



Superior removal of humic acid from aqueous stream using novel calf bones charcoal nanoadsorbent in a reversible process

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HIGHLIGHTS

- Calf bone char (CBC) is a highly reactive sorbent that removed 100% HA in 30 min.
- The highest adsorption was observed at pH 4 with 38.08 mg HA/g CBC adsorption.
- CBC can be fully regenerated without any loss in the adsorption capacity.
- Adsorption occurs by a monolayer formation as explained by the Langmuir model.
- CBC is a cost-effective and sustainable material to design a HA removing process.

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ABSTRACT

While the potable water disinfection regimen has significantly reduced waterborne diseases, development of disinfection byproducts (DBP) during this process has brought a global threat to the environment and human health. The most notorious water pollutant, humic acid (HA), transforms into carcinogenic byproducts during the disinfection process (chlorination) of water treatment. HA removal methods are neither economic nor widely available. This study addresses the most urgent global issue of HA removal by developing an innovative and self-regenerative process based on a low-cost and self-regenerative calf bone char (CBC) that removed 92.1–100% of HA. CBC-based HA removal has not been described yet. The developed CBC, as a super adsorbent of HA, was initially characterized by a scanning electron microscope. Various parameters of adsorption/desorption and self-regeneration of CBC adsorbent were experimentally determined. Results show that prepared CBC with a 112 m²/g surface area exhibited adsorption of 38.08 mg/g (HA = 20 mg/L, pH = 4.0) which is several folds higher than the typical amount of HA present in water. The 30 min reaction time was enough to remove HA which is the shorter HA time in comparison to other similar studies. The increase of HA from 0.5 to 5 g/L, raises % HA removal (36.7–99.8%) while a pH decrease (10–4) increases adsorption (12.3–98.3%). The adsorption data fitted well with the pseudo-second-order model and the Langmuir isotherm which demonstrate that adsorption takes place by a monolayer formation. Thermodynamic constants supported the endothermic, spontaneous and reversible nature of adsorption which can attain 100% HA removal. 100% regeneration of exhausted CBC by

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NaOH further supports the sustainability of the process. CBC as a new adsorbent material thus provides an economical and sustainable water pre-treatment procedure. The present study provides technical guidance for building a cost-effective and scalable process capable of providing clean water.

1. Introduction

Water is the absolute necessity to sustain life, however, providing clean and pollutants free water in developing countries has been the most challenging problem primarily because of population growth and ineffective water treatment methods (Li and Wu, 2019). Natural water resources contain various organic and inorganic soluble ions/compounds and many of them have been classified as pollutants (Lladó et al., 2021). Among these, humic acid (HA), and fulvic acid are the predominant natural organic matter (NOM) or dissolved organic carbon (DOC) in groundwater and surface water resources (Molczan and Szlachta, 2011; Hasani et al., 2019). HA represents up to 90% of DOC (Sounthararajah et al., 2015). The presence of HA in water can be sensed by the yellowishness or brownishness, bad taste/odor (Hasani et al., 2019), the growth of pathogenic microbes and membrane fouling (Camper, 2004).

HA is a polyelectrolytic macromolecule with carboxylic acid and phenolic groups that are formed from the polymerization of various biological residues over the course of a long period (Tang et al., 2020). HA becomes completely dissolved at a pH value above 2 and attains a negative charge in underground water (at 20 µg/L) and surface water sources (at 0.030 g/L) (Brum and Oliveira, 2007). NOM is widely used in agriculture as a soil supplement (Susic, 2016). While HA improves the soil properties as being an organic fertilizer (Li et al., 2019), HA containing water, upon disinfection, could serious health concerns because the disinfection procedure could lead to a production of more than 600 types of undesired byproducts (Richardson and Postigo, 2011). Chlorination, which is a standard disinfection treatment in developing countries, has been reported to give rise to disinfection derivatives such as trihalomethanes (THMs), chloroform and dihaloacetonitriles. These toxic derivatives come into existence due to the interaction of HA with the chemicals resulting from the chlorination process (Zhan et al., 2010).

Recently, various studies have reported the origin of new aromatic halogenated disinfection byproducts (DBPs) forming from the interaction of NOM with chlorine and bromine, which upon decomposition, can form the U.S. EPA regulated DBPs (Pan et al., 2017). Moreover, HA itself could become a serious pollutant as it binds with heavy metals primarily because of its superior binding and electrostatic interactions, resulting in the formation of metal-organic complexes (Sounthararajah et al., 2015). These complexes further complicate their eradication from water. Such derivatives or by-products are toxic to both the environment and humans (Emanjomoh et al., 2019). Because of the environmental and health concerns (Liver/kidney damage, cancer and nervous structure concerns), various jurisdictions have specified the maximum allowable concentrations for these compounds. As per the United States Environmental Protection Agency, THMs (80 µg/L) and haloacetic acids (60 µg/L) are the highest quantities (EPA, 2021) permitted.

WHO has defined the THMs' maximum limit to 100 µg/L in drinking water (Mazloumi et al., 2009). Because of the regulations and potential human health issues associated with HA and its derived disinfectant by-product, this topic has attracted increasing attention in the last few years. Thus, HA removal from water using effective technologies is an important subject worldwide (Bhatnagar and Sillanpää, 2017). Although conventional noneconomical processes such as coagulation and tangential cross-flow microfiltration (Hakami et al., 2019), ozonation (Cui et al., 2019), ion exchange (Wang et al., 2016), adsorption (Derakhshani and Naghizadeh, 2018), filtration (Sutzkover-Gutman et al., 2011), chemical coagulation (Rucka et al., 2019), electro-coagulation (Rezaei et al., 2018) and gas-liquid interface

discharge plasma (Cui et al., 2019) for HA removal are available, the adsorption-based HA removing processes are appropriate considering their implementation cost and tremendous success in effectively removing recalcitrants, metals, organic carbon, turbidity and nutrients (Barhoumi et al., 2019).

A variety of synthetic and environmental adsorbents, including activated carbon (Wu et al., 2002), nanotubes (Wang et al., 2008) and hematite (Qin et al., 2014) have been developed that are promising to remove HA. Among these adsorbents, activated carbon (AC) has gained popularity but the relatively high price tag of this adsorbent and limited application has led to a search for more cost-effective resources. In the quest of economical materials with impressive adsorption capacity, significant efforts have been put forward. In this regard, animal bones (porous solid waste), which are loaded with calcium carbonate (CaCO₃) and hydroxyphosphate have emerged as a viable green material to adsorb heavy metals ions, dyes and other water pollutants (Yang et al., 2020). Bone Charcoal is made from animal bone including pig (Wongrueng et al., 2019), camel (Hassan et al., 2008), sheep (Dawlet et al., 2013), chicken (Herath et al., 2018; Cortés et al., 2019; Niu et al., 2021) has shown effective removal of DBP, Hg, mercury (II), fluoride/fuchsine/Cu²⁺ respectively.

Bone char (BC) has become popular due to outstanding physico-chemical properties, ease of production, significantly low cost, eco-friendliness and outstanding success to remediate water and wastewater contaminated with copper Arsenic (Chen et al., 2008), Fluoride (Shahid et al., 2019), Chromium (Ranjbar et al., 2018) and Mercury (II) (Dawlet et al., 2013). The superior adsorption property of the BC is due to its surface characteristics (functional groups) that allow massive adsorption of a variety of pollutants including HA. Because the BC made from cow's bone provide an extensive surface area, cow bone char (CBC) is promising for solid waste management and the removal of many hazardous pollutants from water (Moreno et al., 2010; Mortazavi et al., 2010; Rojas-Mayorga et al., 2016). Considering the low cost and feasibility of industrial scale up, efficient adsorbents originating from biological wastes such as calf/cow bone charcoal (CBC) serve as plausible green materials.

HA removing process carved from CBC can be adopted, as a pre-treatment of water (prior to disinfection), in developing countries due to its overall low application cost, stable performance and longevity of the process. It's worth mentioning that such a process is going to remove more complex pollutants from water. Despite the appealing potential of BC in treating water, studies exploring the removal of the most notorious pollutant, HA, via BC are still in infancy. In order for this methodology to be successful and affordable continuity of the pollutants removal process without any deterioration in the performance is highly required (Alkurdi et al., 2019). Due to a limited number of studies investigating the reusability of bone char and efficiency after regeneration pose major limitation of this methodology. Additionally, underlying detailed mechanism of HA adsorption on BC, adsorption kinetics, most critical process parameters and chemistry behind regeneration of exhausted BC must be explored to take this technology to the next industrial scale.

To the best of our knowledge, the use of CBC to adsorb humic acid and its total elimination from wastewater has not yet been extensively performed and reported in the literature. Therefore, the present study is aimed to optimize a robust CBC-based HA removing process and build kinetic models explaining CBC's super adsorption efficiency along with a demonstration of the sustainability of the process by regenerating the exhausted CBC materials to fill the knowledge gaps. The study is focused on the development of a sustainable and cost-effective process that is able to self-regenerate for prolonged HA removal from the aqueous

stream. Various process optimizations involving the amount of CBC, HA along with the pH, reaction time were performed. The mechanisms and efficiency of HA removal were further supported by kinetic models, as kinetic models have been useful in establishing statistical relationships between various factors to better characterize a process (Singh et al., 2019). Data in terms of process parameters from the current study are going to be useful in designing large-scale water pre-treatment plants and such water treatment infrastructure will provide HA free potable water to promote good health. Moreover, the data from the current study will provide a theoretical basis and technical guidance for other pollutants removal present in water that crosses share similarities with HA.

2. Materials and methods

2.1. Preparation of calf bone charcoal (CBC)

Local livestock slaughterhouses in Yazd City, Iran were used to obtain fresh femur of the calf. The calf bones were employed for the production of the bio-adsorbent material. De-ionized (D.I.) water was used to remove non-essential materials from bones (residual fat and proteins). Cleaned bones were dried in an oven set at 100 °C for overnight to extract moisture from bones. Afterwards, the dried bones were crushed and milled into small bone particles as described previously (Dawlet et al., 2013). The fine particles were then ignited at 400 °C for 3 h in a muffle furnace under O₂-limited conditions to pyrolyze the materials into porous material as described previously (Cheung et al., 2001). Further, a rise in temperature to 800 °C for 30 m (calcination process) was performed that modifies the properties of bone char and increases the surface area (Rojas-Mayorga et al., 2015). The produced bone ash from the previous step was further triturerated by standard ASTM9 strainers with pore sizes ranging from 10 to 16" using the ball mill for 20–30 s. The final material (40 g/L) was then treated for 1 h with a 100 mM HCl solution. HCl positively charges the surface of the adsorbent which enhances the attraction of humic acid ions. Finally, HCl treated material was rinsed with DI water at least three times to remove residual acid traces. The final material (CBC) was heat dried overnight at ~60 °C. The exhausted calf bone char (CBC) material was regenerated using NaOH solutions (100–500 mM).

2.2. Qualitative and quantitative analysis of CBC

The surface property or morphology of the prepared CBC was examined via a high-quality scanning electron microscope (SEM). The specific exterior area of CBC was estimated via the Brauner-Emmett-Teller (BET). HA content was quantified by a UV spectrophotometer.

2.3. Adsorption experiments

2.3.1. Preparation of humic acid (HA) stocks

HA stock was made by dispensing the powdered HA (Merck) in 100 mL sodium hydroxide (0.1 N) solution. The prepared solution was left overnight, followed by making up the final volume to 1 L with DI water. The solution was clarified via a Whatman filter paper (1.2 µm pore size) to extract any suspended solids. Working stocks of 5, 10, 20 and 30 mg/L were prepared for further experimentations.

2.3.2. HA removal experimental approach and process parameters

The process parameters, such as pH, HA amount, adsorbent amount and reaction period, were studied. 250 mL bottles containing various amounts of HA along with variable amounts of adsorbent (CBC) were incubated in a shaker incubator (150 rpm). pH adjustments of the samples were carried out using HCl (0.1 N)/NaOH (0.1 N). For every sample, a blank sample control was used. At the end of each experiment, solutions were passed through a 1.2 µm cellulose acetate filter (Sartorius, Germany) in order to measure the final content of HA. All assays

were run in triplicates to ensure reproducibility. The calibration curves of experimental and blank samples were acquired under similar conditions to find the appropriate wavelength. Eqs. (1) and (2) were used to calculate the amount of HA adsorbed (%HA removal) on the CBC and the removal efficiency (%), respectively.

$$q_e = \frac{C_i - C_e}{m} \times V \quad (1)$$

$$R (\%) = \frac{C_i - C_e}{m} \times 100 \quad (2)$$

where q_e is the adsorption capacity (mg/g) at equilibrium C_i , HA is amount (mg/L) at 0 h, R , represents % rejection, C_e is amount (mg/L) of HA at equilibrium, V is volume (mL) of the aqueous stream and m is mass (g) of CBC.

2.3.2.1. Adsorption kinetics experiment. Adsorption kinetics are often used to define the relationship between the adsorption process and time. For the adsorption kinetics studies (adsorption mechanism), pseudo-first-order and pseudo-second-order kinetic models, respectively expressed by Eqs. (3) and (4) were used (Al-Shawabkah et al., 2015).

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where q_e is the HA quantity adsorbed (mg/g) onto the CBC when achieving equilibrium q_t , HA is adsorbed (mg/g) at time t , k_1 and k_2 represent the rate constants of pseudo-first-order (min^{-1}) and pseudo-second-order (1/min), respectively.

2.3.2.2. Adsorption isotherm experiments. Adsorption isotherms are typically used to define the relationship between the adsorbate amount and the strength of adsorption. The coined term "isotherm" reveals the equilibrium curves during adsorption conditions at a specified temperature depending on the kind of adsorption (multi-layer, monolayer or chemical/physical adsorption) (Langmuir, 1917). In the present study three isotherms, Langmuir, Freundlich and Temkin isotherm were developed using experimental observations. To determine restrictive and highest adsorption capacities, the Langmuir model has been widely used. The following Eq. (5) represents the simplistic line form of Langmuir isotherm:

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_0} + \frac{C_e}{Q_0} \quad (5)$$

where q_e = HA quantity (mg/g) is adsorbed by CBC when equilibrium is attained, K_L = equilibrium constant (L/mg) and Q_0 = highest adsorption ability (mg/g). In the Freundlich isotherm, a level of heterogeneity with heterogeneous distribution of heat adsorbed into the surface usually occurs in the adsorption process. The following Eq. (6) represents a straight line linear model:

$$\log(q_e) = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

where K_F = adsorption (mg/g) at a unit of concentration and $1/n$ = adsorption intensity (Olsen and Watanabe, 1957; Allen et al., 2004). In addition, the linear Temkin isotherm model (Eq. (7)):

$$q_e = B \ln K_T + B \ln C_e \quad (7)$$

where K_T and B are Temkin isotherm constants. The following Eq. (8) can be employed to quantify the activation energy for HA that is adsorbed onto CBC.

$$k_2 = k_o \exp\left(\frac{-E}{RT}\right) \quad (8)$$

$$k_p = k^* \exp\left(\frac{-E}{RT}\right) \quad (9)$$

where k_2 = pseudo-second order constant (g/mg. min), k_o = adsorption process rate constant (g/mg min), k_p = intra-particle diffusion coefficient (mg/g. min^{1/2}) and k^* = intra-particle diffusion coefficient (endless temperature or the pre-exponential constant), (mg/g min^{1/2}).

2.3.2.3. Thermodynamic parameters estimation experiments. Various thermodynamic determinants such as the standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°) can be estimated using the below following Eq. (10):

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

where R = 8.314 J/mol. K is the standard gas constant, solution temperature T (Kelvin) and distribution coefficient (K_d) is measured as shown below Eq. (11):

$$K_d = \frac{C_{Ae}}{C_e} \quad (11)$$

where C_{Ae} (mg/L) = adsorbed quantity at steady-state and C_e (mg/L) = steady-state concentration. Eq. (12) is for calculating ΔG° is as described previously (Dawlet et al., 2013).

$$\Delta G^\circ = -RT \ln K_d \quad (12)$$

3. Results and discussion

3.1. Characterization of CBC by microscopy and BET

The prepared CBC was further viewed under the SEM to determine the morphology (Fig. 1). Morphology specifically porous structure and surface chemistry determine the efficacy and process cost. Fig. 1 shows the agglomerated structure of CBC. The BC morphologies vary depending on the type of materials used to develop bone char. SEM of Pig's BC developed at 650 °C and 900 °C showed smooth surfaces (Wongrueng et al., 2019) while SEM of Cow's bone char developed between the pyrolysis temperatures of 650–1000 °C produced a rough, non-porous surface with defined geometry (Rojas-Mayorga et al., 2016). The SEM image of the present study is similar to the bone char developed by Rojas-Mayorga et al. (2016), which effectively removed heavy metals (Cd^{2+} , Zn^{2+} and Ni^{2+}) from water. Calcification temperature impacts the surface area and pore volume of bone char, as high temperatures

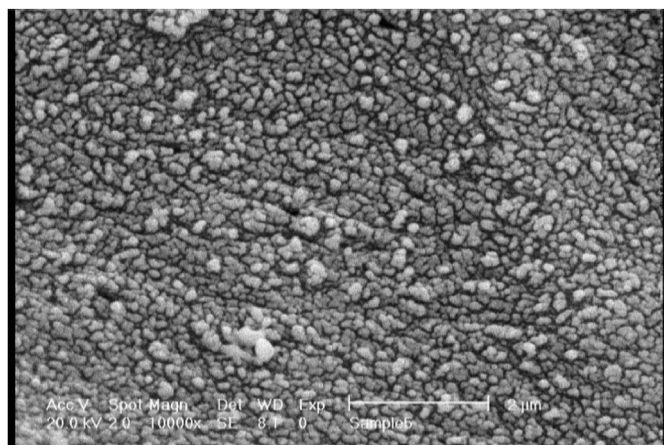


Fig. 1. The SEM image of the synthesized CBC at 10000 × magnification.

tend to remove more carbon and increase the specific area (Rojas-Mayorga et al., 2015). The specific exterior area of the CBC was estimated via the Brauner-Emmett-Teller (BET) method. BET surface area is used as a criterion to determine the quality of the adsorbent. A larger pore volume and increased surface area demonstrate improved electrochemical performance (Tian et al., 2018). BET of CBC in the present study is 112 m²/g which is significantly higher than the previous study (85 m²/g) employing cow's bone (Rojas-Mayorga et al., 2016) and cattle bones (79.34 m²/g) (Shahid et al., 2019).

3.2. Adsorption process performance

3.2.1. Effect of HA content and reaction time on adsorption

To examine how initial HA concentration impacts the adsorption rate, loading capacity and equilibrium concentration, HA solutions of 5–30 mg/L at a constant pH of 4, T of 25 °C and 3 g/L of adsorbent dose (CBC) were used. Fig. 2, reveals that the adsorption process of HA onto CBC was fast and it reached equilibrium in 30 m. This indicates that HA and CBC strongly interacted. Faster reaching equilibrium is beneficial for the effectiveness of a process. Other studies are available where equilibrium time is much higher. Wongrueng et al. (2019) using pig bone char estimated the equilibrium time to be 1 h. Similarly, Dawlet et al. (2013), employed charcoal made from sheep bone (SBC) required twice as much time (2 h) to reach maximum adsorption with a sharp decline in adsorption. A study by Zhang et al. (2018) investigated the humic acid removal by modified aged refuse (MAR) (non BC study) reported the equilibrium time to be 70 m.

A number of studies are available that used non BC material to remove humic acid from water however their equilibrium time is much higher than present study. Maghsoodloo et al. (2011), using activated carbon to eliminate humic acid reported a 100 m equilibrium time. Derakhshani et al. (Derakhshani and Naghizadeh, 2018), using bentonite and montmorillonite nanoparticles as adsorbents observed a 60 m equilibrium time. Wei et al. (2014), using quaternary ammonium cationic cellulose to remove humic acid determined the equilibrium time to be 120 m. Moussavi et al. (2014), determined the HA adsorption equilibrium to be 3 h. In present study, CBC showed an exceptionally shortest equilibrium time that suggests the CBC to be a better adsorbent. Moreover, among all previously used adsorbents (activated carbon, quaternary ammonium cationic cellulose, bentonite and montmorillonite nanoparticles and MAR), CBC is a low-cost superior adsorbent material suitable for wide applications.

From the current study, it is clear that the fraction of HA (residual HA) in the solution decreases as time passes at all HA initial concentrations because it is being adsorbed onto the CBC. However, the continued adsorption slows down as it attains the pseudo-steady state after half an hour. Fig. 2 depicts that the equilibrium fraction of HA remaining in the solution at 25 °C slightly decreases as the starting HA amount increases (5–30 mg/L). The similarities in curves suggest independence of the starting HA amount on %HA removal. This phenomenon is suggestive of a monolayer establishment on the exposed sides of the bone char, as observed previously (Liu et al., 2014) (Lin and Hsien, 2011).

In terms of determining the sustainability and effectiveness of the current method to remove HA, the loading capacity of CBC becomes crucial. From the data presented in the current manuscript, it is evident that CBC remains the robust material to extract HA even at the 6 times higher concentration of HA (30 mg/L). A minor decrease in the efficiency (100–92.1%) was observed when the HA amount was raised from 5 to 30 mg/L. A similar drop in efficiency was described by Moussavi et al. (2014). As shown in Fig. 2, the optimal reaction time is about 30 min where the adsorption rate is the highest and beyond this point, it remains unchanged, without a decrease, for all initial concentrations of HA.

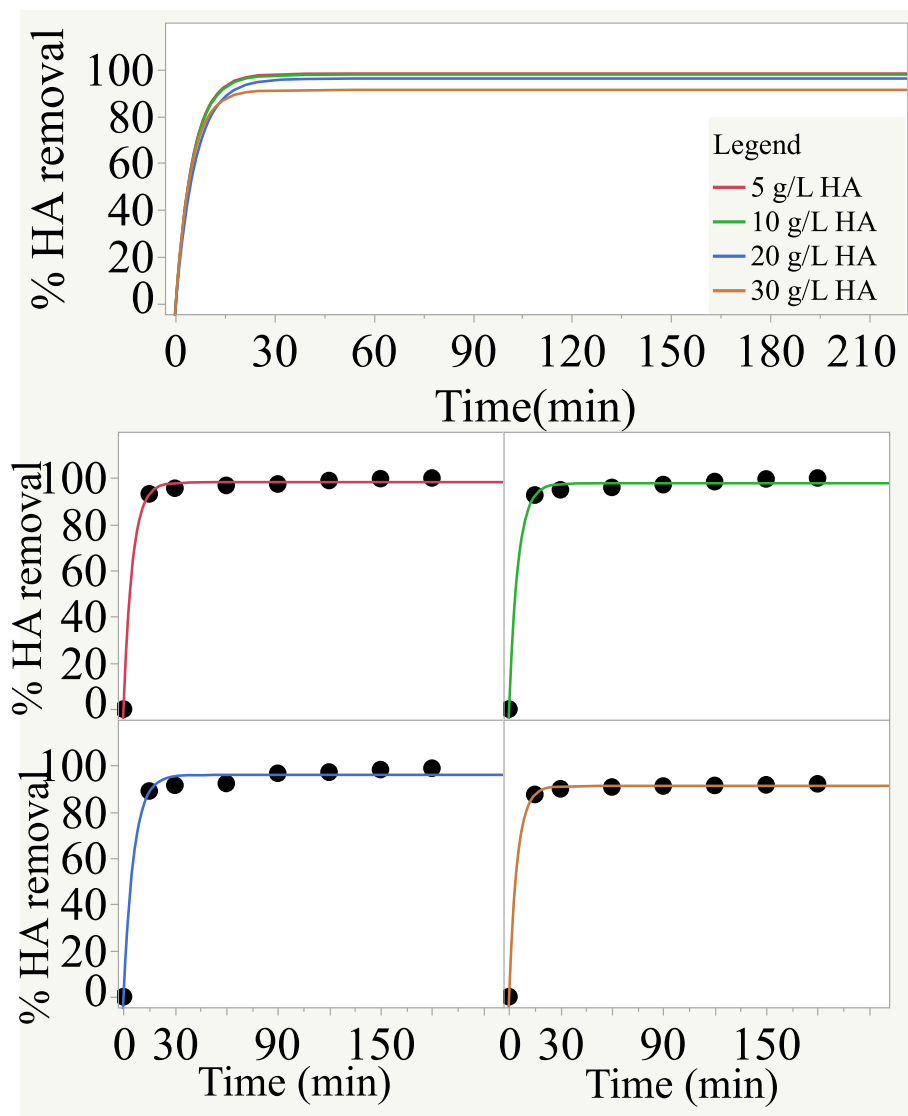


Fig. 2. The effect of HA dose on CBC's adsorption capacity and % HA removal in real time. Percentage HA removal was observed in the presence of 5–30 mg/L HA while keeping 3 g/L adsorbent (CBC) at a constant pH 4.0. Each data point (solid dot) represents three independent experiments.

3.2.2. Effect of adsorbent (CBC) dose and reaction time on adsorption

A differential HA adsorbed fraction was determined with time at different adsorbent (CBC) doses while keeping HA content at 20 mg/L; pH 4.0; reaction time of 180 m and T of 25 °C. According to Fig. 3(A), during the first 30 m, the C/C_0 decreases considerably. % HA removal improves upon increasing the amount of CBC (Fig. 4). As shown in Fig. 3, with increasing doses of CBC from 0.5 to 5 g/L, the % HA removal increases from 36.7 to 99.8%. This improvement in % HA removal might have happened because as the CBC dose increased, the number of active sites for HA adsorption might have substantially increased allowing increased adsorption of HA (Murphy et al., 1992). It is also evident that the adsorption rate of HA onto CBC slowed down and this might have happened because CBC might have provided excessive adsorption sites which rapidly dropped the concentration of HA that ultimately might have altered the chemical adsorption performance of CBC (Zhang et al., 2018). A study by Yu et al. (2017), reported the increase in adsorption of HA when increasing the dose of dual-pore carbon shells. A previous study also reported that increasing the BC dosage enhanced the initial norfloxacin removal rate (Feng et al., 2018). Observations from present study are consistent with prior reports suggesting that CBC material has optimal performance. In the present study, maximum adsorption of 38.08 mg/g was accomplished when HA was 20 mg/L, pH = 4.0,

reaction time was 180 m and the adsorbent dose was 0.5 mg/L.

3.2.3. Effect of solution pH on HA removal

The adsorption capacity is related to the adsorbent's surface load which can be affected by the solution's pH. To study how pH would affect adsorption of HA on CBC, three pH values, including 4, 7 and 10 were chosen. Fig. 5, depicts that adsorption of HA on CBC is completely dependent on the solution's pH such that the % HA removal drops from 98.3 to 12.3% upon changing the pH from 4 to 7. The adsorption of HA on CBC was considerably influenced by the pH value in such a way that the highest removal efficiency is achieved in the acidic environment when pH is 4. This is because pH alters the charges of both adsorbate (HA) and adsorbent (CBC). The carboxylic and phenol groups of HA are most influenced by a pH shift. A pH value more than 4.0 results in dissociation of carboxylic groups of HA whereas pH beyond 8.0 dissociates phenolic groups (Maghsoodloo et al., 2011). Therefore, a negative charge on HA is greatly increased upon increasing pH. This can also affect the morphology of HA because the stretching, caused by an electrostatic repulsion between adjacent negatively charged sites of HA, would decrease at acidic pH leading to shrinking the HA molecules (Lorenc-Grabowska and Gryglewicz, 2005).

It has been reported that HA may exist as a fully stretched molecule

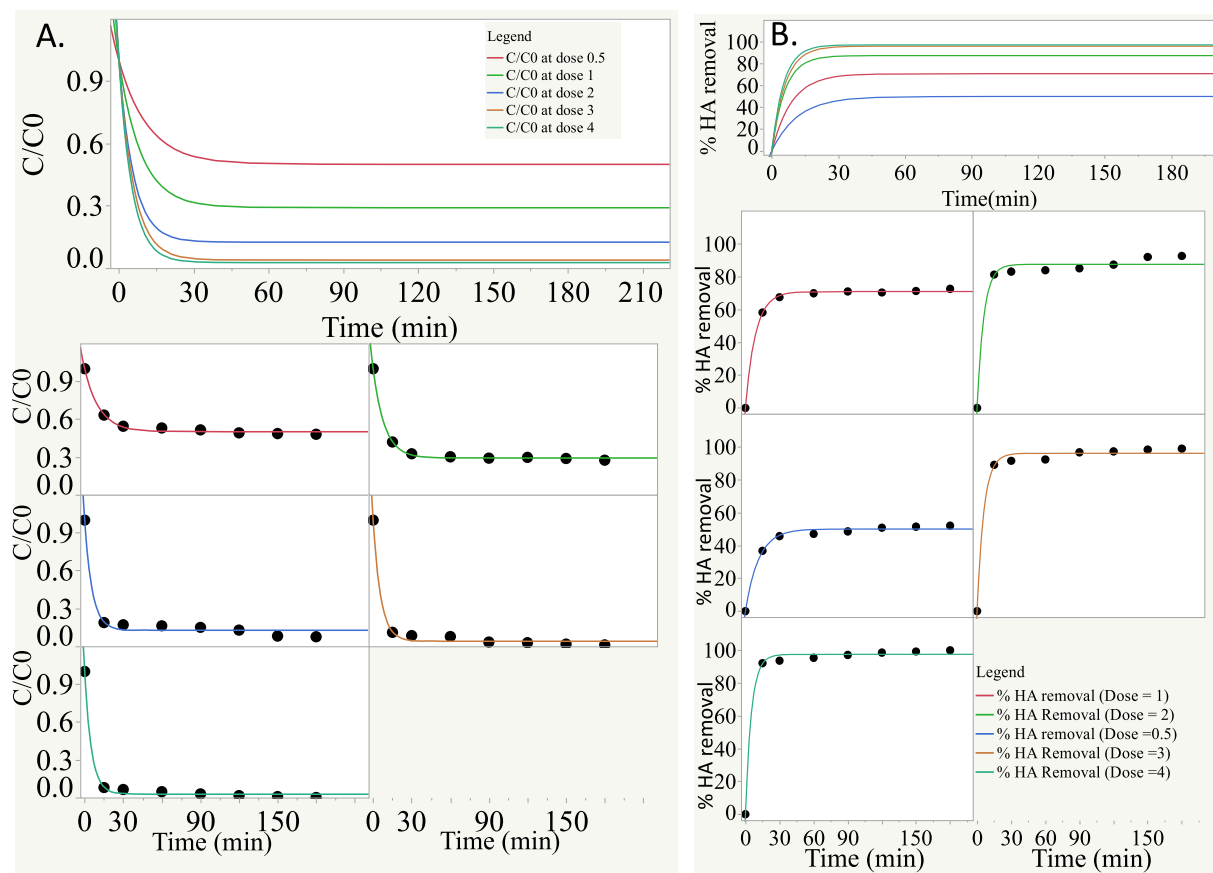


Fig. 3. The effect of CBC dose on the ratio of C/C₀ (A) % removal of HA and (B) in real time. C/C₀ and % HA removal was recorded when increasing the amount of CBC (1–4 g/L) while keeping 20 mg/L adsorbate (HA) at pH 4.0. Each data point (solid dot) represents three independent experiments.

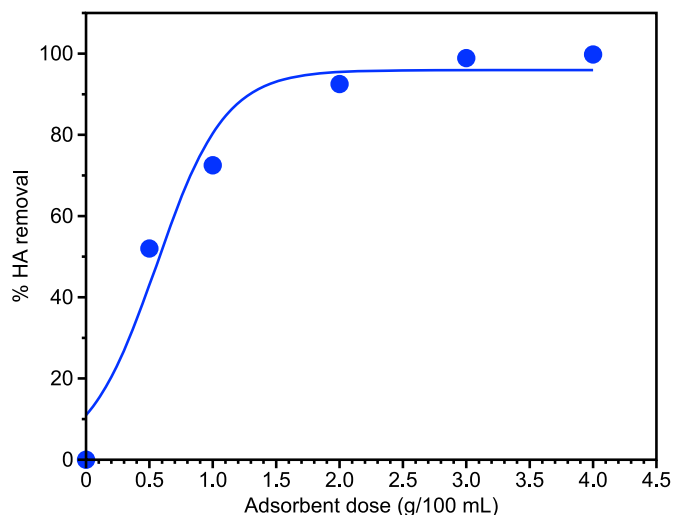


Fig. 4. Effect of adsorbent dose on % HA removal. The % HA removal was recorded at various amounts of CBC while keeping 20 mg/L adsorbate (HA), 180 min reaction time and pH 4.0. Each data point (solid dot) represents three independent experiments.

(linear) at higher pH (Maghsoodloo et al., 2011). This size extension can decrease its adsorption on CBC at higher pH and this is the reason for decreased adsorption at pH 7.0 in present study. Similarly, the physio-chemical properties of CBC are also affected by the solution's pH. At highly acidic pH conditions, several functional groups (carboxyl, amine, and hydroxyl) of CBC gain a positive charge via protonation

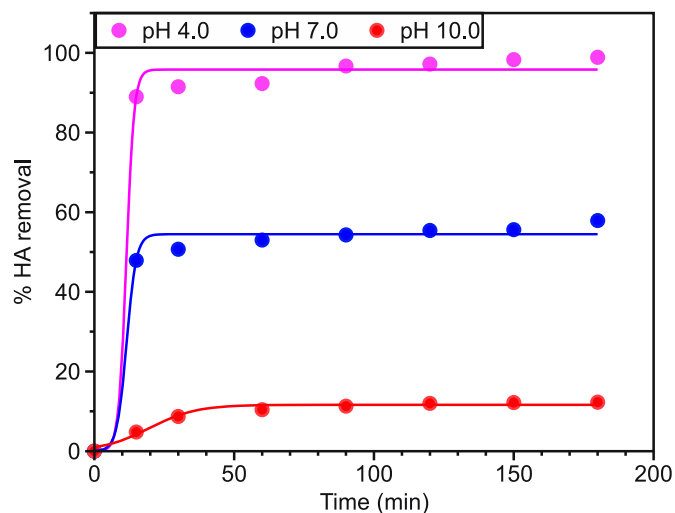


Fig. 5. The effect of pH on % removal of HA in real time. The % HA removal was recorded at three different pH (4, 7 and 10) while keeping 20 mg/L adsorbate (HA) at pH 4.0. Each data point (solid dot) represents three independent experiments.

(Waghmare et al., 2015) which increases the adsorption capacity of CBC. The adsorption capacity of CBC is expected to grow if protonation is accelerated. Additionally, increased adsorption capacity of CBC at pH 4.0 could be related to increased retention time allowing improved HA adsorption. A similar phenomenon was reported by Shams et al. (2010), when using granular ferric hydroxide (GFH) as an adsorbent. Lowering

the pH of the solution and increasing the concentration of adsorbate (Fluoride) prolonged the contact time which resulted in increased fluoride removal efficiency.

Similar to this study, increased adsorption has been observed in many studies. A study using pig bone char (Wongrueng et al., 2019) also observed increased adsorption of DOM and effective removal of DOM at a pH value of <6.5. Niu et al. (2021), determined a 3.0 pH value as optimum that removed more than 95% Cu^{2+} by modified chicken bone char. Ranjbar et al. (2018), also noticed the adsorption decrease (84–63%) of chromium (VI) by bone char-ZnO when pH increased from 3 to 9. Dawlet et al. (2013), used sheep bone char activated with ZnCl_2 to remove mercury (II) and determined that the maximum adsorption was at pH 3.0 because adsorption decreased upon raising the solution's pH. In contrast, a study by Chen et al. (2008) contradicts the majority of studies showing the maximum adsorption at acidic pH. In this study, adsorption of As (V) was found to be dependent on pH dosage and 0.5 mg/L As (V) was removed at pH 10. The reason behind this phenomenon is the complex mechanism in which co-precipitation between calcium hydrogen arsenate and hydroxylapatite in the aqueous solution and ions exchange between calcium hydrogen arsenate and OH⁻ ion.

3.2.4. Adsorption kinetic

To comprehend the adsorption behaviour of HA on CBC, pseudo-first-order and pseudo-second-order kinetic equations were used to fit the experimental data. Fig. 6 (A) and (B) show the pseudo-first-order and the pseudo-second-order kinetics, respectively, along with the correlation coefficients (R^2) at 4.0 pH 4.0, 20 mg/L HA and 3 g/L adsorbent (CBC). The kinetic models were performed at 30, 60, 90 and 180 m. The results of linear regression analyses were 0.809 and 0.901, corresponding to pseudo-first-order and pseudo-second-order kinetic models, respectively. The final kinetic model selection was based on the highest R^2 value. By comparing the R^2 values, the pseudo-second-order kinetic model ($R^2 = 0.901$) is appropriate to explain the adsorption kinetics of HA on CBC. This suggests that physical and chemical adsorption may act in a unified way during the adsorption process. A study by Zhang et al. (2018) that investigated humic acid removal by aged refuse reported similar kinetic model observations. Maghsoodloo et al. (2011), also found the pseudo-second-order kinetic model suitable to describe HA adsorption on chitosan-treated granular activated carbon (MGAC). Niu et al. (2021), also determined the pseudo-second-order kinetic model suitable to be suitable to describe Cu^{2+} adsorption on chicken bone charcoal. Therefore, the model selected in present study is consistent with previous works and appropriately explains the kinetics of HA adsorption on CBC.

3.2.5. Adsorption isotherms

The adsorption power and the adsorption mechanism are typically concluded by the adsorption isotherms (Al-Qodah, 2006; Al-Qodah et al., 2007). The isotherm models inform the dispersion of the adsorbate molecules between the aqueous environment and the adsorbent's surface when the equilibrium is achieved. It also determines how the concentration of equilibrium affects the loading capacity across a wide range of temperatures. Three commonly applied isotherms play a pivotal role in defining the interconnection between the surface concentration (q_e) and the equilibrium concentration (C_e). Among these, as per the Langmuir isotherm (Langmuir, 1917), the equilibrium is reached upon the establishment of a monolayer of the adsorbate over the adsorbent. The other two models are the Temkin isotherm and the practical Freundlich model which has applications in heterogeneous and multi-site surfaces. In the present study, the experimentally recorded observations were analyzed by isotherm models of Temkin, Freundlich, and Langmuir.

The isotherm correlation coefficients of HA adsorption with CBC are shown in Fig. 7(A-C). These experimental data were correlated to these linearized models generating the regression coefficient values of 0.407, 0.731 and 0.943 for Temkin, Freundlich, and Langmuir isotherms, respectively. Considering the goodness of fit, the adsorption of HA onto the adsorbent follows the Langmuir model. Based on the results, the Langmuir isotherm model is the best to define the mechanism of adsorption that takes place by monolayer adsorption on CBC. As per present results, one molecule of HA is adsorbed by one active site on CBC and interactions between adsorbed HA molecules present in the monolayer are unlikely. The surface site adsorption (monolayer) of CBC is consistent with other studies that used bone charcoal to remove a variety of pollutants for example Cu^{2+} monolayer adsorption on chicken bone charcoal (Niu et al., 2021), chromium (VI) monolayer adsorption on bone char Zno (Ranjbar et al., 2018).

3.2.6. Adsorption thermodynamics

K_d is an important determinant for the intra-particle diffusion rate. Table 1 presents how coefficient (K_d) changes when temperature and HA amounts (5, 10, 20 and 30 mg/L HA) are changed. It can be visualized in Table 1 that the quantity of HA adsorbed by CBC, C_{Ae} (mg/L) and consequently Q_{max} increases as temperature increases. These observations verify the endothermic nature of the adsorption of HA molecules onto CBC. This can be attributed to the fact that as temperature increases the liquid phase viscosity decreases and consequently the intra-particle diffusion of solute molecules in the pores increases. In addition, Table 1 shows that K_d increases as temperature increases. Because K_d at 30 mg/L

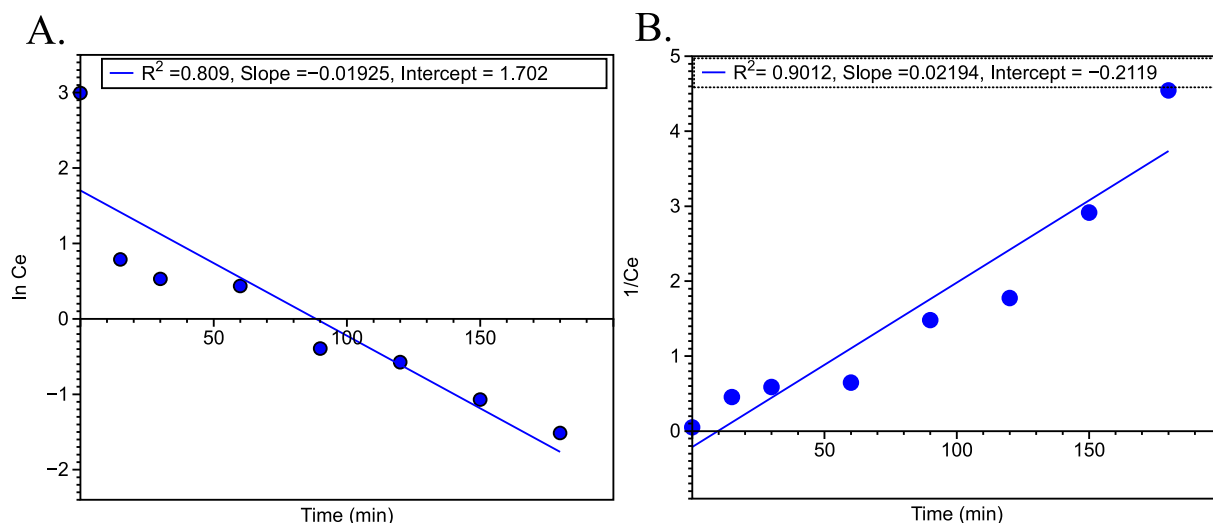


Fig. 6. Correlation coefficient (R^2) of (A) Pseudo-first-order and (B) Pseudo-second-order (pH = 4, HA content = 20 mg/L, adsorbent dose = 3 g/L).

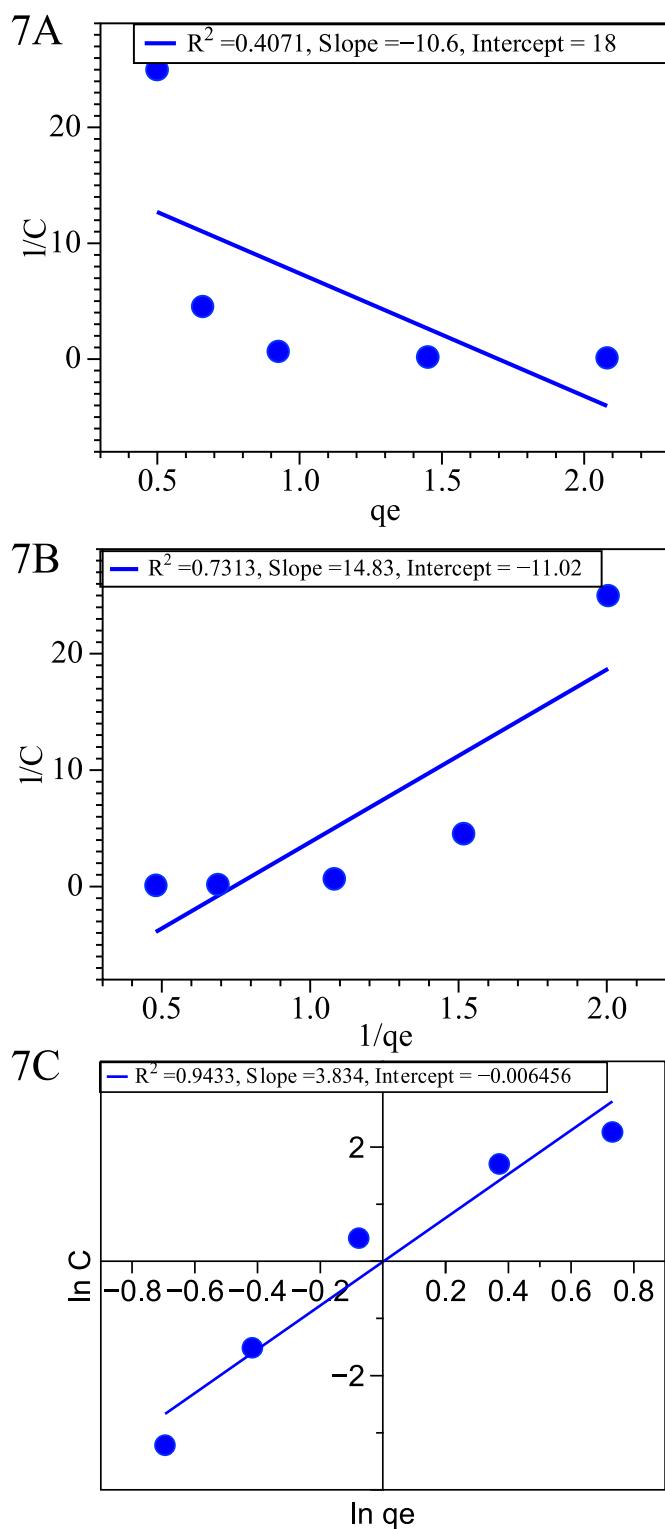


Fig. 7. Adsorption isotherm of HA on CBC (pH = 3 and 3 g/L adsorbent) and fitting of the experimental data by the Temkin (A), Freundlich (B) and Langmuir and (C) isotherm models.

is inferior than 5 mg/L, this suggests that adsorption is feasible when the initial concentration is lower.

To determine the spontaneous nature of the adsorption process, three thermodynamic factors; ΔG° , ΔH° and ΔS° were calculated. A negative value of ΔG° shows the spontaneity of the reaction and a positive value of ΔH° demonstrates endothermic reaction whereas a negative value of

Table 1

Effect of temperature on K_d and HA adsorption.

C_0 (mg/L)	Temperature (K)	C_{Ae} (mg/L)	C_e (mg/L)	K_d
5	298.15	4.99	0.02	332.33
	308.15	4.99	0.01	713.29
	318.15	5.00	0.00	2499.00
10	298.15	9.96	0.04	249.00
	308.15	9.99	0.01	999.00
	318.15	10.00	0.00	3332.33
20	298.15	19.66	0.34	57.82
	308.15	19.85	0.16	128.03
	318.15	19.99	0.01	3332.33
30	298.15	27.51	2.49	11.05
	308.15	28.74	1.26	22.87
	318.15	29.04	0.96	30.15

ΔH° represents exothermic reaction. A positive value for ΔS° represents increased entropy during the adsorption and adsorption may be irreversible (Ranjbar et al., 2018). It was shown above that HA adsorption on CBC follows the pseudo-second-order model. Activation energy associated with HA adsorption and E value was derived from Eq. (8) and the slope of $\ln k$ versus $1/T$, respectively. 5 mg/L HA gives E 82.11 kJ/mol while R^2 is > 0.96. Because E is greater than 42 kJ/mol, this suggests that the reaction kinetics between HA and CBC controls the adsorption process (Zalloum et al., 2008).

The values of $\ln K_d$ were plotted against $1/T$ at four different initial HA concentrations (Fig. 8). It shows that the $\ln K_d$ versus $1/T$ has a linear association as suggested by significantly higher R^2 (0.9806). The slopes and intercepts of the lines calculated the thermodynamic parameters (ΔH° , ΔS° and ΔG° using Eqs. (10)–(12) of the adsorption process. Table 2 shows the obtained values at different concentrations and temperatures. ΔS° values are positive which suggest that elevated randomness at the edge between the solid and liquid phases is the reason for higher affinity of the CBC adsorbents towards HA. Similar results have been previously reported (Ranjbar et al., 2018). These results substantiate the feasibility of the process and its spontaneous nature, especially at 10 mg/L (CBC). At the lowest concentration of CBC while at the high temperature, it is highly likely to obtain the best results (100% removal).

3.2.7. Regeneration of CBC reversible process

To make the whole process sustainable, attempts were made to desorb HA from the CBC surface at the end of each experiment. This will lead to two advantages namely: Regenerating the exhausted CBC to be

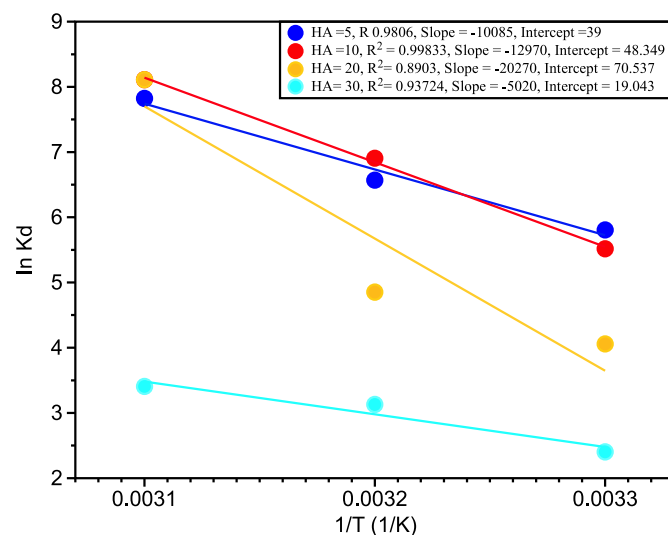


Fig. 8. Thermodynamic parameters with varying temperatures to determine adsorption of different concentrations of HA onto CBC.

Table 2

Thermodynamic parameters for adsorption of HA on CBC.

C0 (mg/L)	ΔH_{a} (J/mol)	ΔS_{a} (J/mol.K)	ΔG_{a} (J/mol)		
			"298.15 K"	"308.15 K"	"318.15 K"
5	67467.3	258.4	-9564.7	-12158.7	-14742.7
10	81746.6	295.7	-6412.6	-9373.4	-12339.4
20	51131.0	193.6	-6605.6	-8526.8	-10464.8
30	65347.0	234.4	-4434.2	-6883.4	-9227.3

re-used multiple times and extracting the valuable HA molecules to be used in some useful applications. Regeneration was achieved by treating the exhausted CBC in a 50 mL NaOH solution (100–500 mM) while continuously stirring at 180 rpm for 2 h at 25 °C. First, for saturating the CBC with HA, 50 g/L CBC was mixed with 500 mg/L HA solution and stirred for 4 h. Afterwards, CBC was incubated with fresh HA solution under the same conditions to achieve higher levels of saturation. Then, deionized water was applied to wash and remove the excess of HA from the saturated bone char surface followed by drying at 60 °C for 24 h. Then, saturated CBC was used for conducting regeneration studies. Fully saturated CBC (~3 g) was treated in a 50 mL NaOH solution (100–500 mM) while continuously stirring at 180 rpm at 25 °C for 2 h.

Having completed the regeneration process, the CBC samples were thoroughly rinsed with DI water until neutral pH was achieved. It was further subjected to drying at 60 °C for 1 day before starting new adsorption experiments. 3 g of regenerated CBC was treated with 5, 10, 20, 30 mg/L HA solutions while continuously stirring (150 rpm) the mixture at 25 °C. The optimum regeneration conditions determined in

the present study were used to conduct an equilibrium test. Fig. 9 depicts how the reaction time and HA contents impact adsorption by regenerated CBC. Regeneration of HA-exhausted CBC is unique to this study. Only a few studies are available to regenerate bone char adsorbent. A study by [Ranjbar et al. \(2018\)](#), attempted regeneration of chromium (VI) adsorbed chicken bone char a by nitric acid solution (pH 2.0).

However, only 10% maximum desorption was achieved and the probable reason is irreversible binding of chromium (VI) to chicken bone char. In some instances, thermal desorption (>500 °C) has been attempted ([Yang et al., 2020](#)) but this has not given success for all the adsorbates. Considering other noneconomic and infective desorption methods, the present study regeneration regimen is economically effective and less time-consuming. The present study findings indicated that the alteration in degradation efficiency of CBC after the first sorption step and further use after reversibility was insignificant. Hence, the reversible CBC can be used to treat water and wastewater containing HA. Therefore, cost-efficacy and simply reversible adsorbent CBC seems to be a promising adsorbent for water treatment ([Table 3](#)).

4. Future prospects and cost of BC

Providing clean and pollutants free water is the most important duty of any country to promote the health of its citizens. In recent years because of population expansion and industrialization pollutants are on the rise. To maintain a healthy status of water, USEPA and WHO has set a maximum contaminant level (MCLs) for most waterborne pollutants. One such pollutant is humic acid that has coexisted with other pollutants in water. The standard chlorination process leads to secondary pollution by generating EPA regulated pollutants such as trihalomethanes

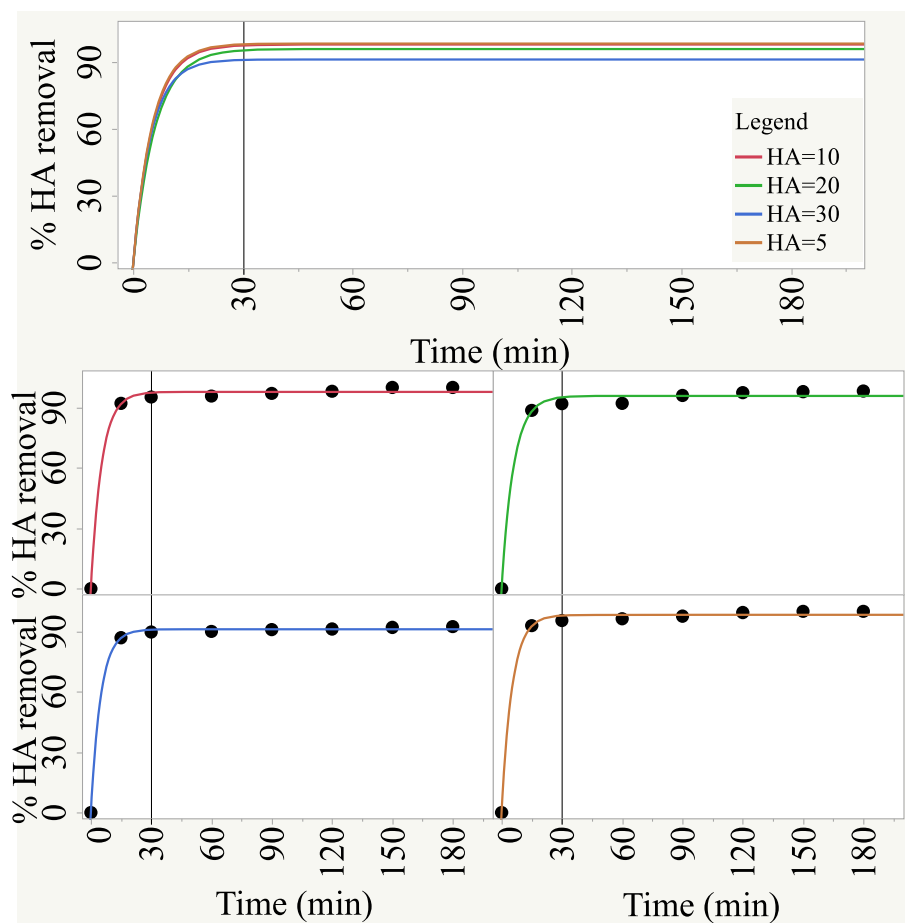


Fig. 9. The performance of re-generated CBC is estimated by % HA removal. % HA removal was observed in the presence of 5–30 mg/L HA while keeping 3 g/L adsorbent (CBC) at a constant pH 4.0. Each data point (solid dot) represents three independent experiments.

Table 3
Comparative analysis of various bone chars to remove various water pollutants.

Bone char type	Pollutant	Surface area (m ² /g)	Reaction time	Maximum adsorption capacity (mg/g)	Regeneration	Reference
Pig bones char	Disinfection byproduct (DBP)	100.63 at 650 °C and 78.00 at 900 °C	1 h	4.40 to 19.97	Not studied	Wongrueng et al., (2019)
Sheep bones with zinc chloride activation	Mercury (II)	83.98	2 h	21	Not studied	Dawlet et al., (2013)
Chicken bones char	Fluoride	Not reported	24 h	11.20	Not studied	Herath et al., (2018)
Chicken bones char	Cu ²⁺	Not reported		15.50	Limited regeneration by HNO ₃	Niu et al., (2021)
Cattle bones char	Fluoride	104	1 day	2.71	Not studied	Medellin-Castillo et al., (2007)
Calf bones char	Humic acid	112	<30 min	38.08	NaOH based 100% regeneration	Current study

(THMs), haloacetic acids (HAAs), halo(acetic acid/ketones/aldehyde) and halogenated furanones (Bhatnagar and Sillanpää, 2017). Therefore, much of the water treatment focus has been shifted towards new water pre-treatment technologies to remove NOM including HA. Several advanced methods such as oxidation, ion exchange, reverse osmosis is superb in removing NOM however the significantly higher application cost has made these technologies limited to only developed countries.

Oxidation based water treatment cost is USD 100–2000 per cubic meter of water however the adsorption technology cost of treatment is significantly lower (USD 50–150 per cubic of water) (Gupta et al., 2012). Adsorption based new methodologies have gained monumental attention recently owing to their extraordinary selectivity for various water pollutants, minimal operational costs and improved efficiency. Bone char has emerged as a superior adsorbent after scoring tremendous success in removing heavy metals including mercury (II) (Dawlet et al., 2013), chromium (Hyder et al., 2014), Cu²⁺ (Niu et al., 2021) fluoride (Shahid et al., 2019), toxic industrial dyes (Reynel-Avila et al., 2016), antibiotics (Dai et al., 2018) and water pollutants such as DBP (Wongrueng et al., 2019) from water. It is considered as an alternative to expensive activated carbon (AC) technology. Expanded surface area and the presence of functional groups make BC one universal adsorbent to remediate various water pollutants.

According to one report (Choy and McKay, 2005) BC's adsorption capacity for metals is 15% higher than that of active carbon. Production of BC is much more feasible due to the abundance of raw materials (animal bones). In 2019, the chicken market achieved a milestone of producing 100 million tons of chicken worldwide which could provide bones for BC production (Kasim et al., 2020). Because of the existence of the meat industries worldwide, millions of tons of bone are discarded annually which can be used for BC production. As per the Organization for Economic Co-operation and Development (OECD) (OECD/FAO, 2018) 40 million metric tons surge in meat production in the next decade is anticipated which will include an increase in 13% poultry, 10% pig meat and >21% sheep meat. The massive availability of animal bones is promising to develop BC that will provide dual benefits (water treatment and bone waste management). Therefore, the future of low cost adsorbent based propitious technology appears bright in developing and under-developed countries.

To build and support bigger plants removing HA from water, large scale production of bone char would be much needed and a proper cost analysis is required. Most of the BC production cost analysis is limited to commercial settings. The overall cost depends on the availability of raw materials, procurement cost and reactor setting cost. As per Arrenberg's (Arrenberg, 2010) cost estimation, it would cost \$1609.87 to produce five tons of bone char of goat, camel, cattle and sheep bone (estimated by CDN's company). Currently, some companies are selling bone char for US\$ 13/kg ("BulkBoneChar@PromolifeInc", 2022) for water treatment however this production cost could be further lowered by using the other products for energy gain (i.e. value added gas production during pyrolysis).

While the CBC is highly effective in sequestering HA from water

(Table 3), more research is needed to extract HA for its further use as a soil fertilizer. It is likely that CBC is also removing other pollutants from water therefore further characterization of the type of pollutant being removed would be needed. According to the nature of pollutant proper disposal of concentrated pollutants must be in place. Additionally, further studies focusing on reactor design, chemical modification of CBC as an effort to increase the surface area, surface chemistry alteration, metal oxide coating, extending CBC's life and cost reduction are encouraged.

5. Conclusions

The present study focuses on the development of a calf bone char (CBC) based process that effectively sequestered HA from water. HA makes the standard disinfection processes ineffective because during the disinfection process HA transforms into tightly regulated and carcinogenic disinfection by products (DBPs) such as trihalomethanes (THMs), chloroform and dhaloacetonitriles. Removal of HA from water is a dire need however due to the cost to acquire and implement advanced technologies, developing countries are struggling to provide pollutants free water. CBC was developed as an economic and super adsorbent material to decimate a high amount of HA present in water. The calcination process involving 800 °C for 30 m generated CBC with a 112 m²/g surface area which supported massive adsorption of HA (38.08 mg/g) on its surface. The adsorption was found to be positively correlated with the HA amount as shown by an increase in adsorption upon increasing the amount of HA from 0.5 to 5 g/L 99% of HA removal was achieved in 30 m at an acidic pH of 4.0 which is superior than similar studies employing various bone char. The optimum conditions to remove 99% HA were found to be pH = 4, HA content = 20 mg/L, adsorbent dose = 3 g/L. A pseudo-second-order kinetic model explains the kinetics of HA adsorption on CBC. The adsorption isotherms were explained by the Langmuir isotherm and the adsorption occurred by a monolayer formation. Thermodynamic constants supported the adsorption of HA. To reuse the HA exhausted CBC, 100% regeneration was achieved via NaOH treatment. Regeneration demonstrates the sustainability of the process. Further optimization such as improving nano-oxides and techno-economic analyses will be useful to apply this technology globally for the HA free water generating infrastructures.

Credit author statement

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Reviewing and Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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