

Original Research

Development of Low-Cost Activated Carbon towards an Eco-Efficient Removal of Organic Pollutants from Oily Wastewater

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Abstract

The current study seeks to investigate the feasibility use of date palm kernels for the development of activated carbon (AC) towards its application, which functions as an adsorbent to treat oil-contaminated groundwater. Biochar derived from date palm kernels (BPK), was prepared by direct pyrolysis of the raw precursor at 600°C for 90 minutes (in oxygen-limited condition). Activated carbon (ACPK) included similar pyrolysis conditions of biochar with subsequent impregnation in H₂SO₄ (as activating agent) at a ratio of acid: biochar (1:1), moderate temperature. The analytical approach was performed through the use of XRD, BET, and FTIR, techniques to evaluate the effect of carbonization and activation process in improving the adsorptive properties of starting materials. Carbonaceous adsorbents obtained were highly porous due to their elevated specific surface area of (333.4 m²/g for BPK and 741.5 m²/g for ACPK) and their amorphous structure. Indeed, the textural properties were significantly improved by the acidic treatment. Further, the adsorption behavior of produced materials was tested by performing batch adsorption tests in contaminated water samples using a ratio of 1:1 (g/L) for 24 hours. The efficiency of adsorbents was evaluated by COD (C₀ = 8568 mg/L), BOD₅ (C₀ = 200 mg/L) concentration, pH and hardness values before and after the treatment. Removal efficiency of COD for the BPK and ACPK samples reached 82.6% and 95.2% respectively, while for BOD₅ was the same (97.0%) for both adsorbents. Additionally, the treated water sample has the same excellent class suitable for irrigation applications according to the Wilcox diagram. In consequence,

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the present study suggests an effective, eco-friendly and economical adsorption process intending to mitigate environmental risk sustainably.

Keywords: environmental remediation, agro-waste, activated carbon, pollutant uptake, water quality, irrigation

Introduction

Toxic pollutant contents in aquatic environments become a thoughtful issue for human health and ecological systems. Several industrial activities worldwide discharge harmful wastewaters without any treatment. For instance in the case of Algeria, water quality adversely affected by petroleum industry growth. Processing operations in Skikda, Arzew, and Algiers oil refineries, constitute the major source of oily wastewater pollution besides to the losses in transport terminals during exportation of petrochemicals to Mediterranean destinations [1]. Several chemicals like sulfides, phenol, ammonia, and hydrocarbons may be found in released petroleum refinery effluents (PRE) at different concentrations. Meanwhile, effluent's composition differs depending on several factors including the type of processed crude, operational methods, and plant configuration [2]. The occurrence of these hazardous pollutants leads to a number of environmental-health and ecological issues in addition to socio-economic difficulties [3-6].

Henceforth, to evade the coming issues associated with water scarcity, the treatment of those industrial effluents until non-risk values are needed before their discharge into waterways. For this motive, various conventional technologies have been utilized for pollutants removal from the aquatic medium like coagulation [7], air flotation [8], chemical oxidation [9], biological treatment [10] and adsorption [11]. In the same vein, novel treatment approaches have been developed recently such as membrane technology [12] and microwave-assisted catalytic wet air oxidation [13]. Particularly, adsorption seems quite attractive due to its efficiency, lower costs and no secondary pollution [14]. The process by which ions, atoms or molecules of liquids, gases or dissolved solids are retained on a specific surface is known as adsorption, where the surface material is named as adsorbent while adsorbate is the substance that will be adsorbed. The selection of adsorbent based first on its porous structure which provides a larger surface area and on its ability to show rapid adsorption kinetics [15]. Activated carbon, Chitosan-based polyacrylamide and polypropylene were used as adsorbents for the treatment of oily wastewater [16]. Among bio-adsorbents, carbonaceous materials are considered as the most popular adsorbent and attracted more attention in the existing literature due to its attractive adsorption characteristics [17]. However, using unrenovable raw materials for activated carbon (AC) production such as coal carbon increases

its costs and restricts its use. Therefore, the reduction of the AC production costs is crucial to develop its use for wastewater treatment applications. In this regard, several agricultural by-products like wood [18], tomato stem [19], banana peel [20], olive stones [21], and carrot waste [22] have been employed as a low-cost precursor to developing green and efficient AC. In Algeria, a large amount of date palm kernels is generated annually without any valorization, which may serve as a good source of carbonaceous materials. Thus, developing the use of date seeds as locally available material for AC production could be considered as an optimal decision towards minimizing input costs and solving waste disposal issues.

This work investigates the development of biochar from date palm kernels (BPK) and activated carbon from date palm kernels (ACPK) and highlights their potential to treat contaminated groundwater by oil pollution. The BPK and ACPK samples were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) techniques. The adsorption tests were performed in batch manner. The adsorption efficiency was evaluated based on the measurements of the chemical and bio-chemical oxygen demand (COD and BOD₅ respectively). Various physico-chemical characteristics of treated water samples were also analyzed and compared to the irrigation standards obtained from the free software database. "Diagrammes version 6.61" developed by Laboratoire d'Hydrogéologie d'Avignon and available in <http://www.lha.univ-avignon.fr/LHA-Logiciels.htm>.

Materials and Methods

Material and Reagents

All reagents used in this work have reagent grade (99%) and purchased from Sigma-Aldrich. Other additives such as HCl (0.1 M) or NaOH (0.1 M) were used to adjust the pH of solutions. All solutions were prepared with deionized water and all chemicals were used without further purification. The groundwater samples used in this study are from Illizi region, Algeria (26°30'33.965"N, 8°28'23.778"E). This water has been contaminated with oil by extraction from local wells. The combination of extracted oil with groundwater produced many changes due to oil composition modifications including the low-molecular-weight fractions spontaneously evaporated, the soluble

components dissolved into contaminated water, the oil droplets combined with water, and photochemical oxidation and biodegradation happened to specific oil elements and not all of it [23].

Raw Date Kernel Precursor

Kernels of the "Deglet Noor" cultivar was selected as a cheap feedstock for the production of adsorbents. The starting material was cut into small pieces, washed with hot distilled water, dried at 75°C (for 24 hours) and then sieved to sizes between 0.08 and 0.25 mm. The biochar (BPK) was prepared through a direct pyrolysis of the obtained powder at 600°C (rate of 10°/min) for 90 minutes using a conventional furnace. On the other hand, activated carbon (ACPK) was made following the same methodology applied for biochar sample but after impregnation of powder in sulfuric acid 5N (for 4 hours at 50°C). After cooling at room temperature, the obtained biochar was soaked in HCl solution (0.1 M). After that, both BPK and ACPK samples were washed with deionized water until neutral pH of filtrate (i.e. pH 6.5-7.5). Finally, the obtained materials were dried at 75°C for 24 hours, ground and sieved to obtain a powder with 0.1-0.8 mm of particle size.

Characterization of Adsorbents

The morphological and chemical properties of the adsorbent samples were studied by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) techniques. The functional groups of the adsorbents surface were identified using Perkin Elmer Spectrometer (Spectrum Two) to determine the chemical structure of produced AC. FTIR spectra were recorded in wave number range of 400-4000 cm^{-1} . Phase state of BPK and ACPK samples were determined through XRD distribution by use of "Bruker D-8 advance diffractometer" with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 30 mA and 40 kV. The N_2 adsorption-desorption isotherm determined apparent surface area and particle size of carbonaceous materials (BPK and ACPK) at 373K for 10 hours (Micromeritics ASAP 2020).

Adsorption Experiments

Adsorption tests were performed by using 250 mL glass Erlenmeyer flask (Pyrex). In each Erlenmeyer, 100 mL of groundwater sample was mixed with 100 mg of adsorbent (BPK - ACPK). The mixture was stirred in a Horizontal mechanical shaker (200 rpm) for 24 hours and at room temperature ($295 \pm 1 \text{ K}$). After that, solutions were filtered by Buchner filtration flask using membrane filter (pore size of 45 μm). The result was obtained from the average of three duplicated assays for each adsorption experiment.

Analysis of Groundwater Samples

Groundwater samples were characterized before and after adsorption treatment to examine the efficiency of BPK and ACPK adsorbents in removing water pollutants. The evaluation of water organic pollution was based on the measurement of biochemical oxygen demand for 5 days (BOD_5) and chemical oxygen demand (COD) of water samples. The BOD_5 and COD measurements were performed on BOD OxiTop Thermostat Box (WTW) and COD3 plus Colorimeter (LaMotte) respectively. The efficiency of pollutant removal (% Removal) from water samples was calculated as shown in Eq. 1.

$$\% \text{Removal} = \frac{C_I - C_F}{C_I} \times 100 \quad (1)$$

...where C_I and C_F (mg/L) are the initial and the final pollutant concentration, respectively.

The groundwater suitability for irrigation was determined according to the Wilcox Diagram which based on the electrical conductivity value and the sodium adsorption-ratio (%Na). This parameter is calculated from Eq. 2 (cations concentrations are expressed in meq/L):

$$\% \text{Na} = \frac{\text{Na}^+ + \text{K}^+}{\text{Ca}^{2+} + \text{Mg}^{2+} + \text{Na}^+ + \text{K}^+} \times 100 \quad (2)$$

The Wilcox diagram suggests that the quality of irrigation water can be excellent, good, permissible, doubtful, or unsuitable. This diagram shows that the water quality decreases with increasing the %Na and electrical conductivity values [24, 25].

The interest ions studied in the water samples were determined by three different techniques: titration technique for alkalinity, hardness, and chloride; sodium and potassium was determined by a flame photometer (PFP-7 Jenway); and a UV-vis spectrometer (LAMBDA 25 Perkin Elmer) was used for nitrate and sulfate determination.

In addition, pH and conductivity values were measured at room temperature ($295 \pm 1 \text{ K}$) using pH meter (CyberScan pH 510) and conductivity meter (CON 510 conductivity/TDS) respectively.

Hydrochemical Analysis

Aiming to identify the quality aspects of the water samples the Piper diagram was used. This diagram is based on the premise that cations and anions in water are generally in chemical equilibrium. Water samples shown on the Piper diagram can be grouped in hydrochemical facies. Additionally, the hydrochemical data have been processed using the method of classification of Stabler. Stabler classification compares

reaction quantities of cations and anions expressed as percentages (%) and separately classifies the anions and cations in descending order to determine the chemical facies. Berkaloff Schöeller diagram was also used for water samples comparison with similar facies but different dilutions. All the hydrochemical diagrams were developed using “Diagrammes” software version 6.61.

Results and Discussions

Characterization of Adsorbents

FTIR spectra give information about the surface properties of adsorbent samples. FTIR spectra of BPK and ACPK adsorbents were recorded in Fig. 1. The wide band observed in the range of 3150-3650 cm^{-1} is due to the hydroxyl groups (-OH) stretching vibrations in the carbonaceous materials structure or adsorbed water. In this region, the -OH band in BPK sample is stronger than the ACPK one, which is attributed to the replacement of water molecules in the porous structure by the activating agent after H_2SO_4 activation of Biochar. The weak peak around at 1500-1750 cm^{-1} is related to stretching of C=C bands in the aromatic carbon structure. The presence of C-H of - CH_3 and - CH_2 of aromatic rings is confirmed by the peaks between 1400 and 1470 cm^{-1} for BPK and ACPK samples. The broad band observed in the region of 1000-1250 cm^{-1} represent the characteristic vibrations of -OH groups [26]. Moreover, the peak at 1150 cm^{-1} corresponds to the C-O stretching vibrations [27].

The BET analysis shows that both of biochar and activated carbon exhibit a well-developed porous structure. The BET surface area reached value of 333.4 (for BPK) to 741.5 m^2/g (for ACPK). This result confirms that the chemical activation improve significantly the textural property of biochar. During activation or carbonization at high temperature, the polymeric structures of the biomass decompose and

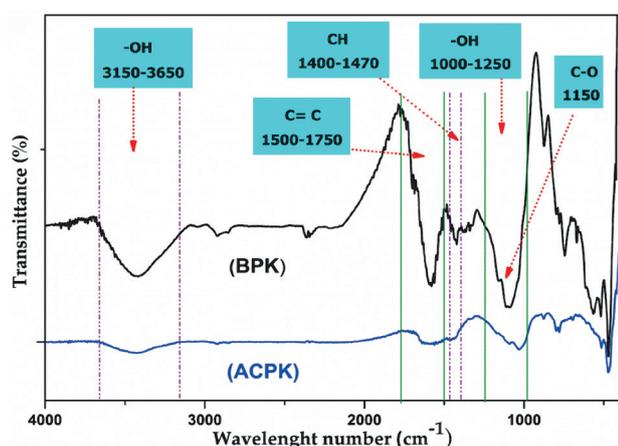


Fig. 1. FTIR spectra of BPK and ACPK samples.

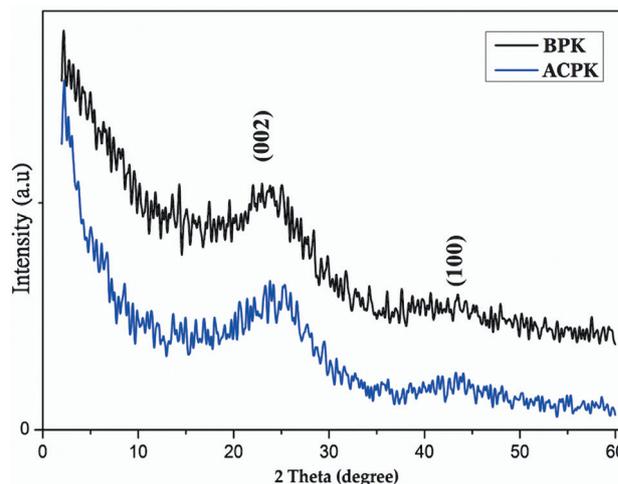


Fig. 2. X-ray diffraction pattern of BPK and ACPK samples.

liberate most of the non-carbon elements (H_2 , O_2 and N_2), leaving behind a rigid carbon skeleton in the form of aromatic sheets and strips. It was also found that the average particle size was 179.5 nm (for BPK) and 17.6 nm (for ACPK). X-ray powder diffraction patterns of the biochar (BPK) and activated carbon (ACPK) samples are provided in Fig. 2. The non-crystallinity of carbon materials structure is confirmed by the absence of sharp reflections in the two patterns. The two broad reflections at near $2\theta = 26^\circ$ and 42° are assigned to the (002) and (100) planes of graphite crystalline, respectively [28, 29]. The d -spacing value of the (002) plane was found to be 0.391 nm (for PBK) and 0.357 nm (for ACBK), which is very close to values reported in literature [30, 31].

Characterization of Groundwater

Fig. 3 shows the efficiency of adsorbents in removing COD and BOD_5 from contaminated groundwater and pH of treated water. The COD removal efficiency of BPK and ACPK samples was 82.6% and 95.2% (initial COD = 8568 mg/L). This result confirms that the carbonaceous material exhibits a high adsorption capacity of COD after the chemical activation, which can be related to the development of their textural properties (surface area and total pore volume). The BOD_5 removal efficiency was the same for both adsorbents (97.0 %) at initial BOD_5 concentration of 200 mg/L and stirring time of 24h (200 rpm). For the two adsorbents (BPK and ACPK), the overall adsorption efficiency is excellent for the BOD_5 removal. This is due to the adsorption of a large fraction of biodegradable organic matter by the employed adsorbents. From results, the ACPK has the high organic adsorption capacity for COD parameter (COD: 95.2%), but for the BOD_5 both adsorbents have the same efficiency (97.0%).

Furthermore, the pH value of the raw groundwater sample was 5.15, which indicates the acidic nature of this water, its tendency to corrosion and it can cause other

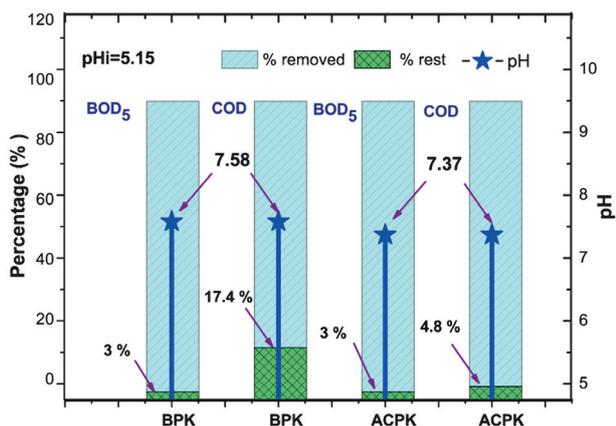


Fig. 3. COD, BOD₅ and pH results of the treated groundwater samples (pH_i = 5.15, [BOD₅]_i = 200 mg/L, [COD]_i = 8568 mg/L).

environmental problems. In addition, the adsorption treatment of contaminated water presents the advantage of increasing the pH value towards neutrality, and the pH of treated water oscillates between 7.37 and 7.58. Values of the BOD₅/COD ratio for the raw and treated water samples are less than 0.3 (Table 1), which confirm the non-biodegradable nature of the oil contamination, it is therefore compulsory to treat this groundwater with a physicochemical technique such as adsorption. The adsorption decreases the BOD₅/COD ratio due to the efficiency of biologically oxidized organic pollution removal more than chemically oxidized organic pollution for both BPK and ACPK. This treatment shows also a decrease in the calcium hardness, such that after adsorption test, those adsorbents have a weak ability to soften the hardness of raw water. This treatment also shows decreased calcium hardness; nevertheless, those adsorbents poorly soften the hardness of raw water.

Assessment of Groundwater Quality

Hydrochemistry

In this study, Piper, STABLER and Schöeller Berkaloff diagrams are constructed to evaluate the variation in hydrochemical facies of water samples (Figs 4-6). The tendency of the cations for the raw and ACPK treated water samples is in order to: Na⁺ > Mg²⁺ > Ca²⁺ > K⁺, and for the BPK treated water is in order to: Na⁺ > Mg²⁺ > K⁺ > Ca²⁺. As shown in Fig. 4, sodium is the dominant cation on all water samples. The tendency

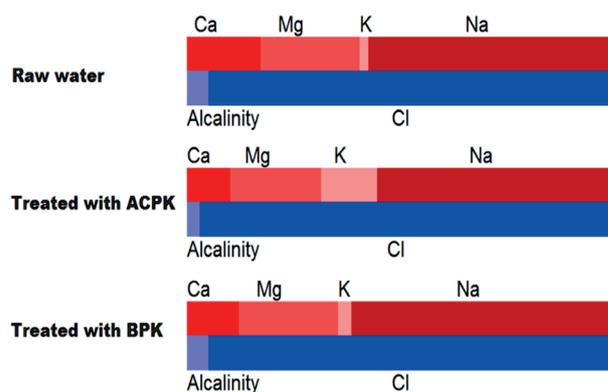


Fig. 4. STABLER diagram illustrating major ionic dominance in all water samples.

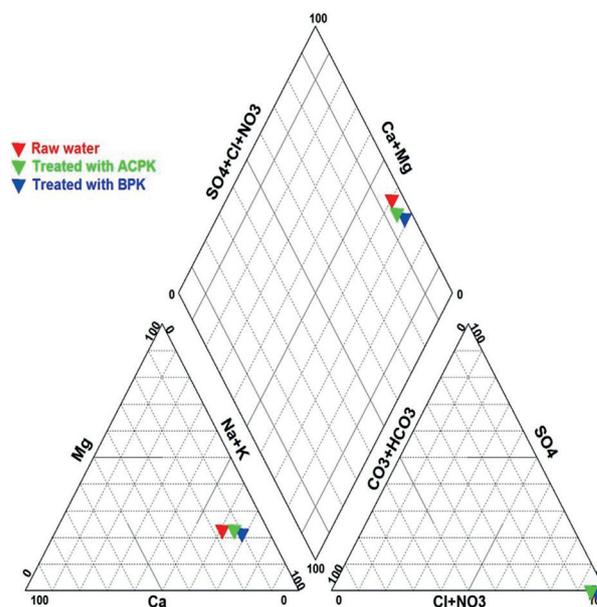


Fig. 5. Piper diagram of all water samples.

of the anions is in order to: Cl⁻ > alkalinity and the dominant anion is chloride. The hydrochemical facies/ water types are the same (sodium chloride type) and influence only by geochemistry of the groundwater (Figs 4 and 5). The Piper diagram also shows that sodium (60%) and chloride (90%) are the most dominant ions and without the presence of sulfate anion on all water samples. The Schöeller Berkaloff diagram (Fig. 6) highlights very similar trends between the

Table 1. Parameters of raw and treated water samples.

Water sample	BOD ₅ (mg/L)	COD (mg/L)	BOD ₅ /COD	pH	Hardness (ppm)	
					Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)
Raw water	200	8568	0.023	5.15	50	70
Treated with BPK	6	1491	0.004	7.58	32	68
Treated with ACPK	6	411	0.015	7.37	38	72

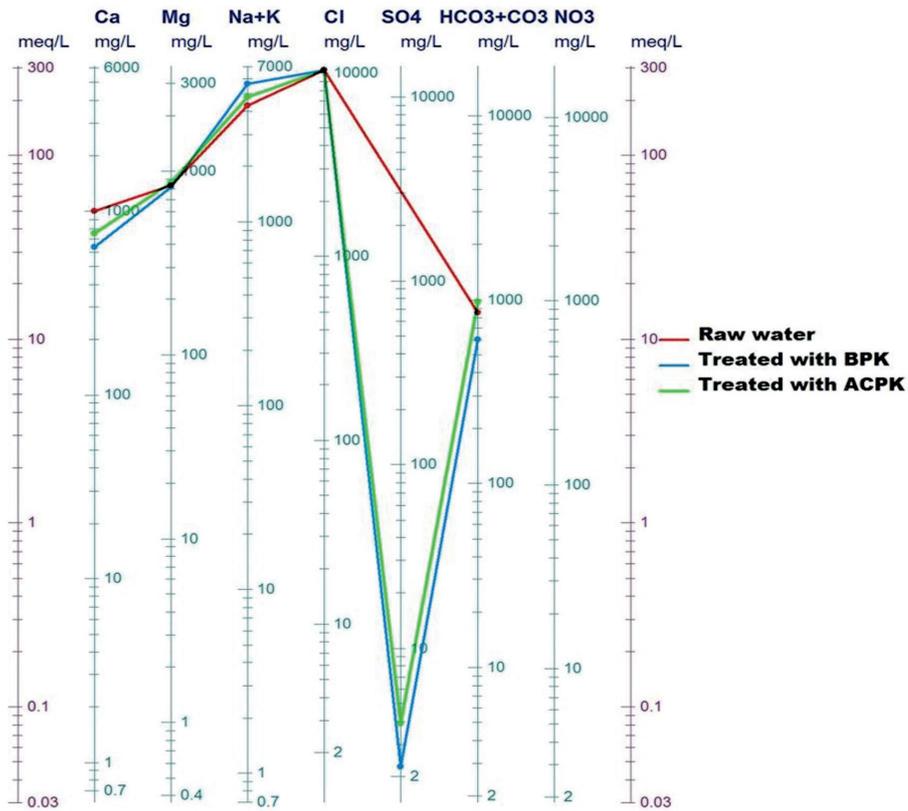


Fig. 6. Schöeller Berkloff diagram of all water samples.

studied groundwater samples, in particular with deferent sulfate concentration on the raw water sample,

confirming the results obtained by using Piper and STABLER diagrams.

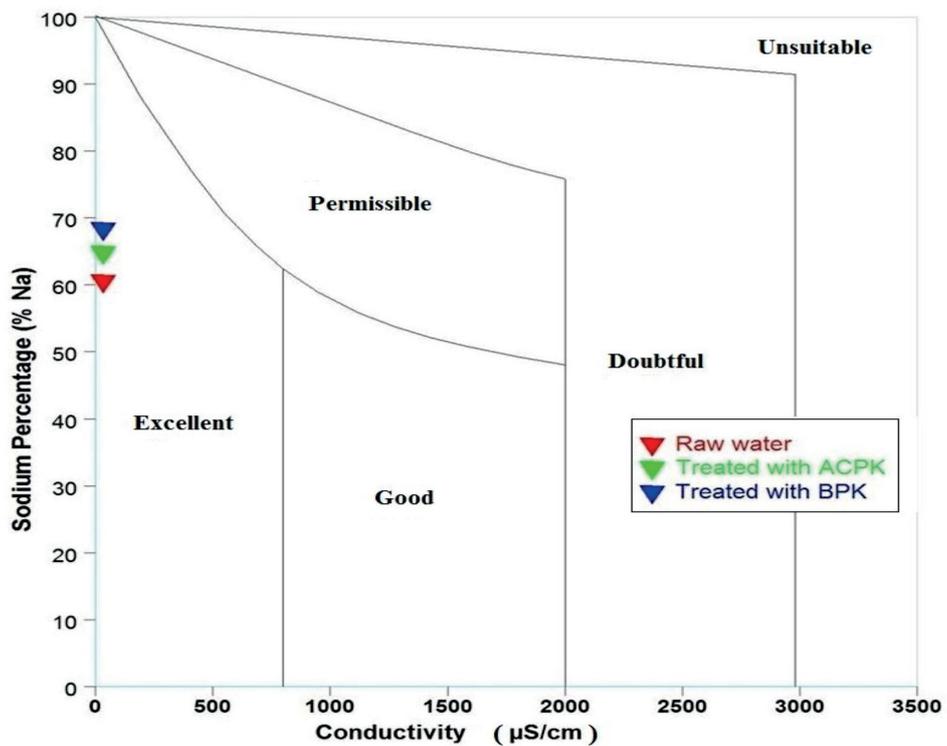


Fig. 7. Wilcox diagram showing the suitability of groundwater for irrigation.

Groundwater Suitability for Irrigation

Fig. 7 shows that all the water samples have adjacent electrical conductivity values (≈ 35 microsimens/cm). The sodium percentage values increase from 60% for the contaminated water to 64% and 68% for the treated water samples with ACPK and BPK respectively, that is related to the increase of sodium and potassium concentrations presented on Schöeller Berkloff diagram. All samples of water fall in the fresh water zone "Excellent" categories for irrigation purposes (Fig. 7). It can be concluded that the used adsorbents can eliminate organic pollution from the studied contaminated groundwater without changing its suitability for irrigation uses.

Conclusions

Biochar (BPK) and activated carbon (ACPK) were developed from palm kernel and used as low-priced materials to treat water samples contaminated with oil pollution. Several analysis techniques characterized the prepared materials, and their absorption efficiency was evaluated by measuring the COD and BOD₅ concentrations before and after treatment. Results showed the ability of chemical activation in improving adsorptive characteristics of prepared biochar.

The COD removal for the BPK and ACPK samples reached 82.6% and 95.2%, respectively, while the BOD₅ removal efficiency was the same (97.0 %) for both adsorbents (for initial BOD₅ = 200 mg/L). Further, prepared adsorbents showed a better ability to remove biologically oxidized organic pollution (BOD₅) compared to chemically oxidized organic pollution (COD) and in optimizing neutral values of pH. Piper, STABLER, and Schöeller Berkloff diagrams indicate that the adsorption manner does not change the hydrochemical type of the oil-contaminated water: sodium chloride type with a reduced presence of the other ions, Wilcox diagram showed that all the studied samples fall in the excellent category of suitability for irrigation with a weak change in sodium percentage.

Overall, the current study reveals that date kernel waste qualified as a suitable feed material for AC generation. Upon chemical treatment, adsorption capability improved, allowing the significant reduction of COD and BOD₅ pollutant levels, accordingly better water quality favorable for irrigation use.

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Conflict of Interest

The authors declare no conflict of interest.

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