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ARUNDO DONAX BASED- BIOCHAR AS A SUSTAINABLE ADSORBENT FOR NATURAL ORGANIC MATTER REMOVAL FROM SURFACE WATER

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ABSTRACT

Natural organic matters (NOM) is one of the major pollutants of the surface water. NOMs cause problems of taste, color and odor. Moreover, they increase the consumption of coagulants and chlorine, causing dangerous disinfectant’s by-products. Humic substances are the main NOM components. One of the most efficient techniques for removing NOMs is the adsorption process. Finding out low cost, high efficiency and eco-friendly adsorbent for NOM removal from surface water is an interesting area of research. Arundo donax has been identified as a naturalized species in the Nile area, Sinai, Western Desert oases, Mediterranean coastal regions, and waste lands throughout Egypt's desert. This study aims to assess the utilization of arundo donax biochar for NOM removal and comparing its performance with the commercial activated carbon. In this study, Arundo donax was pyrolyzed and simultaneously KOH activation was used to produce biochar and used for humic acid (HA) from water. The impact of several operational parameters, including contact time, adsorbent dosage, and initial pH , have been studied. The findings show that for both GBC and CAC, the highest adsorption of humic acid occured at pH 4. At the same operation conditions, the equilibrium time was 40 min and 50 min and the maximum adsorption capacity was 405.86 mg/g and 30.64 mg/g for GBC and CAC respectively. The best-fitting isotherm model was Freundlich model for both adsorbents with R2 = 0.988 for GBC and 0.879 for CAC. The best-fitting kinetic model for both adsorbent was pseudo-second order model. with R2 = 1.0 for GBC and 0.9998 for CAC. The study showed that biochar made from Arundo donax is a promising low-cost, sustainable and ecologically friendly alternative for the removal of NOM from surface water and would provide a new sight for practical application.

KEYWORDS: Natural organic matter, Arundo donax, Biochar, Carbon-based materials, Adsorption.

إزالة المواد العضوية الطبيعية من المياه السطحية باستخدام الفحم الحيوي المشتق من نبات الغاب كمادة مازة مستدامة

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الملخص

تعد المواد العضوية الطبيعية ((NOM) أحد الملوثات الرئيسية في المياه السطحية. المواد العضوية الطبيعية تسبب مشاكل في الطعم واللون والرائحة. علاوة على ذلك، فإنها تزيد من استهلاك مواد الترويب والكلور، مما يسبب تكون منتجات التطهير الثانوية الخطيرة. المركبات الهيومية هي المكون الرئيسي للمواد العضوية الطبيعية. وتعد عملية الامتزاز إحدى الطرق الفعالة لإزالة المواد العضوية الطبيعية. يعد اكتشاف مواد مازة لازالة المواد العضوية الطبيعية من المياه السطحية، منخفضة التكلفة وذات كفاءة عالية وصديقة للبيئة مجالًا بحثيًا مثيرًا للإهتمام. يتواجد نبات الغاب في منطقة النيل وسيناء وواحات الصحراء الغربية وساحل البحر الأبيض المتوسط والأراضي البور في جميع أنحاء صحراء مصر. الهدف من هذه الدراسة هو تقييم استخدام الفحم الحيوي (GBC) المشتق من نبات الغاب لازالة المواد العضوية الطبيعية من المياه السطحية ومقارنة أدائه مع الكربون المنشط التجاري (CAC) . تم تحضير الفحم الحيوي عن طريق الانحلال الحراري لنبات الغاب وتنشيطه بهيدروكسيد البوتاسيوم (KOH) لاستخدامه في إزالة حمض الهيوميك (HA) من الماء. تمت دراسة تأثيرعوامل التشغيل مثل زمن التلامس وجرعة المادة المازة والرقم الهيدروجيني الأولي للمحلول. وقد أظهرت النتائج أن الحد الأقصى لامتصاص حمض الهيوميك حدث عند الرقم الهيدروجيني 4 لكل من الفحم الحيوي (GBC) والكربون المنشط التجاري (CAC) . عند نفس ظروف التشغيل، كان زمن التوازن 40 دقيقة و50 دقيقة وكانت قدرة الامتزاز القصوى 405.86 ملجم/جم و30.64 ملجم/جم لكل من الفحم الحيوي (GBC) والكربون المنشط التجاري (CAC) على التوالي. اوضحت النتائج أن نموذج فريندليك هو النموذج متساوي الحرارة الأفضل ملائمة لكل من الممتزات حيث R2 = 0.988 وR2 = 0.879 لكلا من الفحم الحيوي (GBC) والكربون المنشط التجاري (CAC) علي التوالي وأن نموذج الدرجة الثانية لبوسيدو (Pseudo-second order) هو النموذج الحركي الأفضل لكلا الممتزات حيث R2 = 1.0 و0.9998 لكلا من الفحم الحيوي (GBC) والكربون المنشط التجاري (CAC) علي التوالي . وقد أظهرت الدراسة أن الفحم الحيوي المصنوع من نبات الغاب يعد بديلاً واعدًا منخفض التكلفة ومستدامًا وصديقًا للبيئة لإزالة المواد العضوية الطبيعية من المياه السطحية وسيوفر إضافة جديدة للتطبيق العملي.

الكلمات المفتاحية : المواد العضوية الطبيعية، نبات الغاب، الفحم الحيوي، المواد الكربونية، الامتزاز.

1. INTRODUCTION

Lack of water is becoming a serious global issue caused by a variety of variables including unsustainable water usage practices, population growth, and climate changes. Due to the growing global population and the depletion of freshwater resources, countries that depend primarily on freshwater resources must ensure that the quality of their water is maintained, particularly when it comes to natural organic matters (NOM). Untreated water contains a complex mix of natural and synthetic inorganic and organic substances.[1]. Organic matter that exists naturally (NOM) primarily autogenic and its produced by geological, hydrological, and biological processes., including photosynthetic eukaryotic organisms, detritus litter, and pathogenic organisms [2].

Presented NOM in untreated water could be dissolved or suspended and have an adverse effect on water quality. It change its colour, appearance, odour and taste, make it undesirable also act as a transportation to other harmful particles and chemicals , and responsible for the harmful compounds formation during disinfection process[3,4]. Strong oxidants react with NOM to produce carcinogenic disinfection byproducts (DBPs) [5]. NOM is a complicated substance of several compounds including proteins, lipids, amino acids, fulvic acid and humic acid (HA), and carbohydrates. HA is a compound formed by organic matter decomposition, including plants and animals, through chemical and biological processes. It is a very stable, recalcitrant, and non-biodegradable organic material with high molecular weight [6]. Daifullah et al, have demonstrated that during the chlorination of water supplies, humic materials create trihalomethanes (THMs) and other halogenated organic substances.

Numerous technologies have been developed to remove contaminants from water, including membrane technology, adsorption technology and, advanced oxidation technology [8]. Among these treatment methods, adsorption technology is one of the best treatment technologies because of its low cost, superiority with simple design, wide processing range, and low energy consumption [9]. Adsorption is the process where pollutants (adsorbate) are adsorbed on solid substrate (adsorbent) surface to remove them from the effluent. The adsorption capacity is influenced by a number of variables, including temperature, pH, and adsorbate concentration [10]. Activated carbon, silica zeolite, polymer resin, and other conventional adsorbents are widely utilized in the water treatment. However, their applicability is subject to the restrictions of high cost, limited reuse performance and, complex regeneration. For many decades, commercial activated carbon is the most popular used adsorbent; nevertheless, one of its main drawbacks was the high cost [11].

Biochar is the byproduct resulting from the thermal transformation (through processes like pyrolysis or gasification) of carbonaceous biomass in an environment with restricted oxygen[12,13]. Biochar has been characterized as a cost-effective, sustainable and eco-friendly material including considerable surface area, a high porosity, a high capacity for cation exchange, reusability and stability [17,18]. Such characteristics make it an excellent substrate for environmental applications [14,15]. Several low-cost adsorbents from forestry and agricultural by-products have been reported in recent studies [16-23]

A. donax grows on rather infertile and dry soils, such as roadside areas, however it usually grows along riverbanks, creeks, and in moist soils [24,25]. It has been recorded as a natural plant in the Nile region, Sinai, the Mediterranean coast, roadside areas, railways, and wastelands. It is also found in oasis in the Western Desert and throughout Egypt's desert [26,27]. Consequently, a significant amount of biomass residues are produced annually [20].

The current study aims to evaluate using arundo donax biochar for the removal of natural organic matter from water treatment plants as a cost-effective, sustainable, and eco-friendly material and to compare its performance with the commercial activated carbon. Also, the effect of the adsorption operation parameters has been investigated.

2. Materials and Methods

2.1. Chemicals

All chemicals that were commercially obtained and directly used, including Humic acid potassium salt ($C_9H_8K_2O_4$) (80%, Libox Chem), potassium hydroxide (KOH) (≥ 97.95 %, CDH Fine Chemicals), The deionized water was produced by a high purity water system.

2.2. Biochar preparation and modification

Arundo donax was collected from the Nile River embankment which located in front of Gazerat Eldahab water treatment plant, Giza, Egypt. Before use, Arundo donax was cleaned, rinsed with distilled water then dried at 105 C°. After drying, Arundo donax was cut to ≤ 100 µm. A box furnace was used to elevate the temperature of dried Arundo donax powder to 600 C° for 3 hrs. Following pyrolysis, KOH was used to saturate the biochar, which was pyrolyzed afterwards. Every

5 g of biochar was impregnated using a solution made up of 15 g of KOH and 100 ml of distilled water in a beaker (impregnation ratio 1: 3). After one hour at room temperature, the mixture was mixed. Following the impregnation process, the slurry was dried in an oven at 110 C° in a beaker until a constant weight was reached. The pyrolysis process was carried out in a furnace with a temperature increase of 750 C° for one hour. The preparation method was selected based on other reported study [28].

Characteristics of each GBC, and CAC are shown in Table 1. The GBC's fourier transform infrared (FTIR) spectrum is displayed in Fig. 1.

Table 1. Texture characteristics

Material	GBC	CAC
BET surface area m^2/g	1546.84	703.10
Total pore volume cm^3/g	1.16214	0.52
Average Particle radius nm	0.8815	1.9394

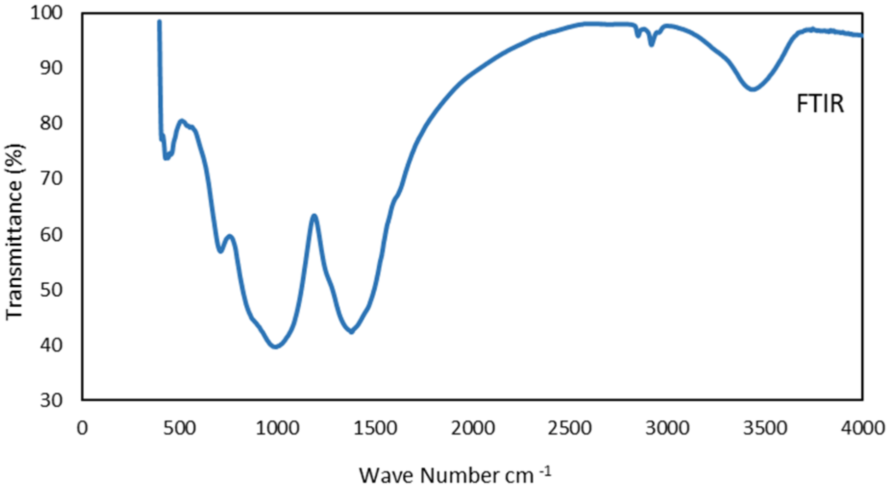

Fig. 1. FTIR for GBC

2.3. Adsorption experiments:

A comparative Batch adsorption experiment was conducted, using green biochar (GBC) and commercial activated carbon (CAC) to determine which sorbent is the most effective for humic acid removal. The experiment was carried out in 250 ml flasks, containing 220 ml of the HA solution at the desired concentration. For adjusting the pH of the solutions, NaOH and HCL solution were utilized. At room temperature, the mixes were stirred at 150 RPM. The adsorbent was separated from the solutions using syringe filter (0.45 µm). the final concentration of HA was measured by using spectrophotometer at λ = 254 nm.

The effects of adsorbent dosage, pH, initial humic acid concentration, and contact time were investigated. Adsorption isotherm was identified by batch equilibrium experiment at the optimum conditions [10].

The following formula was used to calculate the removal efficiency (R%):

$$R\% = \left(C_0 - \frac{C_t}{C_0}\right) * 100 \qquad \text{Eq. (1)}$$

where, R% is the HA removal percent, C_o is the initial HA concentration and C_t is the remaining HA concentration after time (t).

3. RESULTS AND DISCUSSION

3.1. Effect of initial pH

One of the key variables that affects how well organic materials are eliminated is the pH level. [29]. To study how initial pH effect of on the adsorption of HA, the initial pH was adjusted within the range of 3-9. Other operational conditions were GBC dose 25 mg/l, CAC dose 25 mg/l, Initial HA concentration 11 mg/l and contact time 1.5 hr. The efficiency of HA removal in the pH range is shown in Figure 2. The results show that as pH decreased, HA removal efficiency improved from 61 to 91% and from 27 to 56% for both adsorbent, GBC and CAC respectively and at pH 4, the highest adsorption was observed for both adsorbent. Similar findings regarding the increased HA adsorption in highly acidic conditions have been reported in studies [30]. Unanimously, despite of the adsorbent utilized, it was reported that at lower pH values, 78% of the adsorbents exhibited optimal performance.[31]. This pattern has multiple explanations since the quantity adsorbed is affected by both the characteristics of HA and adsorbent surface. At low pH (pH>2), HA is negatively charged due to the existence of carboxylate, aliphatic, and aromatic hydroxyl groups [32]. In addition, it is found that HA was more soluble in a very acidic media, and this characteristic improved HA's adsorption [33,34].

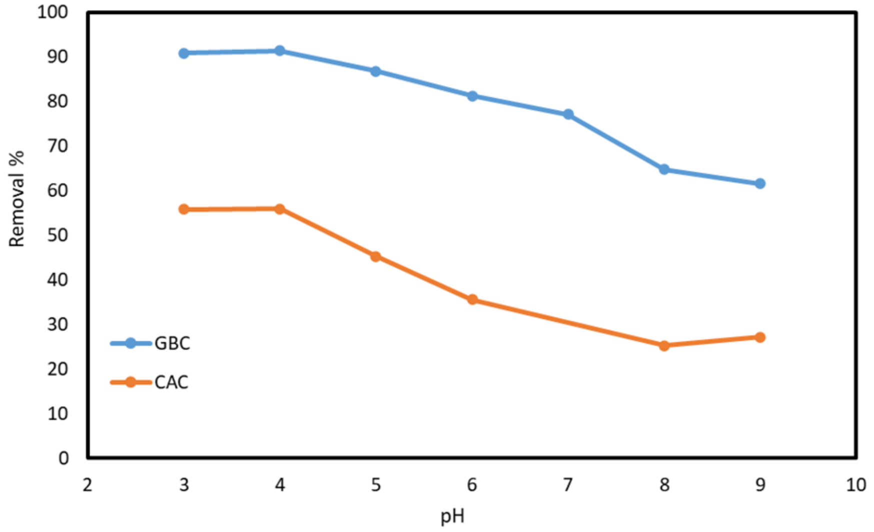

Fig. 2. The removal of HA efficiency with pH range

3.2. Effect of adsorbent dose

The dosage of the adsorbent affects the adsorption process, however this varies depending on the adsorbent [35]. To study how adsorbent dosage affects HA adsorption, adsorbent dose was adjusted within the range of 6.0 - 8000 mg/l. Other operational conditions were initial pH 4.0, Initial HA concentration 11 mg/l and 2.0 hrs. contact time. The removal of HA efficiency in the adsorbent dose range is shown in Figure 3. The results show that the higher dose of adsorbent resulted in a higher removal of HA. This may be explained by the fact that t the surface has a greater number of adsorption sites, which increase the amount of HA that may be adsorbed [31]. At same conditions of dose, pH, and initial concentration GBC achieved the highest HA removal more than CAC.

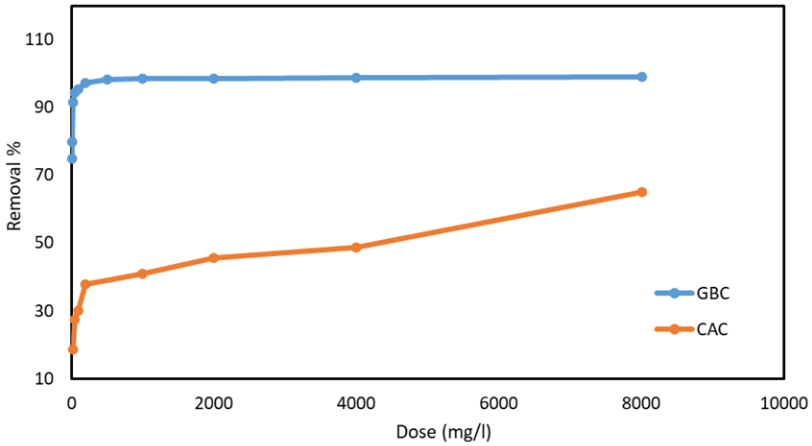

Fig. 3. The removal of HA efficiency with adsorbent dose

3.3. Effect of Contact time and humic acid concentration

The adsorption process is affected by the contact time since it is carried out in batch systems. Also, the adsorption process's efficiency is significantly affected by the adsorbate's initial concentration. To study how contact time and humic acid concentration affect the HA adsorption, humic acid concentration was 2.5, 5, 10, and 20 mg/l, contact time was 5, 10, 20, 40, 80, 160 min. Other operational conditions were initial pH 4.0, GBC dose 25 mg/l and CAC dose 25 mg/l. The efficiency of HA removal in the Contact time and humic acid concentration is shown in Figure 4. The findings indicate that HA removal increases as contact time increases. Increasing contact time further 40 min (GBC), 50 min. (CAC), did not significantly increase the HA removal. This pattern is matched with the literature. Published studies reported adsorption capacity rapid increased at the start of the process followed by a gradual decrease until the adsorption equilibrium is attained where the sorption sites are fully occupied [36,37]. The rapid initial rate of adsorption is due to a substantial gradient between the adsorbent and the adsorbate, as well as the presence of abundance of active sites number on the adsorbent surface. The findings also indicate that HA removal increases as initial HA concentration decreases. the increase in HA molecules causing the saturation of attainable surface active sites of the adsorbent material [38].this findings are matched with the previous studies [39]. The findings indicate that GBC achieved the highest HA removal 98% compared to CAC 17%.

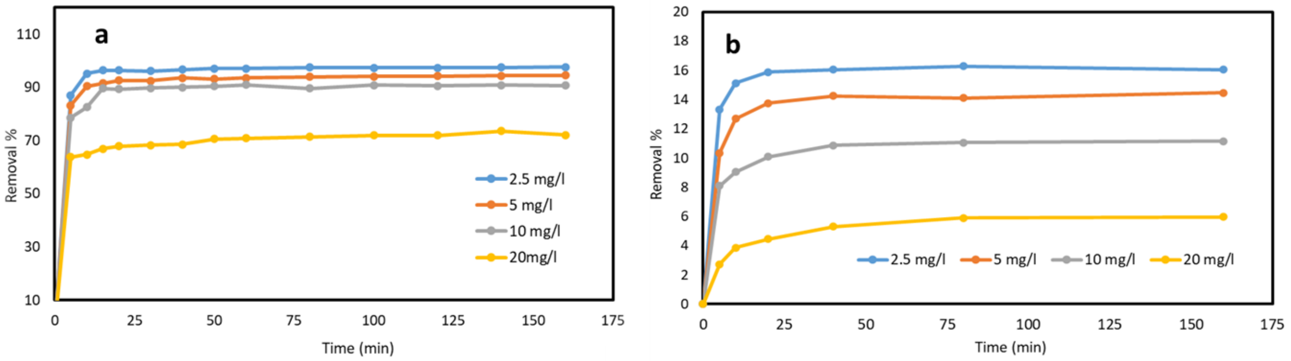

Fig. 4. Effect of contact time & HA concentration

3.4. Adsorption isotherms

Isotherm studies are performed using a batch reaction with a fixed temperature and a variable initial HA concentration. These isotherms provide significant information on the interaction between the HA and the adsorbent surface, including the interaction homogeneity or heterogeneity at the surface and the adsorbent's maximal adsorption capacity. The two isotherms Langmuir and Freundlich have been found to be frequently used in the literature review [40,41]. In this study, both isotherms, Langmuir and Freundlich at various adsorbent dosages were used to predict the equilibrium of HA adsorption onto GBC & CAC.

3.4.1. Langmuir isotherm:

The Langmuir isotherm form is given as [42-44]

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{K_l * q_{max}} \qquad \text{Eq. (2)}$$

where q_e (mg/g) is the adsorption capacity of adsorbent at equilibrium conditions, C_e (g/ml) indicates the concentration of HA at the adsorption equilibrium, q_{max} (mg/g) indicates the maximum adsorption capacity of the adsorbent, and Kl (L/mg) is the Langmuir constant. Adsorption in single layers is assumed to occur in a homogenous condition for the Langmuir isotherm. [45,46]. Fig. 5a, b displays the Langmuir isotherms for GBC and CAC. The correlation coefficient (R2) for HA on GBC and CAC are 0.9437 and 0.0012 respectively in the figure. The R^2 for GBC is close to unity and indicates that Langmuir isotherm can be applied while it is not applicable for CAC. According to Langmuir Equation (2) and the plots, q_{max} for GBC and CAC is found to be 405 mg/g and 30 mg/g, respectively.

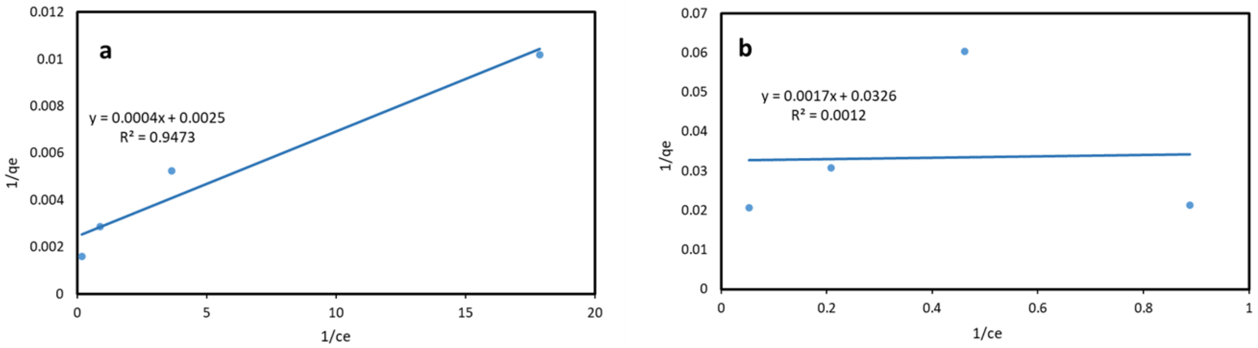

Fig. 5. Langmuir isotherm of HA adsorption into GBC (5a) and CAC (5b)

3.4.2. Freundlich Isotherm

The Freundlich isotherm form is given as [47]

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \qquad \text{Eq. (3)}$$

where q_e (mg/g) is the adsorption capacity of adsorbent at equilibrium, Ce (g/ml) indicates the concentration of HA at the adsorption equilibrium, K_f (mg/g) indicates the Freundlich constant, and, n is the adsorption intensity. The Freundlich isotherm involves the assumption that adsorption takes place in a heterogeneous state and involves multi layers adsorption. Fig. 6a, b displays the Freundlich isotherms for GBC and CAC. The correlation coefficient (R^2) for HA on GBC and CAC are 0.9884 and 0.8789 respectively in the figure. Although both isotherm models were shown to be linear across the HA concentration range, the Freundlich model's R2 value is greater and approaches unity. As a result, the experimental adsorption data is more accurately represented by the Freundlich isotherm.

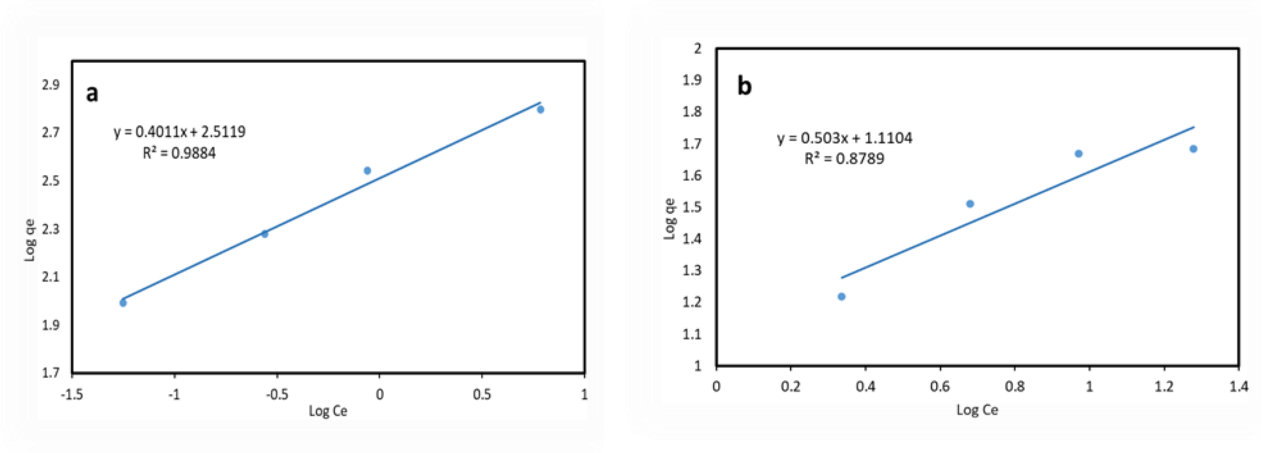

Fig. 6. Freundlich isotherm of HA adsorption into GBC (6a) and CAC (6b)

3.5. *Kinetic models*

Kinetic models play a crucial role in investigating adsorption mechanisms and systems by illustrating and forecasting the rates at which pollutants are removed. Pseudo-first order (PFO) and pseudo-second-order kinetics (PSO) are the two most widely used kinetic models.

3.5.1. *Pseudo-first order kinetic model*

The PFO kinetic model form is given as [40][48]

$$\text{Log}\,(q_e - q_t) = \log\,(q_e) - \frac{k_1}{2.303}t \qquad \text{Eq. (4)}$$

where q_e (mg/g) is the adsorption capacity of adsorbent at equilibrium, q_t (mg/g) is the adsorption capacity at time = t (s) is time, and k_1(min^{-1}) is the rate constant.

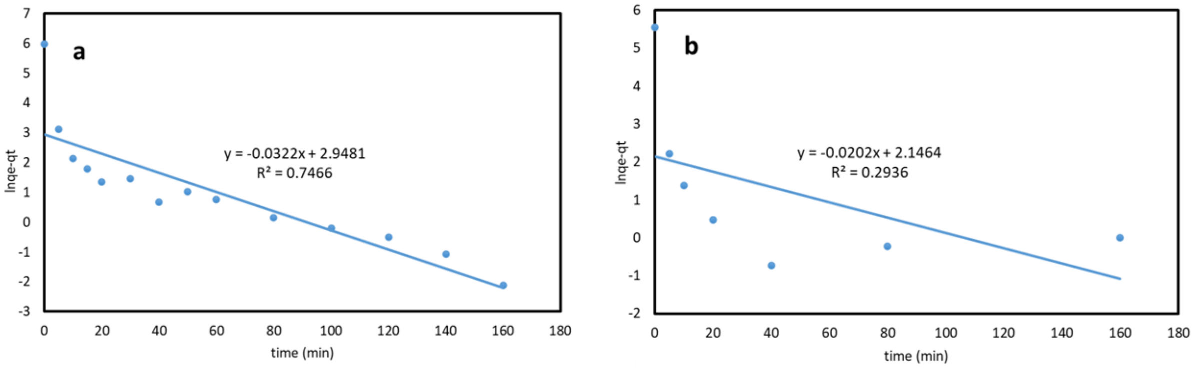

Fig. 7. Pseudo-first order kinetic for GBC (a) and CAC (b)

3.5.2. *Pseudo-second order kinetic model*

The PSO kinetic model form is given as [49,50]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e} + \left(\frac{1}{q_e}\right) t \qquad \text{Eq. (5)}$$

where qe (mg/g) is the adsorption capacity of adsorbent at equilibrium, qt (mg/g) is the adsorption capacity at time t (s), and $k_2(min^{-1})$ is the rate constant.

Most of the kinetic investigations were demonstrated to be fitted as PSO., indicating that HA adsorption mainly involves a chemical adsorption [51] and this is matching with this study.

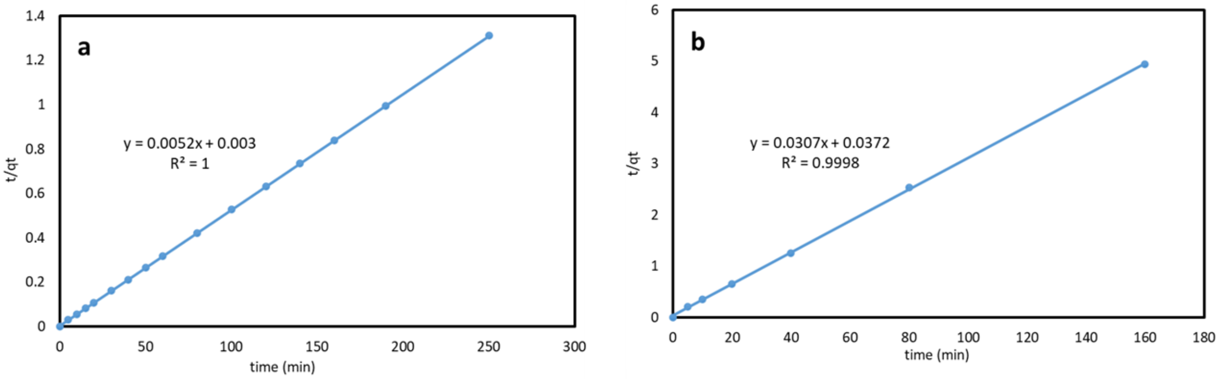

Fig. 8. Pseudo-second order kinetic for GBC (a) and CAC (b)

Conclusions

The synthesized Green Biochar was effectively applied for HA elimination from aqueous solution by chemical activation using KOH. Considering the results of this research and the scientific data presented in the literature, the following conclusions have been listed:

1. pH 4 was the optimum value for HA adsorption.
2. The removal efficiency of HA by GBC (98%) is higher than that of CAC (17%)
3. Both Langmuir and Freundlich are appropriate for describing the HA adsorption by GBC however, the Freundlich Isotherm model was a much better due to the raised correlation coefficient (R2 = 0.9884 & 0.878 for GBC & CAC) and a maximum adsorption capacity for GBC of 405mg/g & 30 mg/g for GBC & CAC was obtained.

4. The higher correlation coefficient (R2 = 1& 0.999 for GBC & CAC) demonstrated that a pseudo-second-order model might be used to fit the sorption reaction's kinetics.
5. A significant improvement in the removal efficiency was observed When the sorbent dosage and contact time are increased, even though a significant decline was observed with raising the initial HA and pH concentration.

The present study showed that green biochar made from Arundo donax is a promising low-cost, sustainable, and eco-friendly alternative for the elimination of Natural organic matter from aqueous solution with a limited ratio.

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