.86% was observed as the contact time increased from 20 to 120 min. The fast adsorption at the initial stage could be because of the presence of a large number of surface sites for adsorption. With increasing initial contact time in a given mass of adsorbent, the adsorption rate increased and then gradually reached equilibrium after 60 min. However, in previous studies using similar adsorbents for the removal of 25 - 50 mg/L of Remazol Brilliant Orange 3R dye from water, the equilibrium was reached after 5 h (Ahmad and Rahman, 2011).

#### 3.2. Effect of pH

The removal efficiency of the adsorbent decreased at higher pH. As shown in Fig. 2, the sorption amount was the highest at pH below 3; 94.5% removal efficiency was recorded at pH 3. This could be because activation can significantly affect HA adsorption by making the external surface of the adsorbent positively charged (Wang et al., 2016). Further increasing the pH dramatically decreases the removal efficiency of the CACH. At high pH, the adsorbent surface could be charged negatively, and the electrostatic repulsion between HA molecules and the adsorbent surface, which may reduce the adsorption of HA (Wang et al., 2014 and Zulfikar et al., 2016).

#### 3.3. Effect of Adsorbent Dose

The removal efficiency increased as the concentration of the sorbent (CACH) increased under experimental conditions. As depicted in Fig. 4, the removal efficiency was increased from 83.3 to 98.7% with increasing CACH concentration from 1 to 25 g/L. This is because

it increases the availability of free adsorption sites (binding sites) for the sorption process (Banerjee and Chattopadhyaya, 2016). On the other side, the HA loading capacity progressively decreased from 8.32 to 0.39 with increasing the adsorbent dose from 1 to 25 g/L. This could be due to a screen effect between the cells; which is the production of the block of active cell sites as the concentration of the adsorbent increase in the system (Berhe, 2009).

#### 3.4. Effect of HA concentration

The effect of the HA concentration was investigated by varying from 0.5 to 20 mg/L at equilibrium conditions. At this concentration intervals, the amount of HA per unit mass of adsorbent was increased from 0.0487 to 1.394 mg/g, in 100 ml solution. This is in agreement with the finding that a more concentrated solution adsorbs better (Mohammed and Firas, 2013). On the contrary, as shown in Fig. 5, the percentage of adsorption was significantly decreased from 97.3 to 69.7% as the concentration of the HA increased from 0.5 to 20 mg/L. This could be because the sites with greater affinity by adsorbate are occupied first followed by other sites with less affinity, until the saturation of the adsorbent (Nsaifabbas and Saeed, 2014, Imyim and Praralimrunsi, 2010).

#### 3.5. Adsorption isotherm models

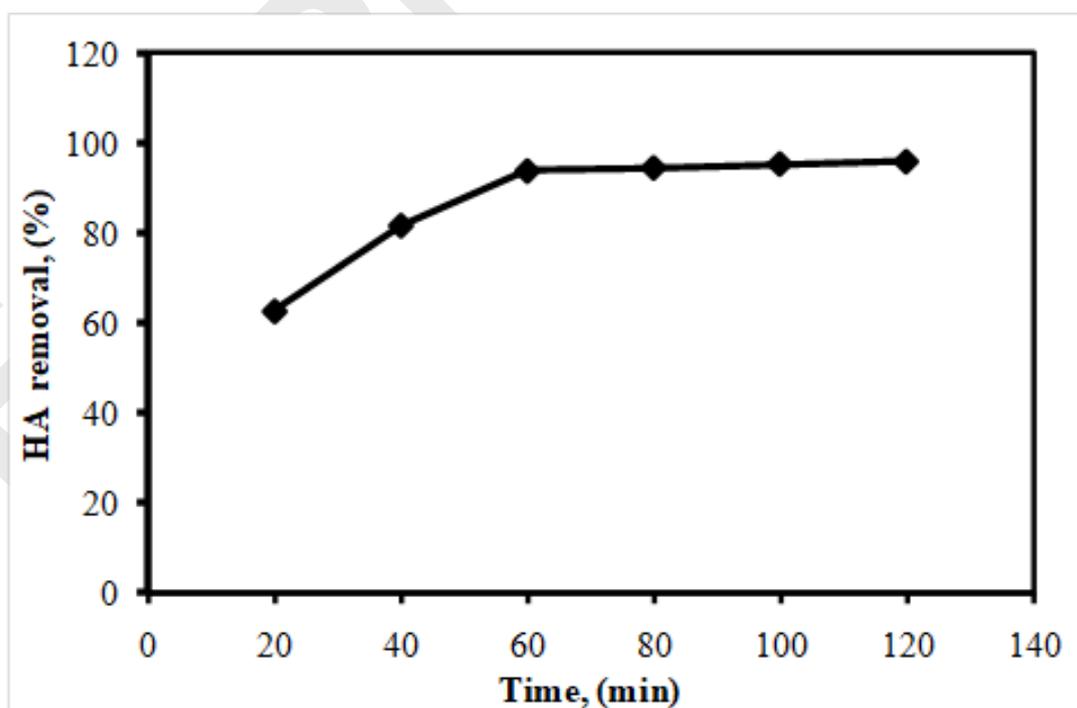
The isotherm plots of the equilibrium adsorption of HA are represented in Fig. 6 and the equilibrium constant computed from the isotherm models using non-linear regression, sum of square error function are given in table 2. Evaluation of the fitting criteria indicates that the Langmuir isotherm has a higher coefficient of determination,  $R^2 > 0.99$ , and low SSE  $\approx 0.006$ . Thus, the experimental data fit well to the Langmuir isotherm equation and describe the equilibrium isotherm of HA adsorption. This indicates that chemical adsorption may be involved in the adsorption process of HA on CACH. From the experimental data, the separation factor ( $R_L$ ) was; it ranged from 0.032

**Table. 1.** Non-linear estimated isotherm parameters for HA adsorption of chemically activated coffee husk

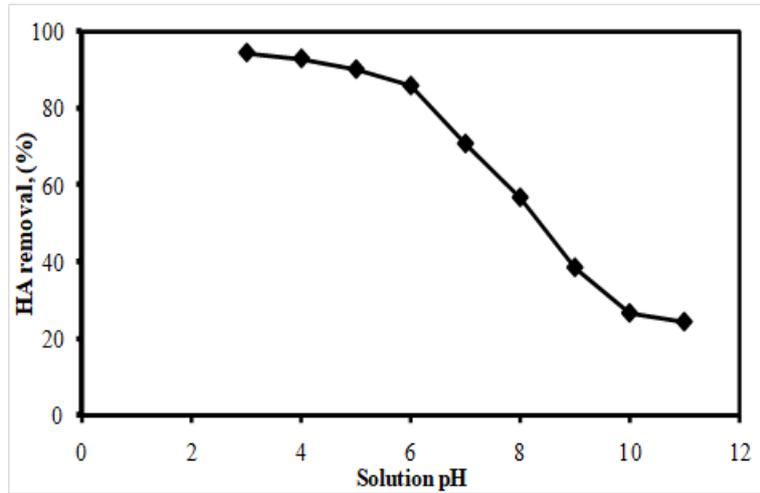
Langmuir Isotherm		Freundlich Isotherm	
Parameters	Value	Parameters	Value
$Q_{max}$	1.495	KF	0.768
B	1.510	1/n	0.365
$R^2$	0.998	$R^2$	0.968
SSE	0.006	SSE	0.058

**Table . 2.** The kinetics parameters for adsorption of HA onto CACH

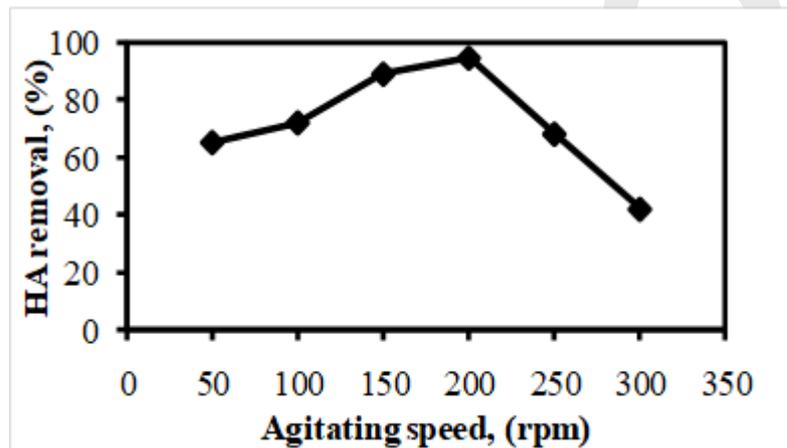
Pseudo-first order		Pseudo-second order		Intra-particle diffusion	
Parameter	Value	Parameter	Value	Parameter	Value
$q_{e,exp}(mg/g)$	0.958	$q_{e,exp}(mg/g)$	0.958	$K_p$	16.39
$q_{e,cal}(mg/g)$	0.941	$q_{e,cal}(mg/g)$	0.972	C	6.22
$K_f[g/(mg.min)]$	0.055	$K_s[g/(mg.min)]$	0.078	$R^2$	0.812
$R^2$	0.961	$R^2$	0.997		

**Fig. 1.** HA removal efficiency versus contact time of CACH ( $C_0$ : 10 mg/L, adsorbent dose: g/L, pH: 6, agitation speed: 200rpm)

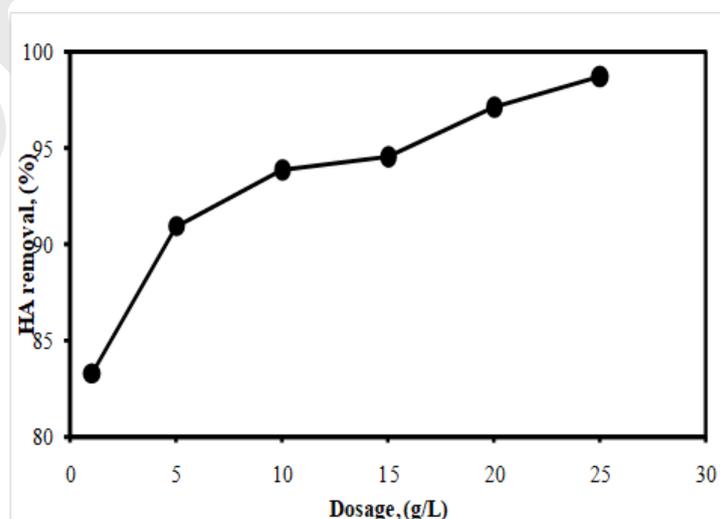
10



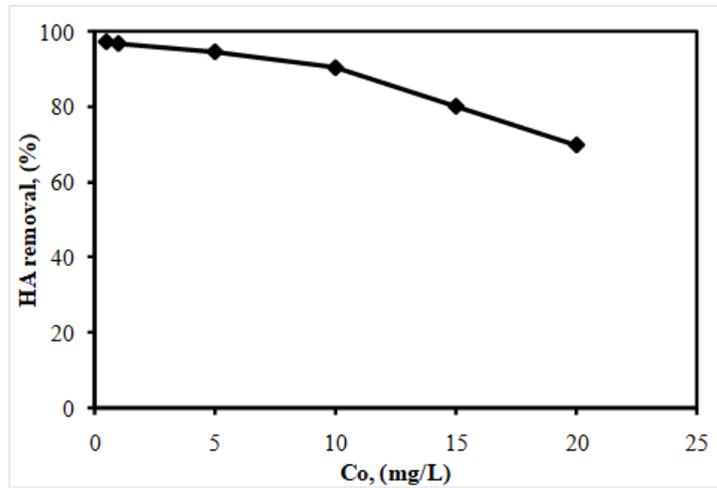
**Fig. 2.** HA removal efficiency versus pH ( $C_o$ : 10 mg/L, adsorbent dose: 10 g/L, contact time: 60 min, agitation speed: 200rpm)



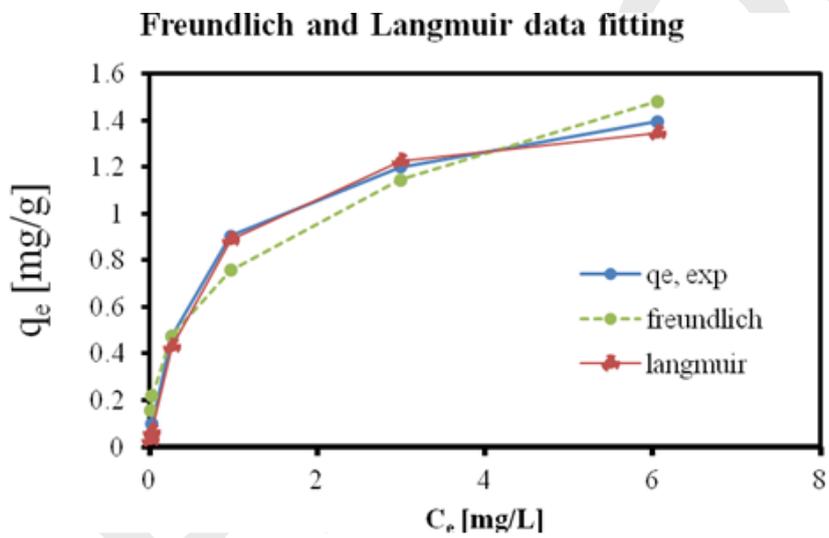
**Fig. 3.** HA Removal efficiency versus agitation speed versus ( $C_o$ : 10 mg/L, adsorbent dose: 10g/L, pH: 6, contact time: 60 min)



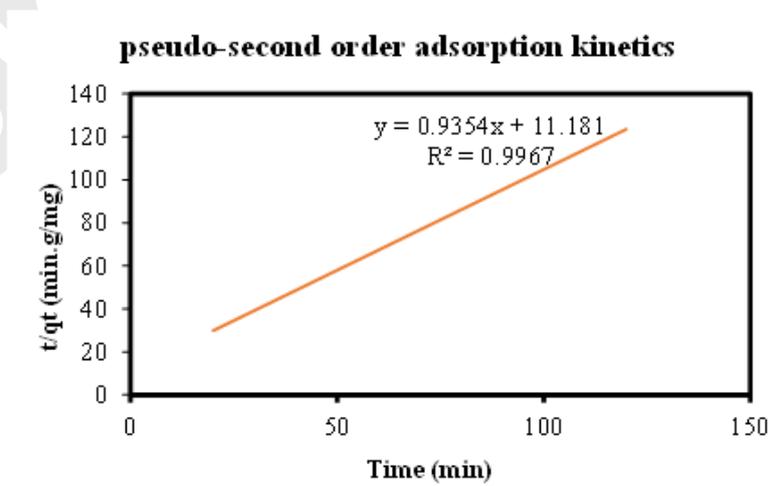
**Fig. 4.** HA removal efficiency versus adsorbent dose ( $C_o$ : 10 mg/L, pH: 6, contact time: 60 min, agitation speed: 200rpm)



**Fig. 5.** Adsorption capacity versus initial concentration (pH: 6, contact time: 60 min, agitation speed: 200 rpm, adsorbent dose: 10 g/L)



**Fig. 6.** Isotherm of equilibrium adsorption of HA on CACH ( $C_o$ : 10 mg/L, pH: 6, contact time: 60 min, agitation speed: 200rpm, adsorbent dose: 10 g/L)



**Fig. 7.** Plot of pseudo-second order kinetics of HA adsorption on CACH ( $C_o$ : 10 mg/L, adsorbent dose: 10 g/L, pH: 6, contact time: 60 min and agitation speed: 200rpm)

to 0.570. This range of  $R_L$  values indicates that the adsorption process is favorable.

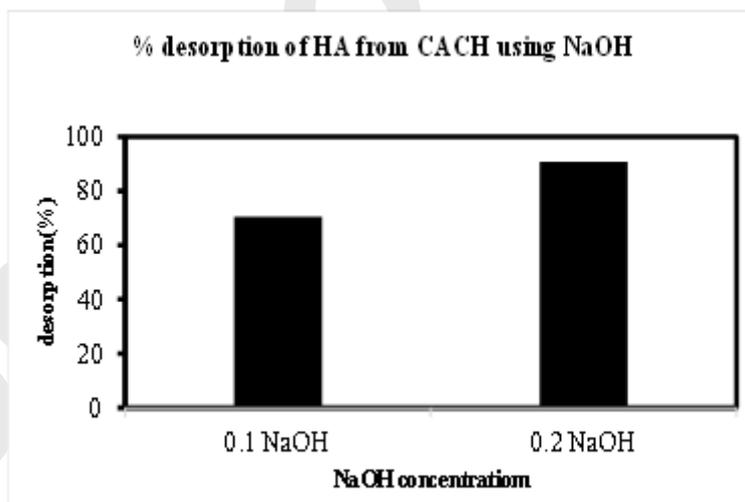
### 3.6. Adsorption kinetics

The linear plots of pseudo-first order and pseudo-second order sorption kinetics constant values of  $K_f$ ,  $K_s$ ,  $q_{e,cal}$  and  $q_{e,exp}$  are given in Fig. 8, Fig. 9 and table 2. The linear plot of pseudo-first order  $\log(q_e - qt)$  vs  $t$  has coefficient of determination  $R^2 > 0.96$  and the modeled equilibrium capacity is  $q_{e,cal}$  (0.941). Furthermore, in the linear plot of pseudo-second order kinetics, the plot of  $t/q_t$  vs  $t$  is a straight line with coefficient of determination,  $R^2 > 0.99$ . In addition, the modeled equilibrium capacity,  $q_{e,cal}$  is 0.972, which is comparable with the experimental equilibrium capacity,  $q_{e,exp}$  (0.958) obtained from pseudo-second order kinetics. Thus, the kinetics of HA adsorption on CACH are well described by a pseudo-second order equation, which assumes that chemisorptions process takes place. Consequently, the overall rate of removal of HA is controlled by chemical adsorption reactions, and not by mass transfer limitations. Similar

results were reported in other studies (Garcia, 2011; Bouras et al., 2015; Liu et al., 2015; Wang et al., 2016; An et al., 2016).

### 3.7. Desorption

The adsorption process was significantly decreased at high pH values. This indicates that HA desorption from the spent CACH can take place in alkaline medium. Series of batch desorption processes were carried out using 100 mL of 0.1, 0.2 and 0.3 M NaOH solution. Fig. 8 shows the percentage removal of HA desorbed by different concentration of NaOH solution. The result showed that desorption increased from 70.4 to 90.7%, where the concentration of NaOH increased from 0.1 to 0.3 M. To test the adsorption potential of the regenerated adsorbent, three more cycles of adsorption-desorption were conducted by maintaining the previous experimental conditions. The experimental study indicated that the regenerated material has an average adsorption capacity of 84.10% and shows the reusability of the adsorbent material.



**Fig.8** . Percentage of HA desorbed from CACH ( $C_o$ : 10 mg/L, dose: 10 g/L, shaking speed: 200 rpm, pH > 11)

### 4. Conclusions

The technological viability of CACH as adsorbent to remove NOM from aqueous solution was investigated at batch level. The effects of various operating conditions like

contact time, pH of the solution, HA concentration, adsorbent dose, agitating speed and desorption study were thoroughly investigated. A maximum adsorption of 94.3% was attained at pH 3. As the dose of CACH

increased from 1 to 25 g/L, the concentration of HA in the aqueous solution was observed to reduce from 10 to 1.67 mg/L, which is below the WHO guideline value of 2 mg/L for dissolved organic matter in drinking water to prevent formation of disinfection byproducts. The adsorption isotherm was most satisfactorily described by a Langmuir isotherm ( $R^2 > 0.99$  and  $SSE = 0.006$ ) and Freundlich models. A pseudo-second order kinetic model successfully explains the kinetic data with  $R^2 > 0.99$ , which suggests the dominance of chemisorptions process. Desorption processes was carried out in alkaline medium by using NaOH. The study indicated that as the concentration of NaOH is increased from 0.1 to 0.3 N, the percentage of desorption was increased from 70.44 to 90.72%, which indicates the regenerability of the adsorbent material. The experimental data demonstrated that CACH could be a potential candidate to be used to remove NOM from aqueous solution.

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