HARNESSING DIFFERENT PRE-TREATMENTS FOR THE PRODUCTION OF ARUNDO DONAX-BASED BIOCHAR FOR REMOVAL OF HUMIC ACID FROM SURFACE WATER, TO MEET THE SUSTAINABLE DEVELOPMENT GOALS

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ABSTRACT

Arundo donax biochar (ABC) is produced through pyrolysis with limited oxygen levels as green biochar (GBC) serves as the raw material. KOH, HCl, and H_3PO_4 were used as alkalin and acidic agents for surface modification. Adsorption experiments were conducted to investigate the impact of these surface modification methods on humic acid (HA) removal from aqua solution compared with ABC without surface modifications and commercially activated carbon. The adsorption experiments were conducted in a pH range from 5 to 9. The findings indicated that the removal of humic acid has been enhanced at lower pH for all cases at the same operation conditions. The HA removal efficiency was higher by CAC than ABC without modification. However, both acidic and alkaline surface modification had higher HA removal compared with CAC. The adsorption efficiency by various treatment reagents on HA was in the order KOH > HCL > H_3PO_4. At a pH value of 5, HA removal efficiency was 97.56 %, 51.3 %, and 48.64 % for KOH, HCL, and H_3PO_4 respectively. The research indicated that biochar derived from Arundo donax represents a promising, cost-effective, sustainable, and environmentally friendly solution for HA removal from surface water, offering a novel perspective for practical implementation.

KEYWORDS: Humic acid, Biochar, Surface modifications, Adsorption, Sustainability.

استخدام معالجات مختلفة لإنتاج الفحم الحيوي من نبات الغاب لإزالة حمض الهيومك من المياه السطحية لتحقيق أهداف التنمية المستدامة

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الملخص

تم استخدام الفحم الحيوي المشتق من نبات الغاب الذي تم إنتاجه عن طريق التحلل الحراري باستخدام مستويات منخفضة من الأكسجين كمادة خام. تم استخدام KOH ، HCl ، H_3PO_4 كعوامل حمضية وقلوية لتعديل السطح. أجريت تجارب الامتزاز لاستكشاف تأثير طرق تعديل السطح المختلفة على إزالة الحمض الهيوميكي من محلول مائي باستخدام الفحم الحيوي المشتق من نبات الغاب دون تعديلات على السطح مقارنة بالكربون المنشط التجاري. تمت التجارب باستخدام الاس الهيدروجيني 5 ، 7 ، 9.

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خلصت النتائج إلى أن إزالة الحمض الهيوميكي قد تحسنت عند قيم الاس الهيدروجيني المنخفضة (pH 5) لجميع الحالات في نفس الظروف التشغيلية. وكفاءة إزالة الحمض الهيوميكي باستخدام الكربون المنشط التجاري أعلى مقارنة بكفاءة إزالة الفحم الحيوي المشتق من نبات الغاب بدون تعديل. ومع ذلك، حققت التعديلات الحمضية والقلوية على السطح كفاءة إزالة أعلى مقارنة بالكربون المنشط التجاري. وكفاءة إزالة المواد الهيوميكية لطرق تعديل السطح المختلفة KOH أكبر من HCL أكبر من H₃PO₄ حيث بلغت كفاءة الازالة97.56 ٪ ، 51.3٪ ، 48.64٪ على التوالي. كما أظهر البحث أن الفحم الحيوي المستمد من نبات الغاب يمثل حلاً واعدًا وفعالًا من حيث التكلفة ومستدامًا وصديقًا للبيئة لإزالة المواد الهيوميكية من المياه السطحية، ويقدم منظورًا جديدًا للتطبيق العملي.

الكلمات المفتاحية : حمض الهيومك، الفحم الحيوي، المعالجة السطحية، الامتزاز، الاستدامة.

1. INTRODUCTION

Surface waters and aquifers are primary sources of drinking water. Most of these sources naturally contain substances such as natural organic matter (NOM), suspended particles, and potentially harmful biological materials including algae, protozoa, and fungi. NOM is commonly regarded as a complex mixture of organic substances that can be found in the majority of natural water bodies. [1]. NOM can arise within water sources due to biological processes [2], predominantly from algae and microorganisms (autochthonous NOM), or it can enter water bodies through runoff from surrounding watersheds, carrying materials produced during the decomposition of land-based organisms (allochthonous NOM) [3]. Therefore, the composition and NOM amount could differ significantly from one location to another even within the same water body. The amount and composition of NOM can vary after seasonal changes such as droughts, floods, and rainfalls [4, 5] All of those biological, hydrological, geological, chemical, and climatic factors are the main reasons for NOM spatiotemporal variations and recurrently monitored increase around the world in the past 20 years [6, 7].

From a water treatment standpoint, humic acids stand out as the crucial constituents of NOM. Humic acids (HA) originate from the decomposition of plants and animals. It alters the color, appearance, odor, and taste of water, rendering it undesirable. Additionally, it serves as a carrier for other harmful particles and chemicals and is responsible for the formation of harmful compounds during the disinfection process [8].

Several methods are used to treat NOM in water, including combined coagulation and flocculation, using activated carbon filters, membrane filters, advanced oxidation techniques, and ion exchange resins. However, some of these options may not be practical due to their cost, challenges like membrane clogging and cleaning, or the building of sludge and frequent filter rinsing [9, 10]. Adsorption technology is considered one of the most effective treatment methods among the available options due to its affordability, straightforward design, versatility in application, and minimal energy usage. [11]. Adsorption refers to the mechanism wherein pollutants (known as the adsorbate) are adsorbed on the surface of a solid substrate (referred to as the adsorbent) to extract them from the effluent. The adsorption capacity can be affected by several factors, including temperature, pH, and the concentration of the adsorbate [12, 13]. Activated carbon remains the most widely utilized adsorbent; however, one of its primary limitations is its high cost [14, 15]

At present, biochar's comparatively large specific surface area (SSA), porous structure, and abundance of functional groups make it a good choice for adsorption. Biochar is recognized as an economical, environmentally friendly material with substantial surface area, high porosity, significant cation exchange capacity, and notable attributes of reusability and stability. [16]. These qualities make it an ideal material for environmental purposes [17, 18]. In recent years, to conserve precious natural resources and utilize waste effectively, a significant quantity of adsorbents has been produced from natural waste sources. These include pinewood [19], loofah peels [20], cotton agricultural wastes [21], waste tea leaves [23], waste paper [22], rice [23], and wheat hull [24], and waste coffee grounds [25] were utilized for the adsorption of pollutants from aqueous solutions.

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Arundo donax reeds, which flourish near water bodies, offer extensive potential applications due to their abundant availability in nature (as eco-biosorbents), low operational costs, and high phosphate removal capacity. Therefore, they offer advantages over other biosorbents [26].

The production of biochar is affected by various factors, including the type of raw materials used, pyrolysis temperature, heating rate, residence time, and modification techniques. These parameters play a vital role in defining the properties of the resulting biochar. Therefore, it is imperative to meticulously consider these factors to guarantee the production of biochar with the desired attributes. [27]. The choice of modification method represents another aspect of the feasibility of biochar engineering. It can be categorized into physical, chemical, and biological modifications. Surface modification includes trimming its structure and modifying surface functional groups. The primary chemical modifications to biochar include those involving oxidizers, metal salts, acids and alkalis, and organic reagents [28]. These techniques aim to alter biochar's structure via chemical processes [29].

This study aims to produce a novel Arundo donax biochar for humic acid adsorption by selecting the optimum surface modification method as a sustainable, eco-friendly, and cost-effective material. Also, compare the HA removal efficiency for both commercial activated carbon (CAC) and Arundo donax biochar.

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 distilled water was produced by a high purity water system.

2.2. Synthetic water

Synthetic water was created by mixing a specific amount of humic acid solution with distilled water to reach the desired concentration for the experiment.

2.3. Synthesis of Biochar

Arundo donax was collected from the Nile River embankment which is located in front of Gazerat El Dahab water treatment plant, in Giza, Egypt. Before use, Arundo donax was cleaned, rinsed with distilled water then dried at 105 C°. After drying, Arundo donax was ground up to ≤ 100 μm. A box furnace was used to elevate the temperature of dried Arundo donax powder to 600°C for 3 hrs. After cooling to room temperature, Surface modification of the activated biochar was performed by the following three methods for comparison.

2.3.1. HCL Surface modification method

The Arundo donax samples were taken out after the pyrolysis and then soaked in 10% (w/w) HCl solution for 12 h. Subsequently, samples were washed with distilled water to neutralize pH and dried at 80 °C to obtain the Arundo donax biochar.

2.3.2. H$_3$PO$_4$ Surface modification method

The Arundo donax samples were taken out after the pyrolysis and then soaked in 45% (w/w) H_3PO_4 solution for 12 h. Subsequently, samples were washed with distilled water to neutralize pH and dried at 80 °C to obtain the Arundo donax biochar.

2.3.3. KOH Surface modification method

Following pyrolysis, KOH was used to saturate the biochar, which was pyrolyzed afterward. 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.

2.4. Instruments and Analytical methods

1. The measurement of humic acid was conducted by the standard method (APHA, 2012) utilizing a Double beam UV spectrophotometer (UVD-2950).
2. The measurement of pH was conducted by the standard method (APHA, 2012) utilizing a pH Meter (JENWAY-3510).
3. Tap water was distilled using PO3El WATER STILL MODEL 720 - 4 L/H.

| Arundo donax plant | Arundo Donax after grinding | Biochar after pyrolysis |

Fig. 1. biochar Preparation from Arundo donax

2.4. Adsorption experiments:

Batch experiments were conducted to investigate the humic acid (HA) removal efficiency. These experiments involved keeping the initial concentration of humic acid (HA) constant at 10 mg/L and the biochar dose at 5g /l. The experiments were carried out at variable pH values of 5,7 and 9, using green biochar (GBC) with variable surface modification methods and commercial activated carbon (CAC) to determine a) which surface modification method is the most effective for humic acid removal and b) to compare the humic acid removal efficiency via GBC and CAC. For adjusting the pH of the solutions, NaOH and HCL solutions were utilized. At room temperature, the mixes were stirred at 150 RPM. The adsorbent was separated from the solutions using a syringe filter (0.45 μm). the final concentration of HA was measured by using a spectrophotometer at $\lambda = 254$ nm.
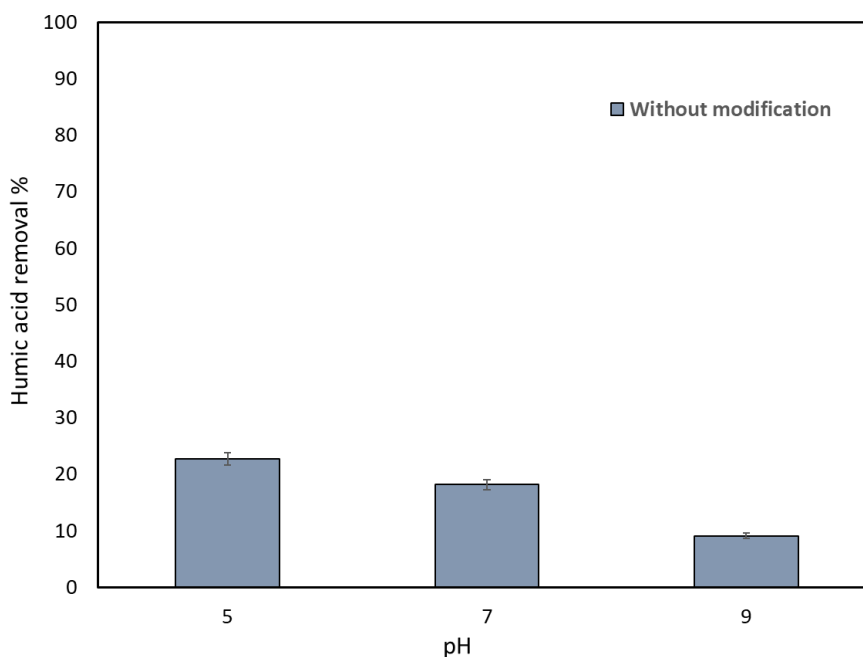
3. RESULTS AND DISCUSSION

3.1. Effect of GBC for HA removal without any surface modification versus the use of commercial activated carbon
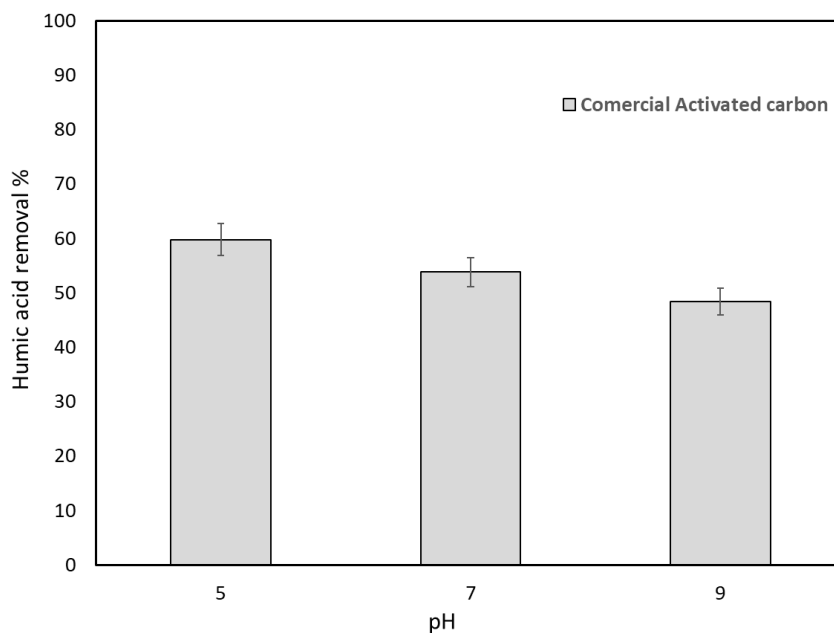
The efficiency of GBC without surface modifications on HA removal in the pH range of 5,7 and 9 is shown in Figure 2. The operating parameters were a 1.5-hour contact period, an initial HA concentration of 10 mg/l, and a GBC dose of 5 g/l. The findings demonstrate that HA removal effectiveness was 22.73 %, 18.18 %, and 9.09 % at pH 5,7 and 9 respectively, where the greatest adsorption was shown for both adsorbents, as pH dropped. This finding confirms that using GBC without any modification was not significant as the removal percent of humic acid was very limited it shows that surface modification play a vital role in the adsorption process. However, the removal of humic acid has been enhanced after using commercial activated carbon as shown later in the current manuscript.

The efficiency of CAC on HA removal in the pH range of 5,7 and 9 is shown in **Fig. 3**. The operating parameters were a 1.5-hour contact period, an initial HA concentration of 10 mg/l, and a CAC dose of 5 g/l. The findings demonstrate that HA removal effectiveness was 59.78 %, 53.80 %, and 48.37 % at pH 5,7 and 9 respectively where the greatest adsorption was shown, as pH dropped. The removal of humic acid has been enhanced at lower pH for both cases (unmodified surface and commercial activated carbon) and this could be due to the treatment of the humic acid for the two types of biochar without any modification at the surface and the removal efficiency was not significant (not exceed 60 %). The surface modification of the biochar will lead to an increase surface functional groups [28, 29] and area [32, 33] which will lead to enhanced removal percent as will be discussed later in the current manuscript.

Fig. 2. HA removal efficiency with biochar without surface modifications

Fig. 3. HA removal efficiency with biochar using commercial activated carbon

3.2. Effect of GBC on HA removal with different acid pretreatment H_3PO_4 acid and HCL acid for surface modification

The efficiency of GBC with H_3PO_4 surface modifications on HA removal in the pH range of 5,7 and 9 are shown in Figure 4. The operating parameters were a 1.5-hour contact period, an initial HA concentration of 10 mg/l, and a GBC dosage of 5 g/l. The findings demonstrate that HA removal effectiveness was 48.64 %, 45.65 %, and 40.21 % at pH 5,7 and 9 respectively. As shown, there was no big and significant difference between the humic acid removal at different pH's and this confirms that the pH in the case of phosphor pretreatment was not the main factor for the humic acid removal. However, as shown in the same figure, the efficiency of GBC with HCL surface modifications on HA removal in the pH range of 5,7 and 9 are shown in Figure 4. The operating parameters were a 1.5-hour contact period, an initial HA concentration of 10 mg/l, and a GBC dosage of 5 g/l. The findings demonstrate that HA removal effectiveness was 51.3 %, 49.46 %, and 44.84 % at pH 5,7 and 9 respectively. The difference in the humic acid removal was only around 6% for all different pHs and this confirms that the pH in the case of HCL pretreatment was not the main factor for the humic acid removal, however, in comparison to using HCL or Phosphoric acid for pretreatment of biochar to remove humic acid, HCL was the best in the acidic pretreatment and it could be refereeing to the high power capacity of the HCL as it is considered strong acid than the low power capacity of the phosphoric acid as it is considered a weak acid [34]. This finding verifies that chemical activation through both acidic modification methods has a substantial impact on converting a non-porous structure into a well-developed porous structure [35].
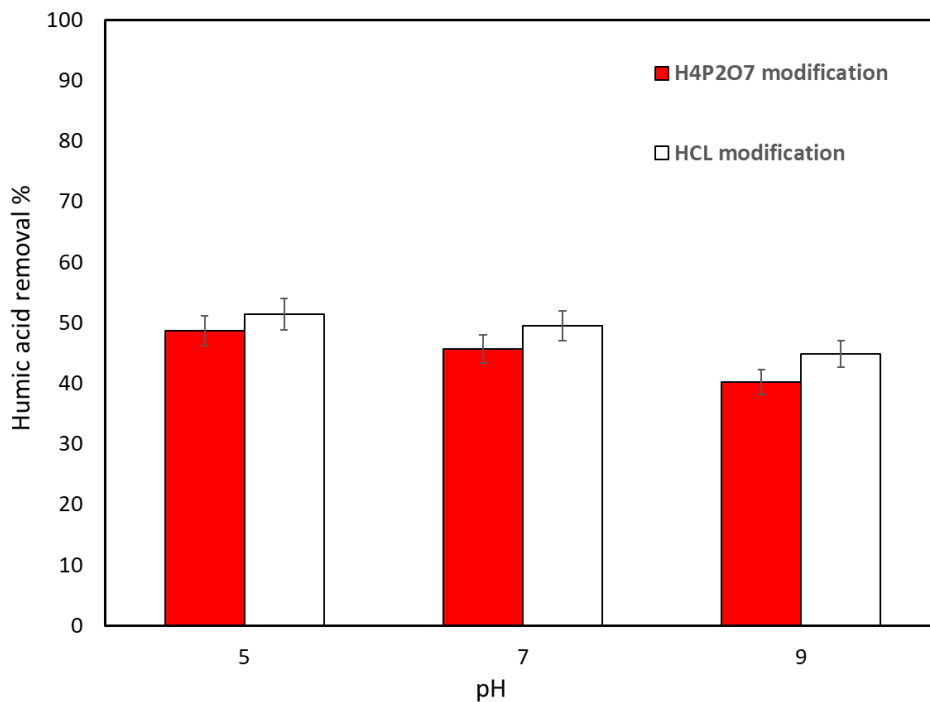
**Fig. 4.** HA removal efficiency with GBC with H_3PO_4 and HCL surface modifications

3.4. Effect of GBC on HA removal with alkaline pretreatment - KOH surface modification with comparison of all other pretreatment.

The efficiency of GBC with KOH surface modifications on HA removal in the pH range of 5,7 and 9 are shown in Figure 5. The operating parameters were a 1.5-hour contact period, an initial HA concentration of 10 mg/l, and a GBC dosage of 5 g/l. The findings demonstrate that HA removal effectiveness was 97.56 %, 82.61 %, and 55.16 % at pH 5,7 and 9 respectively where the greatest adsorption was shown, as pH dropped. Using alkaline pretreatment with KOH affects mainly on the removal of HA at the different pHs and the difference reaching around 50% than using acidic pretreatment. This phenomenon may be ascribed to the fact that the acidic activator typically interacts more readily with the amorphous cellulose present in the wood, resulting in the corrosion of the wood, collapse of its pores, and reduction of its specific surface area [36]. Furthermore, KOH has a significant capacity for hole expansion in the pretreatment phase[35, 36]. This confirms that the HA removal was mainly affected by pHs by using the alkaline pretreatment and this theory was confirmed by many researchers such as [39]. In comparison for all pretreatments for the removal of humic acid, as shown in figure 6, the alkaline pretreatment was the best choice for further studies.
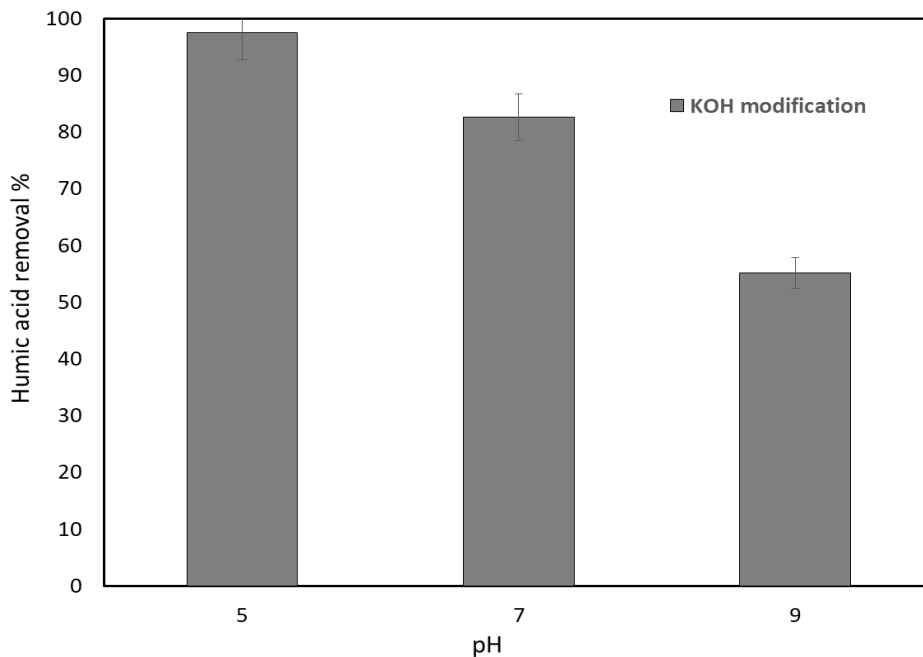
Fig. 5. HA removal efficiency with biochar with KOH surface modifications
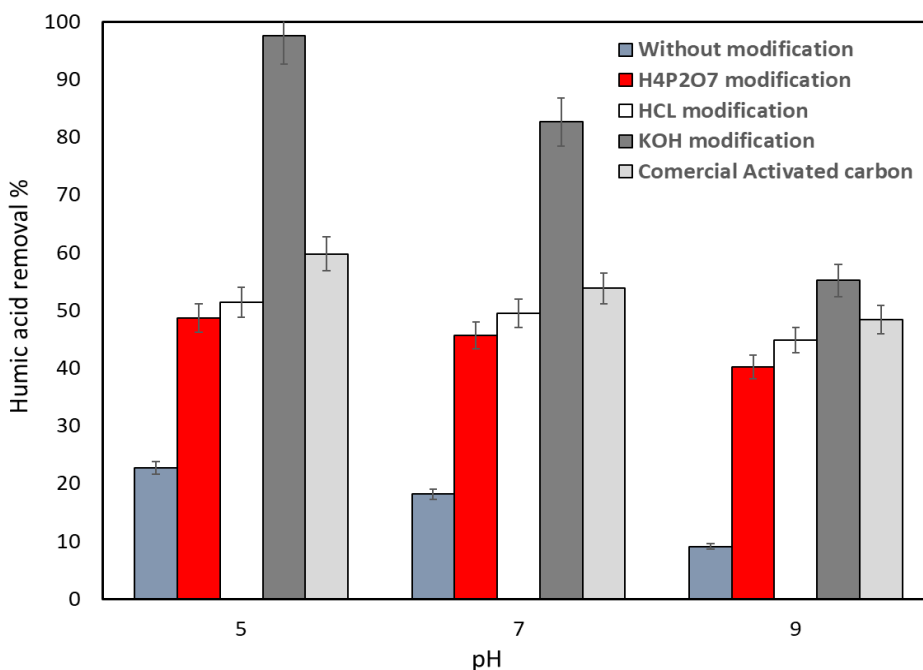
Fig. 6. HA removal efficiency using biochar with different surface modifications

3.6 Meeting the Sustainability Dimensions from the removal of NOM using biochar as an adsorbent

The results of this study maintain several benefits that could fulfill the sustainable development goals dimensions. For instance, the treatment of humic acid as a part of natural organic matter from the surface water before reaching the network that reaches the consumers. This approach has a positive correlation with SDG14 "Life Below Water" by protecting and conserving the human and aquatic species as well from any increase in the humic acid or any natural organic matter to be

included in the water source and become very harmful after years of consumption. Moreover, this adsorption treatment facility meets the aims of SDG3 "Good Health and Well-being" because removing these materials leads to a secure food chain and secure good health as well [30]. Also, the study confirms that adsorption by a novel modified biochar could be an innovative tool that could optimize the treatment of surface water facilities and reduce the operational costs, meeting SDG9 "Industry, Innovation, and Infrastructure". Protecting the water-related ecosystems and improving water quality by minimizing ASSW pollution comply with the targets of SDG 6 "Clean Water and Sanitation".

Conclusions

The biochar was prepared by pyrolysis using Arundo donax as a raw material for humic acid removal. The GBC without surface modification has been tested for HA removal. The removal efficiency was low so many surface modification methods have been used to increase the specific surface area and functional groups to achieve HA optimum removal efficiency. A significant improvement in HA removal efficiency was observed when surface modification with KOH was used. It was more effective compared to H_3PO_4 and HCL surface modification methods. The surface modification by H_3PO_4 was less effective in HA removal however, it achieved twice the removal efficiency in case no modification was made. Under the same conditions, GBC removes HA more effectively than CAC. The lower pH value was the optimum for HA adsorption.

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