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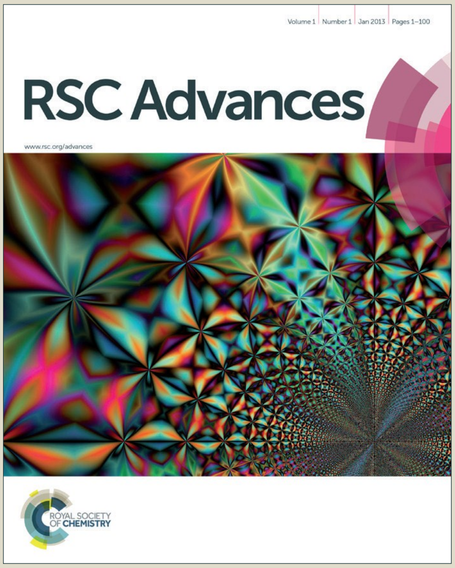

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A green adsorbent for the removal of BTEX from aqueous media

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Abstract

This study reports on the application of the covalently modified ostrich bone wastes (OBW) with citric acid as bioadsorbent for the uptake of various volatile organic compounds such as benzene, toluene, ethylbenzene, and *p*-xylene. The influence of experimental parameters on removal behavior was assessed by changing the contact time, amount of adsorbent, initial pH, temperature, chemical modification process, and initial pollutants concentration. The order of the adsorbates removal on OBW-NaOH-CA was obtained as follow: *p*-xylene > ethylbenzene > toluene > benzene. The adsorption kinetics of the organic pollutions has been studied in terms of pseudo-first- and -second-order kinetics, and the Freundlich and Langmuir isotherm models have also been applied to the equilibrium adsorption data. The results showed that the adsorption process was spontaneous and endothermic in nature and followed pseudo-second-order kinetic model. The present of free carboxyl groups of citric acid raise the density of electron donating group (carboxylic oxygen as an electron-donor) on the modified ostrich bone, that is, increasing its favorable interaction with the organic pollutions due to their weakly positively charged at different pHs. The results showed that the immobilized CA on OBW shifted the surface charge towards negative value, which promoted the adsorption of BTEX. Furthermore, the prepared bioadsorbent could also be utilized to remove the organic pollutions from the real water (*Persian Gulf* water).

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Introduction

Contaminated water with toxic organic compound has been a crucial cause of treat. The wastewater from industrial, transportation and domestic is in charge for source of several harms to the environment and certainly affecting the ecosystem and human health. The volatile organic compounds (VOCs); benzene, toluene, ethylbenzene, and p-xylene are mentioned as priority contaminants because they are detrimental to organisms at trace concentrations and have been categorized as flammable, carcinogenic as well as hazardous pollutants due to their potential to harm human health. Hence, due to their toxicity, the Agency for Toxic Substances and Disease Registry, of the U.S. Department of Health and Human Services, has designated these compounds as priority contaminants [1]. Several techniques, such as condensation, thermal oxidation, catalytic oxidation absorption, and adsorption have been developed to remove volatile organic compounds (VOCs) [2]. Among these methods, the adsorption process has been considered as low-cost processes for the remediation of organic pollutants in wastewater. A number of material such as activated carbon, modified clays, polymeric resins, waste materials, and zeolites have been described as adsorbents [3,4].

Recently, attention has been focused on the application of pristine biomaterial. However, modified bio-originated waste materials have also been taken great attention as sorbents due to their low-cost and easy regeneration potential. Generally, removal capacity of pristine biomaterial is low. Covalent modification can greatly increase the sorption capacity of biomaterials. Indeed, the advantages of utilizing waste-based biomaterial would not only be a significant depletion in remediation technology operational costs, but also the advantages of valorization of these wastes should be taken into account [5].

The present work explains the possibility of modified ostrich bone waste (OBW) by citric acid (CA) as a low-cost biocomposite for VOCs removal from industrial wastewater. OBW was chosen because Iran is the world's third largest breeder and producer of ostrich meat, after South Africa and China [6] Food industry and animal slaughtering supply meat and bone meal as by-products which are obtained by cleaning of fat from animal carcasses throughout the procedures of cooking, grinding and crushing. By-products included nearly 60% to 70% of the slaughtered carcass by weight, of which nearly 40% contains edible and 20% inedible products [7]. In fact, no study has been published for examining the adsorption capacity of materials with biological origin, such as OBW treated and covalently modified with CA to remove VOCs from aqueous solution.

CA is a tricarboxylic acid, with $pK_{a1} = 3.13$, $pK_{a2} = 4.76$, $pK_{a3} = 6.40$, which can form several species (H_3Cit, H_2Cit^-, $HCit^{2-}$, and Cit^{3-}) according to solution pH [8]. CA can be utilized as an environmentally friendly cleaning agent. Also, CA exists in human plasma (0.1 mM) which can result in its interaction with exotic species get into the body [9]. In fact, CA will be dehydrated by heating and give a reactive anhydride that could react with the reactive sites (amine and hydroxyl groups) on the surface of OBW to attach covalently [10]. The present free carboxyl groups of citric acid raise the density of electron donating group (the carboxylic oxygen as the electron-donor) on the modified ostrich bone that increasing its favorable interaction with the organic pollutions. Other mechanism could be included such as hydrogen bonds (due to the functional groups of CA), and electrostatic interactions (because of the charged modified surface with CA) [11]. It is believed that the π–π electron-donor–acceptor interaction at the surface of adsorbent is responsible for adsorption of the VOCs; due to the weakly positively charged of BTEX molecules (benzene ring) at the pH range 3–12 [12-14]. Based on the above phenomena, we have covalently immobilized CA on the modified OBW in order to remove the VOCs from aqueous. However, the carboxylic groups as the electron-donor could have favorable interaction with the aromatic ring of the VOCs as the electron-acceptor.

Here is reported a full account of the synthesis, characterization, and adsorption activity of OBW functionalized with CA groups towards benzene, toluene, ethylbenzene and p-xylene. This study highlights the role of reactive sites of the immobilized CA (carboxylic groups) as the potent adsorbent of the VOCs from the real wastewater.

2. Experimental section

2.1. Materials

All reagents (A.R.) were purchased from Merck or Aldrich and were used without further purification, except for solvents, which were treated according to standard methods.

2.2. Modification processes of OBW

Ostrich bone waste (OBW; leg bone and breastbone) was obtained from a local store and was cut and then its fat and flash were removed cleanly. After separating the fat and their flesh, all remaining ostrich bone waste was put in the oven for 24 hours in 70 ^{o}C, and after drying they were ground and were passed through different sieve size. The fraction of particle between 250 and 400 µm (geometric mean size: 305 µm) was selected. Fresh OBW was washed thoroughly with hot distilled water and was dried at 65 ^{o}C. The sorbent thus obtained was designated pristine ostrich bone waste (OBW). Preliminary studies using OBW treated with base was carried out in order to optimize the sorption of organic compounds. The OBW was treated with 0.1 M NaOH solution at reflex for 2 h. A typical experimental procedure was as follows: 30 g of OBW were dispensed in 0.5 L of distilled water. Then a certain amount of 0.1 M NaOH was added and the suspension was subjected to mechanical stirring for 2 h on heater. The final material was separated by centrifugation and washes with distilled water. Excess of NaOH was removed with distilled water and the material was dried at 50 ^{o}C. NaOH treated OBW was designated as OBW-NaOH.

The modified pristine bone with CA was synthesized by reacting OBW-NaOH with solution containing CA. In a typical experimental procedure which is as follows: 25 g of OBW-NaOH is dispersed in 0.5 L of distilled water. Then a certain amount of CA (loading levels between 0 and 30 wt.%) is added and the suspension is subjected to mechanical stirring for 1 h at 70ºC. The modified bone sample (OBW-NaOH-CA) is separated by centrifugation and washed with 50% (v/v) of water and ethanol mixture. The resulted sample is dried at 60 ºC overnight, and mechanically ground with a mortar and then passes through 100-mesh sieve.

2.3. Characterization techniques

The point of zero charge for the adsorbents was determined from the addition method [15]. Nitrogen (99.999%) adsorption experiments were performed at -196 ºC using a volumetric apparatus (Quantachrome NOVA automated gas sorption analyzer). All samples were degassed under vaccum at 120ºC for 16h before the adsorption experiments. The specific surface areas of the adsorbents were calculated using the BET method and the pore size was calculated using the Barrett-Joyner-Halenda (BJH) method. FTIR spectra were recorded using a Jasco FT/IR-680 plus spectrophotometer as KBr pellets. XRD studies were carried out using a Philips X'PERT MPD diffractometer. SEM-EDX analyses were accomplished on a Seron microscope, model AIS2100.

Hydrophobicity of the bone samples at various coverages were studied by a liquid–liquid partition (water/hexane) and determined the mass distribution in the two phases [16]. Therefore, a sample of 1 g was placed in a separation funnel with 100 ml of water under sufficient stirring to keep the suspension stable. Then, 100 ml of hexane was added and stirred for another 3 min. The obtained mixture was then let to stand for 10 min, the time required for separation of the phases. The quantity of bone sample transferred to the organic phase was measured by filtration followed by drying and weighing. The results are expressed in terms of the mass ratio of the bone sample transferred to the organic phase or remained at the interface. This value is an estimation of the degree of hydrophobicity of the bone samples.

2.4. Adsorption measurements

The organic chemicals were freshly prepared in a solution mixture of deionized water/ethanol (80:20). Adsorption experiments were carried out in batch conditions as follows: 0.75 g of modified bone sample was shaken with 75 ml of the organic pollutants, at a concentration of between 0.5 and 300 mg/L, at a controlled temperature of 25 ºC. In all experiments, the temperature was controlled to within ± 0.5 °C by circulating thermostated water through Erlenmeyer flasks which were closed with parafilm to avoid evaporation. Blank experiments without the prepared biomaterials were performed to prove that the reduction in the concentration of BTEX was in fact resulting from the uptake of bioadsorbents, rather than the adsorption on the Erlenmeyer flasks wall or through evaporation and volatilization. Each experiment including blanks was performed three times, and displayed a relative standard deviation lower than <2 %. The required time to reach the equilibrium conditions was determined by preliminary kinetic measurements. No significant variation in sorption capacity was observed after 24 h of contact. After centrifugation at 3000 r.p.m. for 7 min, the liquid phase was rapidly separated and the solute concentration determined using a UV–vis spectrophotometer at the following wavelengths: benzene, 252 nm; toluene, 260 nm, ethylbenzene, 262 nm; *p*-xylene and 267 nm. The calibration curves for BTEX were constructed by diluting the solution to various known concentrations and recording their absorbance [4].

The amount adsorbed was calculated as:

$$q_e = V.(C_0 - C_e)/ m \tag{1}$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations (mg/L) of adsorbates; V is the volume of the solution (L); and m is the amount of adsorbent (g). This equation assumes that the change in volume of the bulk liquid phase is negligible as the solute concentration is small and the volume occupied by the adsorbent is also small. A similar procedure was adopted for the CA adsorption experiments on the OBW-NaOH [17].

3. Results and discussion

3.1. Characterization of the prepared biomaterials

Preliminary experiments showed that the pristine ostrich bone has the low capacity to adsorb BTEX from the wastewater. Pristine ostrich bone contains more than 80% organic compounds which can block the inorganic phase as well as suitable active sites of the bone. Therefore, in this study various processes of pretreatment are designed to ostrich bone with the aim of enhancing the BTEX adsorption capacity by opening up the physical structure and framework to give more active sites and/or by obtaining suitable chemical modification of the available functional groups.

Alkali modification with (0.1 M NaOH) will have the stronger effect of removing the fat tissues and creating more active sites and either converting of carboxylic and sulfonic groups into their Na salts, which further accelerate immobilization of CA as well as BTEX adsorption from aqueous solution. CA was believed to clean some soluble organic compounds from the pristine bone without suffering the nature and amount of active sites which already present in the pristine bone. Therefore, CA opening up the pores and framework of the pristine bone as well as increasing the number of available binding sites such as carboxylic groups (as consequence of the binding of some carboxylic groups to free alcoholic groups in the pristine bone).

The structures of the bone samples were confirmed by Scanning electron microscopy (SEM), BET (N_2 adsorption–desorption technique), TG, FT-IR, EDX, zeta potential, and XRD. SEM has been a primary tool for studying the changes of surface morphology, distribution and fundamental physical properties of the adsorbent before and after the chemical modification.

3.1.1. Scanning Electron Microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX)

Fig. 1 shows the morphology of pristine and modified ostrich bone. It is clear that ostrich bone has an assemblage of fine particles of irregular shape and size with plenty of small ravines (Fig. 1A). On the other hands, Fig. 1B showed that modification of OBW by NaOH and CA have changed dramatically the surface morphology of OBW-NaOH-CA to a more irregular and porous structure with plate like shape, that is, increasing the surface area and pore volume which all could be due to the removing of organic compounds and chemically immobilized of CA and increasing the inorganic phase.

The chemical composition of the pristine and modified ostrich bone after base extraction (0.1 M NaOH) and acid oxidation (CA) were determined by EDX. The ostrich bone contains relevant amounts of animal nutrients like C, Ca, P, K, and Mg (Fig. 1C). In addition, the bone contains a number of elements that are vital to animal in small doses, i.e., micronutrients, but also generally contain small amounts of undesirable heavy metals. EDX analysis of ostrich bone from an average of scanned points showed the strong C signal originates from the fat tissues and organic compounds adhesive the framework of pristine bone. NaOH and CA treatment removed fat tissues as a change in the color of the extraction liquid can also be visualized (the extraction liquid is dirty brown) during the modification reactions (the carbon content of pristine bone after chemical modification decreased from 83 to < 23 wt %). Also, the base treatment may induce negatively charged by dissociation and ionization of the functional groups (i.e., -O-H converts to $-O^{-}Na^{+}$), which increasing the active sites of the modified bone. In the CA treatment process, CA was first dehydrated to form an anhydride which then reacted with the hydroxyl groups of the ostrich bone to add carboxylic sites [10] (Scheme 1). In fact, the immobilized CA groups readily react with wastewater contaminations BTEX to give the heterogeneous organic compounds.

3.1.2. Specific surface area (BET)

The textural properties of the samples, evaluated from the low temperature nitrogen adsorption revealed a more than fivefold increase in the specific surface area (SBET) and either a one and half fold increase in the average pore size of OBW-NaOH-CA to 17.73 m^2/g and 67.43 Å, respectively, than that the pristine one, which again demonstrates the removing of organic compounds from the pores of the ostrich bone after chemical modification (Table 1). However, the greater specific surface area and average pore size of OBW-NaOH-CA give an increase in the approachability of active sites of the adsorbent in contact with contaminated water, which lead to a better efficiency of the modified bone in removing of BTEX.

3.1.3. Fourier transform infrared spectroscopy (FTIR)

Inspection of infrared wave numbers (cm^{-1}) of significant valence vibrations of bone powder before modification and after modification with NaOH and CA showed striking changes promising with chemical modification, which is collected in Fig. 2. The bands at 1625-1665 cm^{-1} are related to organic tissue and water, while the $–CO_3^{-2}$ band intensities of unmodified bone appear at 1413 and 872 cm^{-1}. However, the bone shows the characteristic absorption bands of symmetric and asymmetric stretching vibration of the CH_2 and CH_3 at around 2922 cm^{-1}, 2852 cm^{-1} and 1470-1455 cm^{-1}, while the presence of a definite band at 1744 cm^{-1} is due to carbonyl groups (–C=O). The spectrum in the C-H stretching region showed absorption maxima at 3065 cm^{-1}, which is typical of the C-H stretching vibration of the aromatic ring.

As can be seen from the Fig. 2A, the characteristic vibration bands of O–P–O bonds of calcium phosphate appeared in all the samples as follow: 1165cm^{-1} (HPO_4^{-2} group, P–O–H in-plane and out-of-plane deformation modes), 1028 and 1100 cm^{-1} (v_3, P–O asymmetric stretching vibrations), –960 cm^{-1} ($v_1$sym, P–O stretch), -603 cm^{-1} (v_4, P–O stretch), -564 cm^{-1} (v_4, P–O stretch and P–O bending) [18]. FT-IR also bestows an indication of the inorganic phase of the bone (mineral crystallinity of hydroxyapatite). In fact, two bands in the regions 1028-1100 cm^{-1} attribute to hydroxyapatite while amorphous calcium phosphate appears a broad single band. However, the characteristic vibration bands of hydroxyapatite are hardly obvious in unmodified bone which could be due to the high content of organic phase (collagen, fat and organic tissue) which disguises the features of the mineral phase and decreasing the crystallinity of hydroxyapatite. Furthermore, infrared wave numbers of bone powder comprise of some characteristic absorption bands related mainly to the peptide bonds (–CONH–) which known as amide I, amide II, and amide III. The weak intensity of the vibration bands in the range of 1700–1600 cm^{-1}, attribute to C=O stretching vibrations of the amide I and are assigned as a useful indicator of different types of protein secondary structure [18]. In fact, the a-helical and the 1-sheet structure of the protein gave a maximum near 1655 cm^{-1} and 1630 cm^{-1} respectively, where the peaks of amide I were appeared at 1641 and 1646 cm^{-1}. The amide II which appears in 1540–1520 cm^{-1} range is assigned to N–H and C–H bending and stretching vibration, respectively. The amide III band which falls in the range of 1220–1300 cm^{-1}, is attributed to the phase combination of C–N stretching, N–H in plane bending and some contribution from C–C stretching and C=O bending vibrations. Natural proteins and peptides contain a disulphide bond (–S–S–), which have stretching vibrations near 510, 525 and 540 cm^{-1} [19]. Therefore, the main band at 507 cm^{-1} and the ones at 521 and 530 cm^{-1} with lower intensities were attributed to the disulphide bond of pristine bone (Fig. 2A).

The band intensities of 2922, 2852, 1744, 1625-1665, 1470-1455 related to the organic tissue decreased and the main S–S bond at 507 cm$^{−1}$ disappearance (an extra band at 534 cm^{-1}, in the IR spectrum of OBW-NaOH, assigned to *v* (C–S$_{\text{mercapto}}$) appeared) with modification of bone with alkaline hydrolysis (0.1 M NaOH). The broad band from 3400 to 2450 cm$^{−1}$for NaOH-bone attributes to stretching modes of hydrogen bonded of adsorbed H_2O molecules which demonstrates increasing hydrophobicity of modified bone with NaOH rather unmodified one (the molecules of H_2O are more adsorbed over modified bone than to the unmodified one). Indeed, treatment of OBW with NaOH broadens the peaks, especially those near 1566, 1462 and 1385 cm^{-1}. This demonstrates that NaOH enhances the negative charge of the active sites through deprotonation of –C–O–H bond, which result in the increased polarization of the –C–O–H bonds and leading to rapid replacing of H^+ with sodium cation (–C–O$^−$ Na$^+$), however, alkaline hydrolysis treatment increases the liquid-solid interface available for interaction between active sites of bone and CA with BTEX. The modification of the bone powder with NaOH and CA were an efficient procedure in reducing the amount of organic phase and destroys the organics that cover the framework of bone, increasing inorganic phase and consequently raising the accessible amount of the active sites of the bone (the organic content seems to be lower in modified bone as compared to pristine bone). In fact, the treatment of OBW by base and CA increased the hydroxyapatite (HAP) crystallite, which was in agreement with some decreasing in the XRD peak broadening of OBW-NaOH-CA (will be discussed later).

To prove the proposed mechanism in Scheme 1, the immobilization of CA on OBW-NaOH was studied by FTIR (Figs. 2B and 2C). In the equilibrated sample with CA extra strong characteristic stretching vibration bands at 1642, 1617, 1566, 1538, 1436, 1385, 1313, 1303, 1275, 1265, 1184, 1148, 1076, 926, 916, 887, 836, 743, 665 and 536 cm^{-1} were observed showing the presence of CA attached to the samples (Fig. 2C) [20,21]. The FT-IR spectra of alkaline hydrolysis treatment of unmodified bone and CA modification show the broad band at 2500–3500 cm^{-1} confirms the existence of carboxylic O-H groups (or removing organic phase and increase the hydrophilicity); hydroxyl (-OH) deformation vibration of carboxylic groups at 1462 cm^{-1}; asymmetric and symmetric stretching motions of the carboxylate (C–O) group at 1566 and 1387 cm^{-1}; coupled stretches and bends of the carboxylate group (from skeletal vibrations) at 1275 cm^{-1} and the C–O–C stretching vibration of ester groups at 1184 cm^{-1} [22]. As a consequence, the appearance and disappearance of different peaks shows that chemical immobilization of CA successfully introduced some functional groups (–COOH and –OH) into the framework of bone as shown in scheme 1.

3.1.4. X-ray diffraction (XRD)

The X-ray diffraction patterns of pristine and modified ostrich bone are given on Fig. S1A. Comparison of XRD pattern to JCPDS file confirms the presence of a major calcium hydroxyapatite (CaHAP) phase [$Ca_{10}(PO_4)_6(OH)_2$], while the broad and intense background were attributed to the collagen, fat tissues and other organic compounds [18]. These results clearly show the poor crystallinity of pristine ostrich bone even after chemical modification, however the XRD patterns of the modified samples show that calcium phosphate peaks become somewhat sharper after treatment by NaOH and CA (due to the removal of inward organic compounds from the framework of ostrich bone and increasing the mineral phase), however, the chemical modification did not create notable changes of HAP original crystallinity (Fig. S1A).

3.1.5. Thermo gravimetric analysis (TGA)

Thermal stability of the pristine bone and OBW-NaOH-CA were studied with TGA (thermo gravimetric analysis) in Ar atmospheres, which heated from the room temperature to 800 ℃ with a ramping rate of 10 °C/min (Fig. S1B). Thermal analysis (TG) of bone showed third stages of weight loss, stage I (81.9–231 ^{o}C) corresponds to the desorption of physically held water (3.3 wt.%), mainly the attracted and loosely bound water removes from inward framework and surface of bone, and Stage II (231–494.5 ^{o}C), proving a process of fast degradation and burning of organic components (bone marrow, fat tissue and collagen are pyrolyzed to water and carbon dioxide) as well as the liberation of some strongly bounded crystal water. At the third stage (494–800 ℃), weight loss decreased with lower rate than the stage II and the weight loss was very slow above 625 ℃ (14.0 wt.%). The additional weight losses in stage III could be explained due to the several phenomena; burning of the residual organic components, the oxidation of carbonated from the framework of bone to carbon dioxide and releasing of the possible lattice water [23]. However, OBW-NaOH-CA showed third distinct steps: at 81.1–294.0, 294.0–466.3, 466.3-800 ˚C (Fig. S1B). Stages I and II (81.1–466.3 ◦C) are due to desorption of water molecules from the framework of OBW-

NaOH-CA and also decomposition of the immobilized organic functional groups induced by CA (–OH and –COOH). The additional weight losses in stage III could be explained due to the calcination of coke and decomposition of the remained organic and carbonic compounds. As a result, from the comparison of thermogram analysis of samples, it could be concluded that the weight losses of the modified bone at stages II and III significantly decreased and ,in fact, thermal stability and mineral content of modified bone with NaOH and CA improved (mineral content, 69.0 wt.%) rather than unmodified one (mineral content, 52.4 wt.%).

3.2. Adsorption study

3.2.1. Effect of initial concentration of BTEX on the removal capacity

The results of the experiments with varying initial BTEX concentrations (2.5–300 mg L^{-1}) over the bone samples are illustrated in Fig. S2. When the initial BTEX concentrations were increased, the removal efficiencies of organic compounds increased at 25 °C for 24 h. The increase in the loading capacities of sorbents with increasing BTEX concentrations is due to the interaction between BTEX and adsorbents which provides the vital driving force to defeat the resistances to the mass transfer of BTEX between the aqueous and the bone samples. However, the removal of BTEX in this study were in the order of *p*-xylene > ethylbenzene > toluene > benzene, with the same trend of decrease in solubility (benzene, 1790 mg/l > toluene, 530 mg/l > ethylbenzene, 152 mg/l > *p*-xylene, insoluble), and the increase in molecular weight (benzene, 78 g < toluene, 92 g < ethylbenzene, *p*-xylene, 106 g) [24] and boiling point (benzene, 353.1 K < toluene, 383.7 K < ethylbenzene, 409.2 K < *p*-

xylene, 417 K) [25]. The BTEX removal increased dramatically and the adsorption equilibrium was achieved much faster with the chemical modification of ostrich bone. The strong affinity of the modified bone samples especially OBW-NaOH-CA for the BTEX arises from the removal of organic compounds from the framework of pristine bone and also adsorbed CA, which could change the property of ostrich bone from hydrophobic to hydrophilic and either increasing accessibility of the adsorbent active sites. This indicates that the adsorption of BTEX to the biomaterials is dependent on the surface chemical nature [26].

It is believed that the interactions between organic molecules and water interrupt the normal hydrogen-bonded arrangement of water molecules. The increase of this phenomenon is higher for large molecules of high molecular weights, where, a large molecule of high molecular weight disrupts the aqueous solution to a greater extent than a small molecule and larger nonpolar molecules are “pushed” out of solution onto surfaces more completely than small ones [27]

The adsorption mechanism may be partly a result of the ion exchange or complexation between the BTEX and carboxylic groups on the adsorbent surface. It may be involved that H^+ ions present on the adsorbent (-OH groups) are exchanged by BTEX. Surprisingly, the equilibrium pH values indicated no changes than the initial pH values in the solution under the detection limit of pH meter used in this study, pronouncing that BTEX are in the molecular forms through adsorption process and that ion-exchange mechanism does not play a role in BTEX adsorption.

3.2.2. Effect of equilibrium pH on BTEX removal and the zeta potential

To evaluate the influence of pH on the adsorption capacity of the OBW-NaOH-CA, experiments were performed at initial concentrations of 100 and 250 mg/L and pH range 2.0–12 (Fig. 3). The lowest BTEX sorption capacity of OBW-NaOH-CA were found at an initial solution pH of 2.0, on the other hand, as the initial pH increased to 8.0 for BTEX sorption capacity increased and varied little in the initial pH range above 8.0, and the removal efficiencies were in the range of 55–95%. It is obvious that alter in pH has unremarkable effects on BTEX adsorption, demonstrating high stability of OBW-NaOH-CA as BTEX adsorbents in a wide range of solution pH. As typical pH range of groundwater is reported as 6–9 [28], the pH values would hardly affect BTEX adsorption capacity of the OBW-NaOH-CA. The effect of BTEX concentration on the efficiency of adsorbent was also studied. As the BTEX amount increases in solution (250 mg/L) the removal efficiency decreases at constant pH. This phenomenon could be explained by the following reasons: at low BTEX / OBW-NaOH-CA ratio, the BTEX adsorption performs on the high-energy sites, but with increasing the BTEX / OBW-NaOH-CA ratio the higher energy sites are saturated and adsorption commences on the lower energy sites, concluding in a decrease in adsorption efficiency (the similar results have been previously published in the literature) [29-32].

The observed lower uptake in an acidic medium may be attributed to the partial protonation of the active sites (the dominant active sites of OBW-NaOH-CA are -COOH, -C-OH,-P-OH and ≡Ca-O-H species) and the competition of H^+ with organic compounds for adsorption sites on the modified bone (the active sites are closely associated with hydronium ions H_3O^+, that is, restricted the approach of BTEX) and therefore fewer groups are available for BTEX to interact with.

In order to a better comprehending of the net charge of the adsorbent surface at the different pH solution, the point of zero charge (pH_{pzc}) of the bone samples were measured. Zeta potentials of the POBW, OBW-NaOH and OBW-NaOH-CA (0.1 mg/mL) were measured in 10^{-3}M NaCl aqueous solution at different pH. The solution pH was adjusted by NaOH or HCl. As shown in Fig. 4, the pH value of point of zero charge (pH_{pzc}) of POBW is about 7.8. After being modified with NaOH and CA, the pH_{pzc} have been shifted to 5.74 and 6.76, respectively, indicating that the immobilization of CA onto OBW-NaOH is successful. Therefore, the modified samples yield negative surface since pH_{pzc} of them are lower than that of the pristine one and the negative surface charge is due to the introduction of several oxygen-containing functional groups.

3.2.3. Effect of CA concentration on the removal capacity

The effect of the CA on the adsorption of the benzene ant *p*-xylene was investigated by adding various amounts of CA on the pristine ostrich bone waste in the concentration range between 0 and 30 wt.% (Table 2 and Fig. 5). The adsorption of benzene ant *p*-xylene by the pristine ostrich bone were 14.68 and 23.16%, respectively, indeed, these low affinity to adsorbed organic pollutions could be due to strong dipole interaction between unmodified bone and water and also unavailable reactive sites for the interaction by the used pollutions, which exclude organic solutes from this portion of the bone and finally decrease the adsorbed amount. Thus, BTEX is not amenable for adsorption on the pristine ostrich bone, when the

CA loading level is 0%. After pristine ostrich bone was modified by CA, the amount of BTEX adsorbed was significantly increased. In fact, it is believed that by increasing the amount of CA from 1% to 30 % the chemically immobilized of CA on the OBW increased too and the surface progressively loses its positive charge with increasing adsorbed CA, while becomes more hydrophilic. At CA loading level between 8 and 30 wt.%, the surface of OBW-NaOH-CA showed maximum hydrophilicity (>83%) and increasing BTEX adsorption which may correspond to the increase of loading of CA on the surface of OBW. However, the increase in adsorption capacity is due to the surface modification with CA which induces higher interaction between reactive sites of the immobilized CA on ostrich bone surface with the BTEX molecules (Fig. 5). It is believed that the presence free carboxyl groups of citric acid raise the density of electron donating group (the carboxylic oxygen as the electron-donor) on the modified ostrich bone that increasing its favorable interaction with the organic pollutions. Other mechanism could be included such as hydrogen bonds (due to the functional groups of CA), and electrostatic interactions (because of the charged modified surface with CA) [11]. It is believed that the π–π electron-donor–acceptor interaction at the surface of adsorbent is responsible for adsorption of the VOCs; due to the weakly positively charged of BTEX molecules (benzene ring) at the pH range 3–12, removal of the used organic compounds could be accelerated by a negative surface charge (OBW-NaOH-CA 8 %).

To support the above explanation the results of zeta potential of OBW-NaOH-CA are shown in Fig. 4B. The surface modification of pristine ostrich bone with increasing of CA loadings result in the change of particles zeta potential from positive to negative charge reflecting, which could be explained by the presence of reactive sites of CA (carboxylic acid groups) on OBW-NaOH-CA (Fig. 4B) [33]. According to these results, loading level of 8 wt.% of CA is chosen for the surface modification of ostrich bone waste in this study.

3.2.4. Effect of adsorbent dosage

The adsorbent dosage is one of the important factors because it presented the capacity of the adsorbent for a given initial concentration of the adsorbate. To determine the dependence of BTEX sorption on OBW-NaOH-CA, various dosages (0.10-2.0 g) of the sample, at a controlled temperature of 25 ± 1°C, was added into 10 mL of 250 mg/L BTEX solution without any changes on the solution pH at 30 min. The relation between the adsorbent dosage and removal percentage of BTEX by the OBW-NaOH-CA is shown in Fig. 6, where the removal percentage of BTEX increased with increasing the adsorbent dosage due to increase in the number of adsorption sites. As the adsorbent dosage increased from 0.1 to 1.25 g, the removal efficiency of BTEX increased significantly from 25.92 % to 70.0 %, 37.48 % to 74.9 %, 48.4 % to 78.5 %, and 63.6% to 90.0 % for benzene toluene, ethylbenzene and *p*-xylene, respectively. It is apparent that removal efficiency of BTEX is increased by cleaning process with NaOH and CA, where *p*-xylene was removed 90.0 % by OBW-NaOH-CA. The removal efficiency of BTEX by OBW-NaOH-CA after 0.75 g of sorbent dosage was negligible because it achieved the equilibrium adsorption capacity at higher adsorption dosages. It is believed that at the low adsorbent dosage the dispersion of OBW-NaOH-CA particles in bulk solution is better, that is, all of the active sites on the adsorbent surface are completely uncovered which may accelerate the approachability of BTEX molecules to a large number of the adsorbent active sites. Therefore, the adsorption on the surface active sites is reached to a saturated point, performing a high removal capacity. However, at higher adsorbent dosage, the accessibility of adsorbent active sites with higher energy decreases and a larger portion of the active sites with lower energy becoming occupied; leading to a decrease in adsorption process. Therefore, 0.75 g of adsorbent dosage was chosen as the optimal dosage for the rest of the study.

3.2.5. Adsorption kinetics

BTEX adsorption capacities were investigated as a function of time (0-360 min) to determine the adsorption equilibrium time for the adsorption of BTEX (250 mg/L) onto OBW-NaOH-CA (0.75 g) in the solution of pH 7.0 at 25^{o}C (Fig. 7A). It is easily seen that the amount of BTEX adsorption were significantly increased onto the OBW-NaOH-CA with increasing the contact time. Studies conducted on the adsorption kinetics of BTEX removal revealed that the majority of organic pollutions were removed within the first 0-40 min contact with the adsorbent. Percentage of maximum adsorption was 65.8, 74, 77.4 % and 91.2 % for benzene, toluene, ethylbenzene and *p*-xylene, respectively, at 60 min. The initial rapid adsorption declines at a much lower rate approach to equilibrium and gradually levels-off (360 min) towards the end of the experiment (a dynamic equilibrium is reached between OBW-NaOH-CA and organic pollutions remaining in the liquid phase). In fact, the fast adsorption at the initial stage is probably due to the increased concentration gradient between the adsorbate in solution and adsorbate in adsorbent as there must be increased number of vacant active sites available in the beginning, where removal of the BTEX in the solution carried out completely within 360 min. In fact, the swift kinetics has consequential applicable importance, because it will promote smaller designed-system volumes pledging high efficiency and economy. In the order to optimize the adsorption process, the adsorption isotherms for the rest of initial concentrations were obtained for a time of 30 min.

In order to determine and interpret the mechanism of BTEX adsorption processes over the bone samples and major parameters governing sorption kinetics, kinetic sorption data obtained empirically were fitted to the pseudo-first-order, pseudo-second-order, and intra-particle diffusion models (Table S1).

Where k_1, k_2 and k_{int} are the adsorption rate constants of first, second order kinetic and intraparticle diffusion models, in min^{-1}, L/mg min and mg/(g^1 min$^{1/2}$), respectively; q_e and q_t in mg/g, are equilibrium adsorption uptake (at time $t = \infty$) and adsorption uptake (at time t), respectively.

The calculated kinetics parameters for adsorption of BTEX onto the OBW-NaOH-CA, at initial concentration of 250 mg/L is tabulated in Table 3. As can be observed, the second-order equation appeared to be the best-fitting model than those for the other two equations (the correlation coefficient is extremely high for the second-order equation of OBW-NaOH-CA; $R^2 > 0.999$). The plots of linear form of the pseudo-second-order for the adsorption of BTEX is shown in Fig. 7B.The pact of the experimental data with the pseudo-second-order kinetic model (the pseudo-second order equation is based on the sorption capacity on the solid phase) indicates that the adsorption of BTEX onto the OBW-NaOH-CA controlled by chemisorption (as the rate-limiting step of the adsorption mechanism and no involvement of a mass transfer in solution) involving valence forces through sharing or exchange electrons between adsorbent and adsorbate (scheme 1). Consequently, the adsorption of the organic pollutions onto the OBW-NaOH-CA may be considered to composed of two processes with initial adsorption rate of 98.03, 69.30, 73.58 and 67.29 mg/(g min) for benzene, toluene, ethylbenzene and *p*-xylene, respectively, OBW-NaOH-CA This adsorption rate is related to the content and type of active adsorption site on the matrix of adsorbent; carboxylic (-COOH) sites of the immobilized CA are the main reactive groups for the removal of BTEX from aqueous solution (Scheme 1).

3.2.6. Adsorption isotherms

The equilibrium adsorption isotherms are known one of the most important data to understand the mechanism of the adsorption and describe how adsorbates interact with adsorbents. The experimental adsorption equilibrium data of BTEX on the OBW-NaOH-CA were fitted by applying the Langmuir and Freundlich isotherm models, which are usual models for aqueous-phase adsorption (Table S1). These adsorption models give a representation of the adsorption equilibrium between an adsorbate in solution and the surface active sites of the adsorbent.

Where qe (mg/g) is the specific equilibrium amount of adsorbate, C_e (mg/L) is the equilibrium concentration of adsorbate, qm is the maximal adsorption capacity and K (K_L and K_F) (L/mg) and n are empirical constants that indicate the extent of adsorption and the adsorption effectiveness, respectively. The constant n gives an idea of the grade of heterogeneity in the distribution of energetic centers and is related to the magnitude of the adsorption driving force. High n values therefore indicate a relatively uniform surface, whereas low values mean high adsorption at low solution concentrations. Furthermore, low n values indicate the existence of a high proportion of high-energy active sites.

Langmuir equation relates the coverage of molecules on a solid surface to concentration of a medium above the solid surface at a fixed temperature and adsorption is limited to monolayer coverage, and intermolecular forces decrease with the distance from the adsorption surface. On the other hand, the Freundlich model supposes that the adsorption surface is heterogeneous, that interactions among adsorbed molecules can occur, and that multilayer adsorption is possible. The Langmuir and Freundlich adsorption isotherms exhibit an approximately linear relationship for all the bone samples. The data obtained from the modified bone systems revealed that the Langmuir isotherm model fitted the experimental data better than Freundlich isotherm (Table 4 and Fig 8). The maximum adsorption capacity (*qm*) obtained by Langmuir isotherm for *p*-xylene (425 mg/g) was much higher than the values found for other organic pollutions onto the OBW-NaOH-CA and it also suggests that there is a high thermodynamic stability for *p*-xylene immobilized on the active sites of the OBW-NaOH-CA (Table 4).

3.2.7. Effect of the temperature on the removal capacity

Furthermore, the equilibrium adsorption capacity of BTEX onto the favored adsorbent, OBW-NaOH-CA, was studied at higher temperatures of 288, 298, 312 and 353 K in pH = 7.0 (Fig. 9A). The increase in the temperature of solutions of BTEX from 288 to 353 K leads to an increase in the adsorption capacity of the OBW-NaOH-CA. This may indicate that adsorption of organic pollutions onto active sites of the bone sample are endothermic and could be elucidated by availability of more active sites of adsorbent, the enlargement and activation of the adsorbent surface at higher temperatures. This could also be due to the easily mobility of organic pollutions from the bulk solution towards the adsorbent surface and enhanced the accessibility to the active sites.

In order to better understand the effect of rising temperature on the adsorption of the BTEX onto the active sites of the OBW-NaOH-CA, three basic thermodynamic parameters were studied: the Gibbs free energy of adsorption (ΔG), the enthalpy change (ΔH), and the entropy change (ΔS).

The thermodynamic parameters ΔG, ΔS and ΔH for this adsorption process were determined by using following equations.

$$\Delta G = -RT \ln K \qquad (2)$$

where K is the thermodynamic equilibrium constant. The values of K can be determined by plotting $\ln(q_e/C_e)$ against qe and extrapolating to zero, where q_e is the adsorbed BTEX concentration at equilibrium and C_e is the equilibrium concentration of BTEX ions in solution.

The ΔH and ΔS values were calculated from slope and intercept of the linear plot, of lnKvs 1/T as shown in Fig. 9B.

$$\ln K = \Delta S/R - \Delta H/RT \qquad (3)$$

and Gibbs free energy is given by Eq. (4), where ΔG is the free energy change (J/mol); R and T is the universal constant (8.314 J/(mol K)) the absolute temperature (K), respectively.

$$\Delta G = \Delta H - T\Delta S \qquad (4)$$

The corresponding values of thermodynamic parameters are presented in Table 5. This shows that ΔH and ΔS are positive for all the experiments and ΔG is negative in most systems. The positive values of ΔH revealed that the adsorption process was endothermic in nature; hence with increasing temperature the adsorbed amount at equilibrium increased.

The positive value of ΔS revealed the increased randomness and an increase in the degrees of freedom at the solid-solution interface during the immobilization of the BTEX on the active site of the adsorbent, which indicate the partial dehydration of the BTEX before adsorption and either the adsorbed solvent molecules that were released by the adsorbate, therefore, enabling commonness of randomness and spontaneity in the system. The necessity of a large amount of heat to remove the BTEX from the solution makes the sorption process endothermic.

It was also observed that with increase in temperature the value of ΔG decreases, which indicated that sorption processes was spontaneous and thermodynamically favorable by an increase in temperature. In fact, the value of ΔG for physisorption is in the range $-20 < \Delta G < 0$ kJ/mol, while for the chemisorption process ΔG is between $-400 < \Delta G < -80$ kJ/ mol [34]. The calculated ΔG values based on Eq. (4) for the adsorption of BTEX onto the OBW-

NaOH-CA were in the range of physisorption (Table 5). Therefore, based on the values of ΔH and ΔG both suggested that adsorption of BTEX onto OBW-NaOH-CA might be a physisorption process.

3.2.7. Effect of ionic strength

The ionic strength of solution is one of the most important factors that influencing on the adsorption efficiency of adsorbent in natural waters, where the effect of ionic strength on BTEX adsorption by OBW-NaOH-CA could help to clarify the removal capacity of immobilized CA. The sorption of BTEX (250 mg/L) on OBW-NaOH-CA in solutions having various concentrations of NaCl was studied ([NaCl] = 0.0, 0.05, 0.10, 0.20, 0.40, 0.60 and 0.80 M) (Fig. 10). Increasing ionic strength of solution increases the adsorption of BTEX (Fig. 10). At the NaCl concentration of 0.8 M, 72.4, 79.88, 79.36 and 86.8 % was removed, while that in the absence of NaCl was 63.84, 71.82, 74.34 and 83.96 % for benzene, toluene, ethylbenzene and *p*-xylene, respectively. At higher ionic strength the high removal capacity of OBW-NaOH-CA is likely to be due to the decrease in organic pollutions solubility that could be explained by postulating that some of the H_2O molecules cannot participate in the solvation of the BTEX and even active sites of the adsorbent (carboxylic acid groups of the immobilized CA) because they are involved in dissolution of NaCl ions. In fact, water is reported to have very high salinity, if the amount of NaCl is about > 0.1 M [35], thereby, at these concentrations, the adsorbed BTEX increases in the presence of OBW-NaOH-CA.

3.3. Mechanism study

In order to better understand the adsorption properties of OBW-NaOH-CA, adsorption of Pb(II) and BTEX in a binary solution with initial pH 7.0 by OBW-NaOH-CA was investigated (Fig. 11). Pb(II) is a highly toxic substance that can produce a wide range of adverse health effects in both adults and children upon exposure. Thus, very low levels of exposure can result in reduced intelligence quotient, learning disabilities, attention deficit disorders, behavioral problems, stunted growth, impaired hearing, and kidney damage in children under the age of six years. At high levels of exposure, such children may become mentally retarded, fall into a coma, and even die from lead poisoning. In adults, lead can increase blood pressure and cause fertility problems, nerve disorders, muscle and joint pain, irritability, and memory or concentration problems.

From the Fig. 11, it is clearly observed that OBW-NaOH-CA showed lower removal efficiency for BTEX in the presence of Pb(II) ions. The decrease of the removal efficiency for BTEX in binary solution was because that Pb(II) may occupy the available active sites, thereby lowering the organic pollutions removal efficiency. However, the effect of Pb(II) ions on BTEX adsorption was calculated as $DI = (K_{d\ BTEX} - K_{d\ BTEX\ \&\ Pb}) \cdot K^{-1}_{d\ BTEX}$, where $K_{d\ BTEX\ \&\ Pb}$ and $K_{d\ BTEX}$ correspond to the removal coefficients of BTEX with and without Pb(II) ions, respectively (Table 6; $K_d = q_e/C_e$). Pb(II) ions decreased the adsorption capacity of benzene (42.07 %), toluene (37.28 %), ethylbenzene (19.03 %), and *p*-xylene (32.73 %) by OBW-NaOH-CA. This could be explained through the formation of inner-spher or surface complexes of Pb(II) by oxygen-containing active sites and hydration, thereby may block some hydrophilic adsorption active sites on the surface of OBW-NaOH-CA. Indeed, the metal cation hydration shells may interfere or cover the OBW-NaOH-CA active sites and so indirectly make interference for removal of BTEX, leading to the inhibition of BTEX adsorption around the metal-complexed portions.

In this work, the percent of hydrophobicity and zeta potential of OBW-NaOH-CA after adsorption of benzene and p-xylene was measured to evaluate the mechanism of adsorption. From the results of Fig. 12A it was observed that with increasing the initial concentration of pollutions (benzene and p-xylene) the percent of hydrophobicity of adsorbent increased which confirmed that organic compound immobilized on the active sites of OBW-NaOH-CA and decreasing its hydrophilicty (block the hydroxyl group through electrostatic and hydrogen bond interaction) [11]. However, in order to further demonstrate the above interactions zeta potential of OBW-NaOH-CA after adsorption of benzene and p-xylene were analyzed (Fig. 12 B), where the surface charge of the adsorbent after exposure to the organic compounds altered to a positive value. It is believed that organic compounds were removed by the positive interactions between the reactive sites of the immobilized CA and benzene ring from aqueous solution which eventually decreased the negative charge of the pristine OBW-NaOH-CA, due to the weakly positively charged of BTEX molecules (benzene ring) at the pH range 3–12.

3.4. Comparison of different adsorbents for BTEX removal

The adsorption capacity of the present adsorbent with some recently reported BTEX adsorbents including SWCNT, MWCNT, GAC and ACF are compared in Table 7. In most cases, the materials that were utilized in the papers are not low-cost. The adsorption capacity of OBW-NaOH-CA for BTEX is higher than that of the majority of other adsorbents mentioned. However, it is anticipated that modified carbon nanotubes (CNTs) could offer remarkable BTEX removal properties because of their significant active surface area (Table 7), while these synthetic materials could not be applied for drinking water filtration at present as their separation is not simplistic and the toxicity of CNTs to humans is currently not fully evaluated. Therefore, it can be concluded that OBW-NaOH-CA has potent potential for the removal of BTEX from aqueous solutions.

3.5. Real water sample

The suggested adsorbent in this study was also implemented to remove BTEX from the Persian Gulf water as a function of time (Fig. 13). The Persian Gulf water gathered from the coast of Bushehr and was filtered using a 0.45 mm filter membrane and then stored in polyethylene bottles. The concentration of BTEX in the real sample was measured by the UV-vis and GC. Identification of compound was done by comparing the GC retention times of expected compound with those of standard samples. As observed in Fig. 13, removal tests were performed by spiking known amount of standards (25 and 80 mg/L BTEX) in the sample matrix and then analyzing it. The removal percentage of BTEX from the Persian Gulf water reached 58.1%, 97.2, 98.3% and 99.9% for 25 mg/L BTEX and 55.2%, 80.6%, 85.2%, and 98.1 % for 80 mg/L BTEX, respectively, after 30 min. The results confirmed that OBW-NaOH-CA has reliable and potent efficiency to uptake BTEX from real water.

As a consequence, it is believed that the combined treatment of pristine ostrich bone with NaOH and CA would more likely opening up the pores and increasing the active sites of the pristine bone. Besides, the CA modification of pretreated bone with NaOH could induce more active sites on the surface of the modified bone (the carboxylic acid groups of immobilized CA), which show very effective tendency in order to react with BTEX.

3.6. Economic evaluation

The relative production cost of the proposed bioadsorbent in this work was way much lower than that of traditional and commercial adsorbent (i. e. activated carbons (AC) and carbon nanotubes (CNTs)). The OBW and CA are accessible with low cost, replicable without the need of high technology facility, and after adding expenses like chemicals treatment by alkali and CA, transport; and the operation cost, the price of the modified OBW would be approximately US$ 120 ton^{-1}. The value of the AC and CNT utilized for wastewater remediation in Iran is above US$ 900 ton^{-1}. Moreover, OBW-OH-CA is low-priced and allegedly effortless to provide in large weights, thus presenting the potent occasion to exploit this bio-adsorbent in the third world drinking wastewater remediation to reduce the adulterating and damaging of millions of people worldwide.

Conclusion

The data obtained in this work confirmed that the covalently immobilized CA over OBW can be prosperously utilized for the removal of hazardous organic compounds from aqueous media. The existence of CA on the OBW was verified by FTIR, XRD, BET, SEM, Zeta (ζ) potential and EDX analyses. Experimental results showed that the physicochemical properties of OBW-NaOH-CA such as crystallinity, surface charge and surface area were changed with the presence of CA. Several removal parameters such as initial BTEX concentration, adsorbent dosage, pH, temperature, and contact time on the removal efficiency of BTEX by OBW-NaOH-CA have been studied. The order of adsorbates removal on OBW-NaOH-CA was obtained as follows: *p*-xylene > ethylbenzene > toluene > benzene. The kinetic data showed that the pseudo-second order kinetic model was resulted to be well suited and provide high degree of correlation with the experimental results for the adsorption process of BTEX. The present free carboxyl groups of citric acid raise the density of electron donating group (the carboxylic oxygen as the electron-donor) on the modified ostrich bone, that is, increasing its favorable interaction with the organic pollutions due to their weakly positively charged at different pHs. The results showed that the immobilized CA on OBW shifted the surface charge towards negative value, which promoted the adsorption of BTEX. The prepared bioadsorbent could also be utilized to remove the organic pollutions from the real water (*Persian Gulf* water).

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Figure

Fig. 1. SEM–EDX analyses of POBW (A and C) and OBW-NaOH-CA (B and D).

Fig. 2. FT-IR spectra of POBW (A), OBW-NaOH (B) and OBW-NaOH-CA (C).

Fig. 3. Effect of pH on BTEX adsorption from aqueous solutions by OBW-NaOH-CA at initial concentration of 100 mg/L (A) and 250 mg/l (B).

Fig. 4. Zeta potential of the bone samples (A), and OBW-NaOH-CA (B) as a function of pH ($C_{\text{Bone samples}}$ = 2.5 g/L and 10^{-3} mol/L solutions of KNO_3). Experimental error: ±4 mV.

Fig. 5. Effect of the amounts of CA on the adsorption capacity of benzene and p-xylene on OBW-NaOH-CA. Adsorption experiments-organic compound concentration, 250 mg/L; sample dose, 0.1 g/100 L; pH = 7.0; temperature, 25 ^{o}C; equilibrium time, 30 min.

Fig. 6. Effect of the adsorbent dosage on the adsorption of BTEX on the OBW-NaOH-CA from aqueous solutions.

Fig. 7. The adsorption kinetics (A) and pseudo-second order plot (B) of OBW-NaOH-CA for the adsorption of BTEX at room temperature.

Fig. 8. Equilibrium absorption of BTEX on OBW-NaOH-CA at 25 ^{o}C and pH = 7.0.

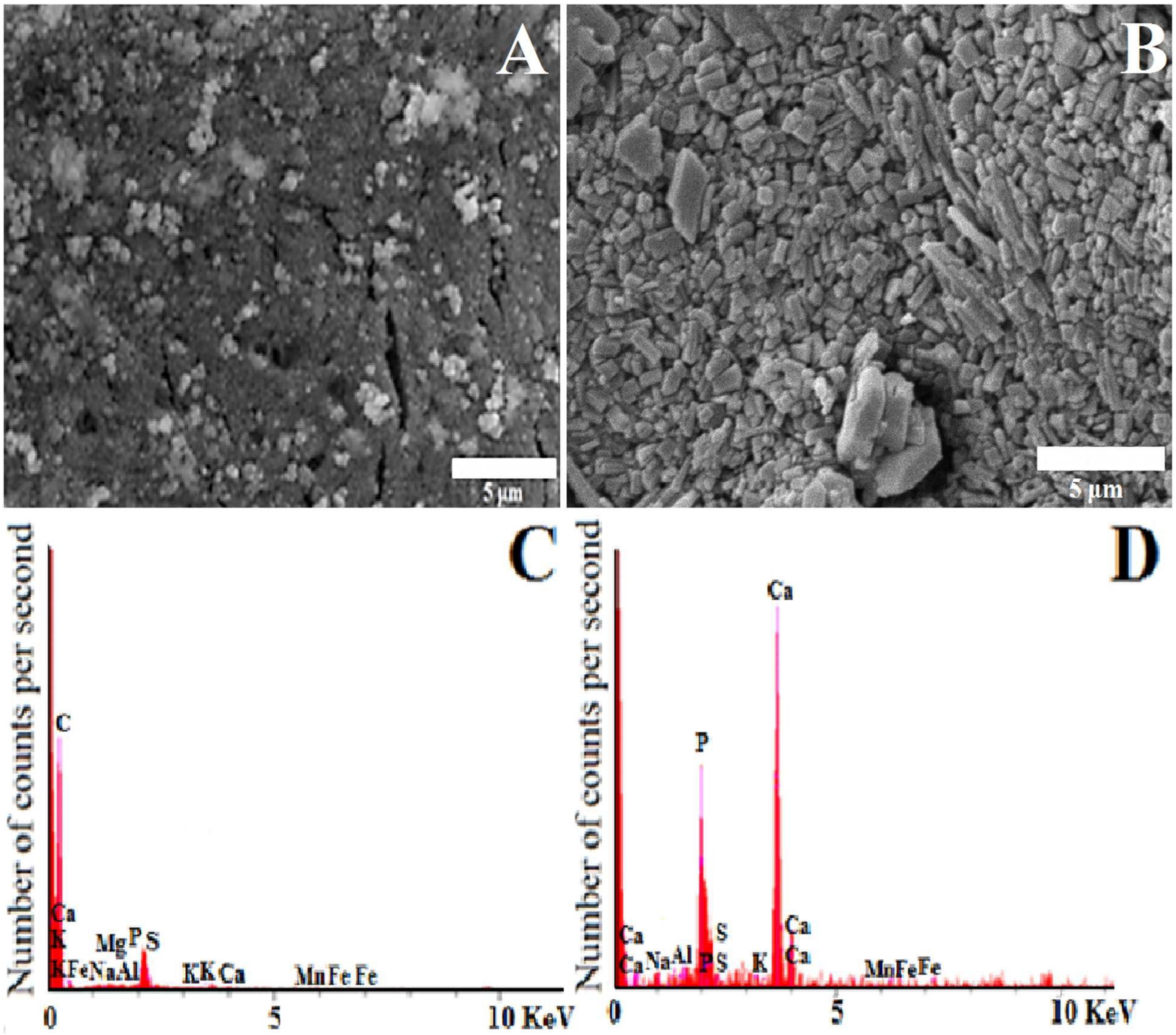
Fig. 9. Effect of temperature (A) and plot of lnK vs. 1/T (B) on the adsorption of BTEX by OBW-NaOH-CA at different initial concentrations.

Fig. 10. The effect of chloride ion on the removal of BTEX by OBW-NaOH-CA; pH = 7.0, contact time = 24 h, T = 25 ^{o}C.

Fig. 11. , Adsorption of Pb(II) and BTEX by OBW-NaOH-CA in a binary solution with initial pH 7.0.

Fig. 12. The % hydrophobicity and Zeta potential of OBW-NaOH-CA after adsorption of benzene and *p*-xylene.

Fig. 13. BTEX removal from Persian Gulf water at initial concentrations of 25 mg/L (A) and 80 mg/L(B) after exposure to OBW-NaOH-CA at varying times.



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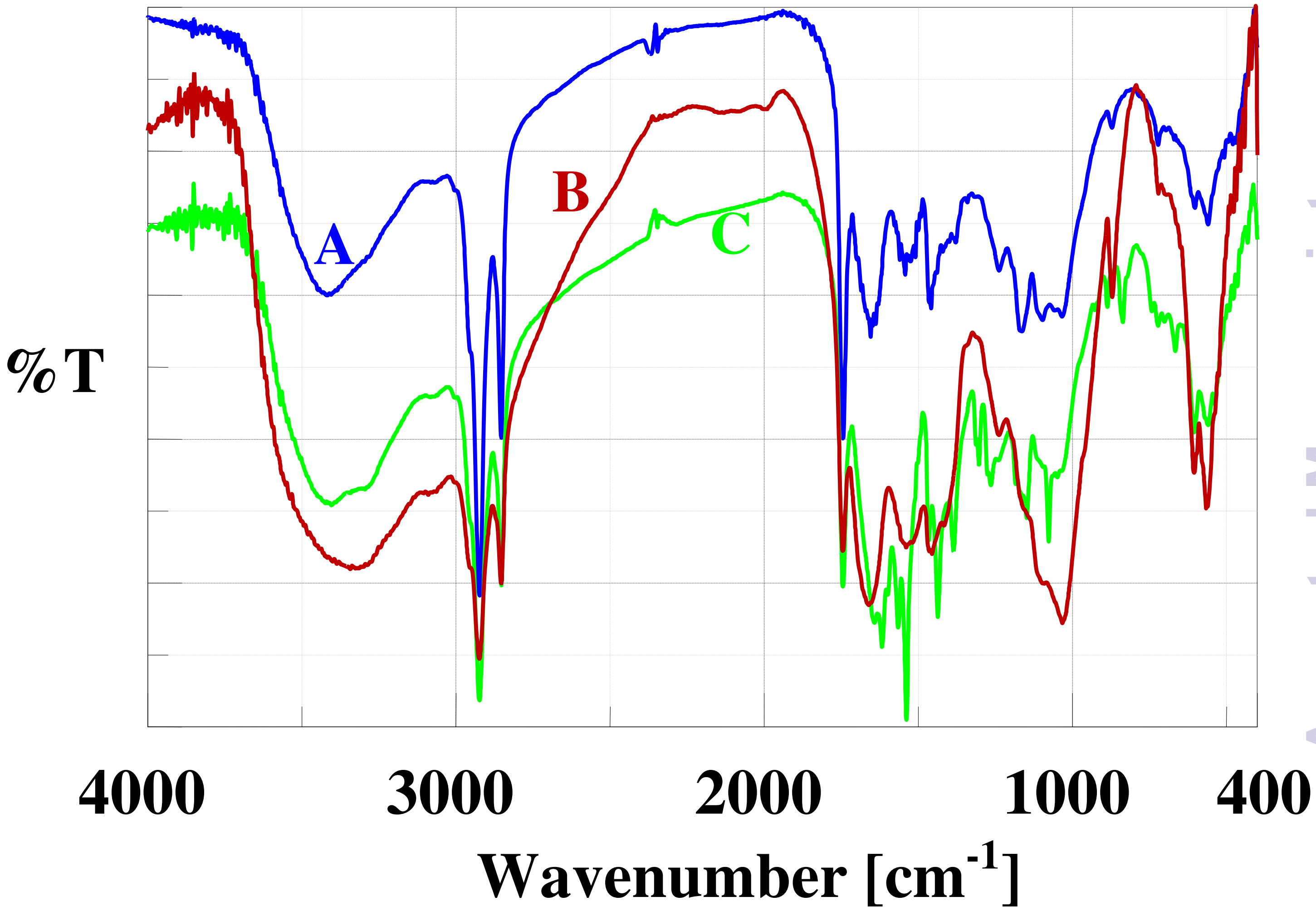

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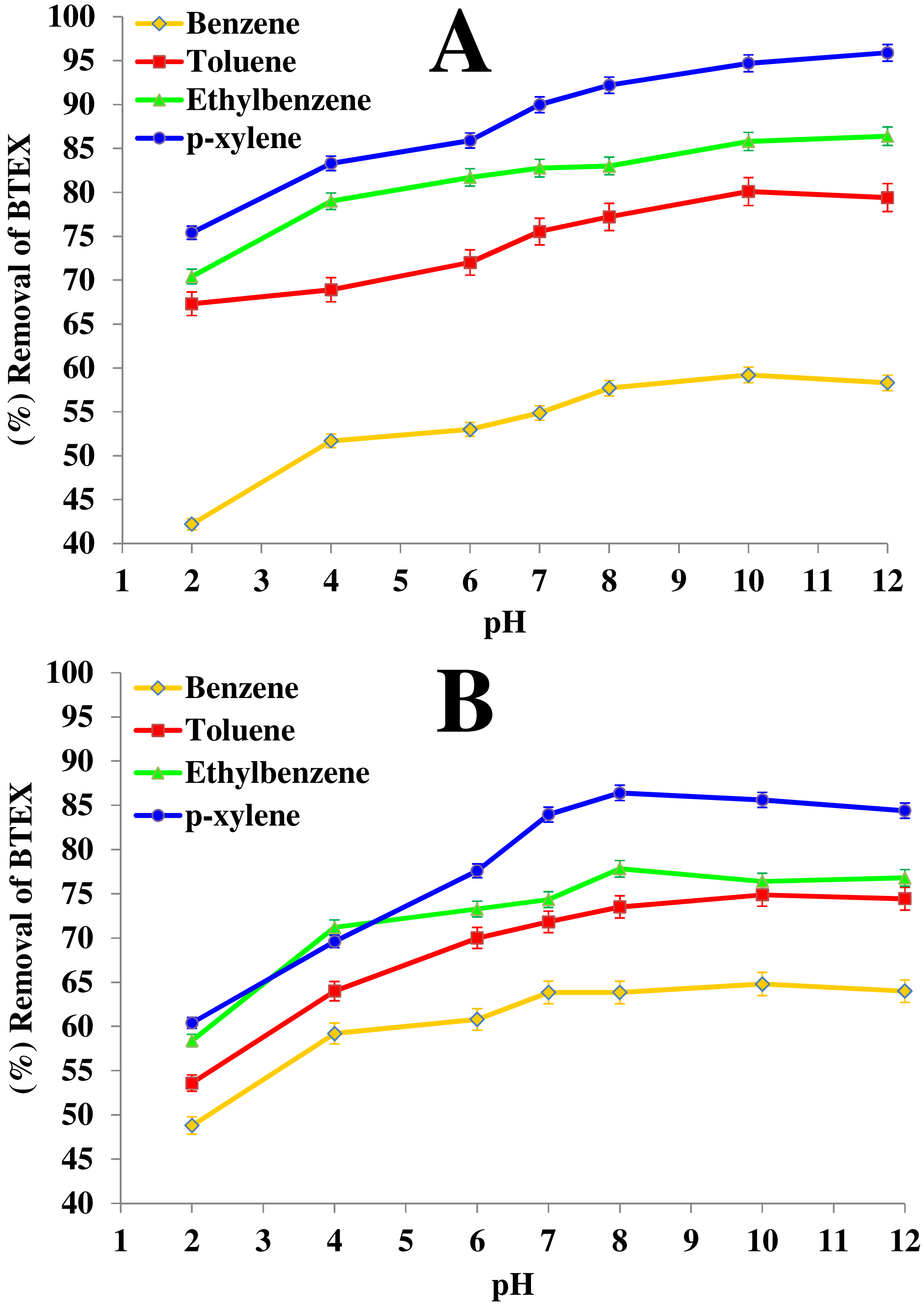

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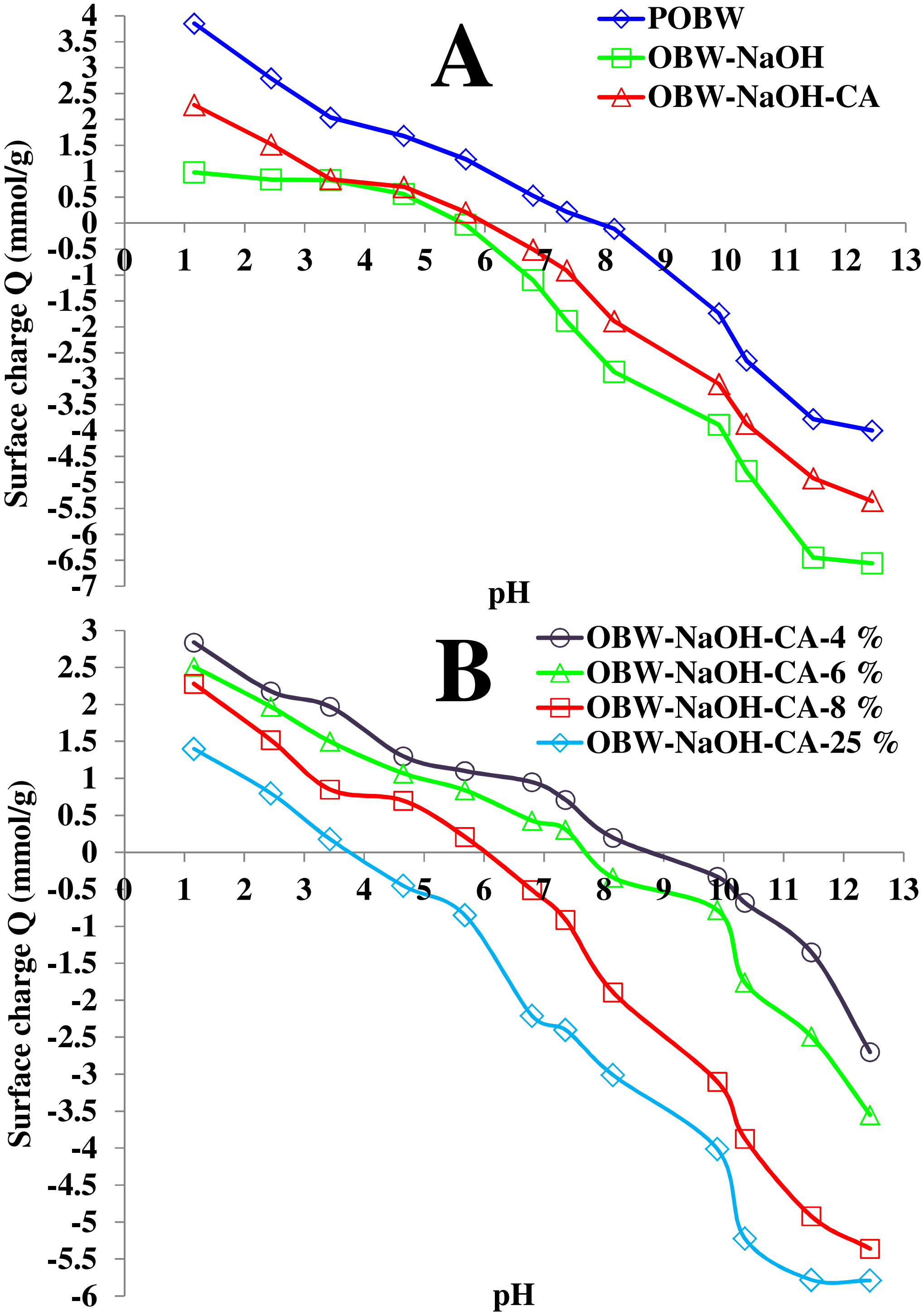

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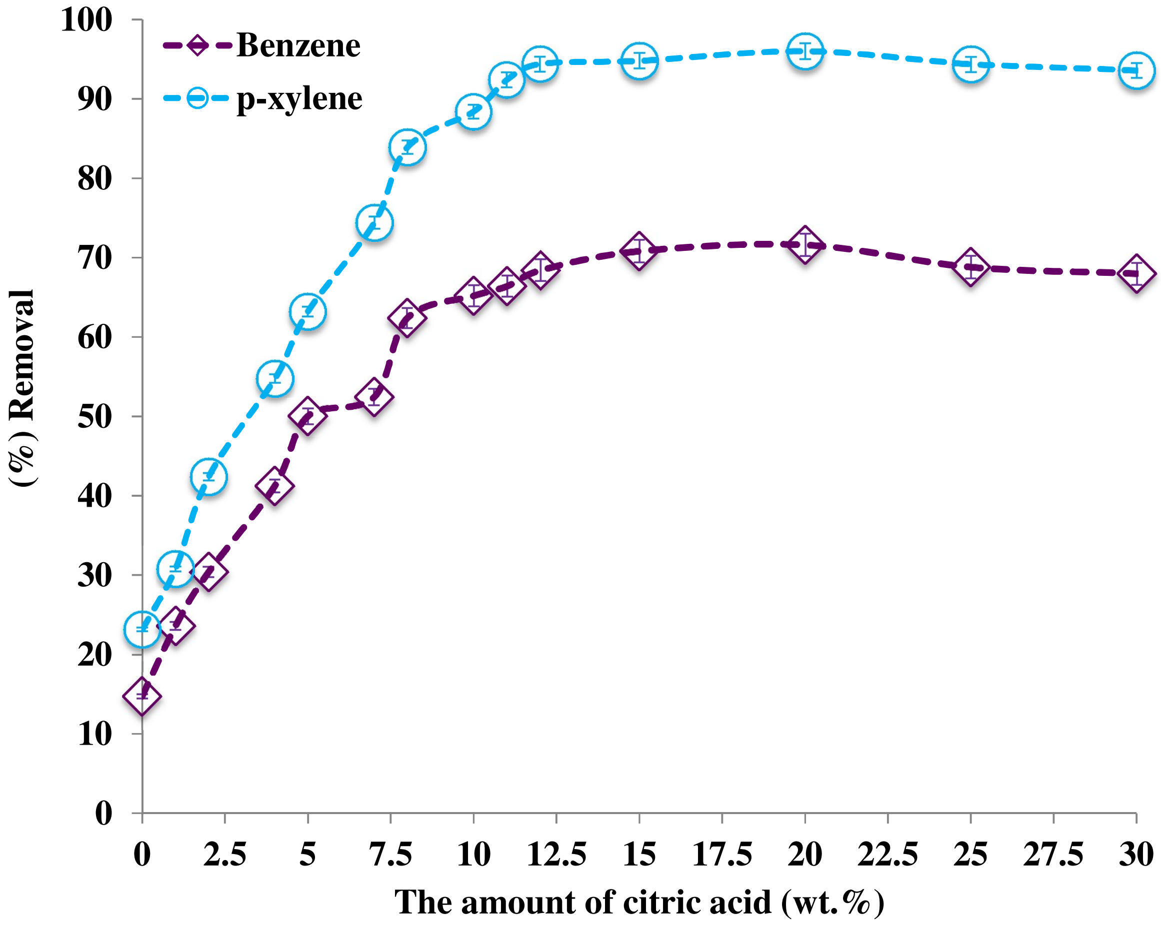

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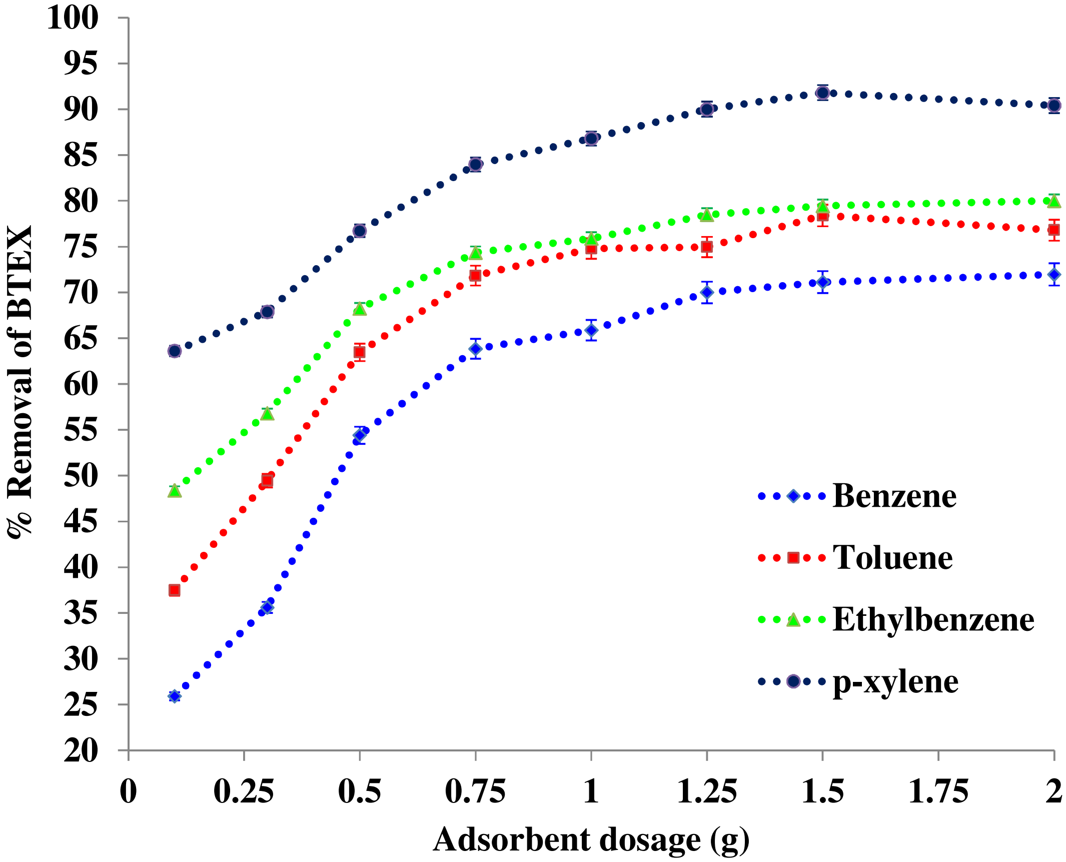


Fig. 6. Effect of the adsorbent dosage on the adsorption of BTEX on the OBW-NaOH-CA from aqueous solutions.

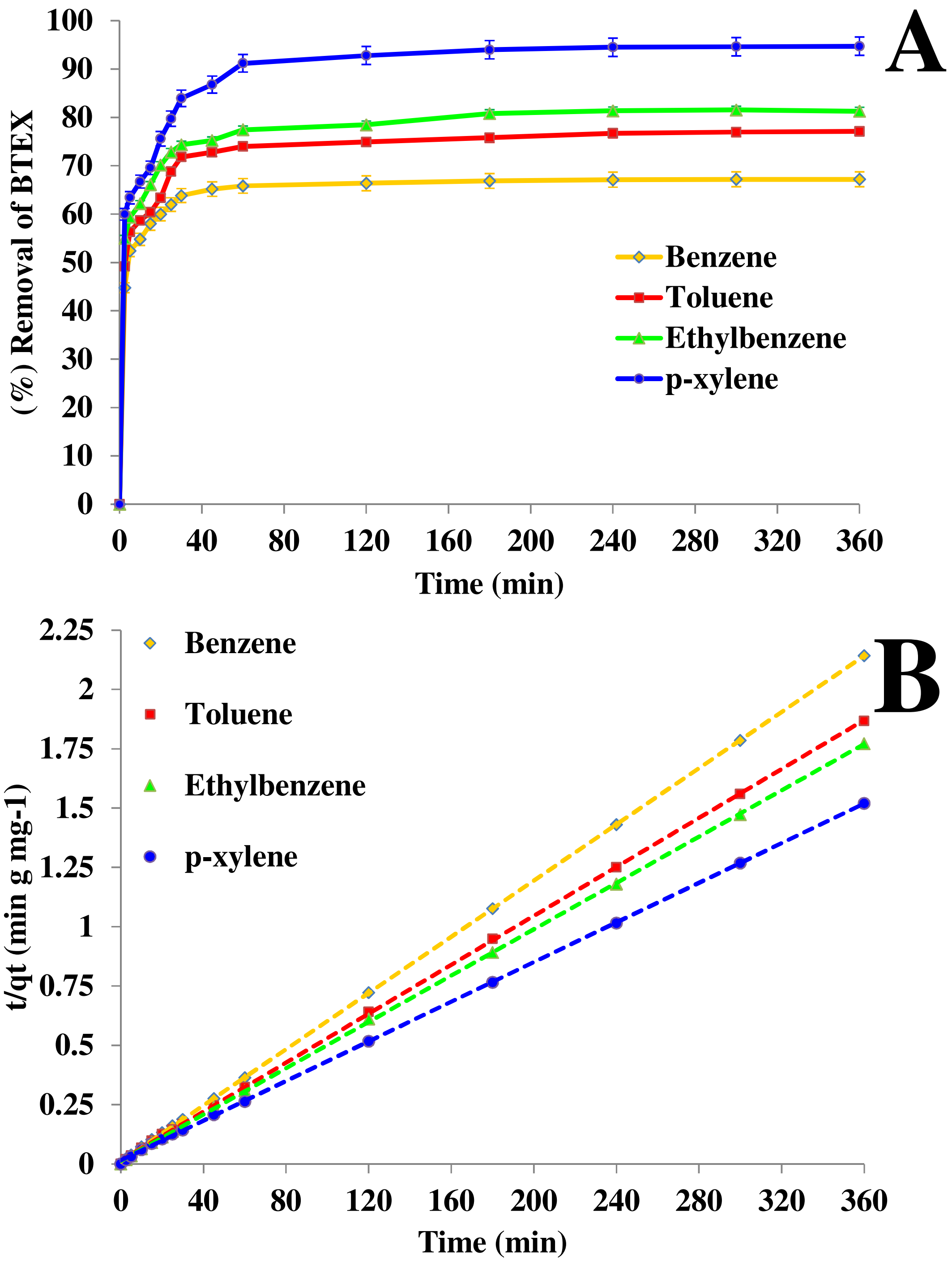


Fig. 7. The adsorption kinetics (A) and pseudo-second order plot (B) of OBW-NaOH-CA for the adsorption of BTEX at room temperature.

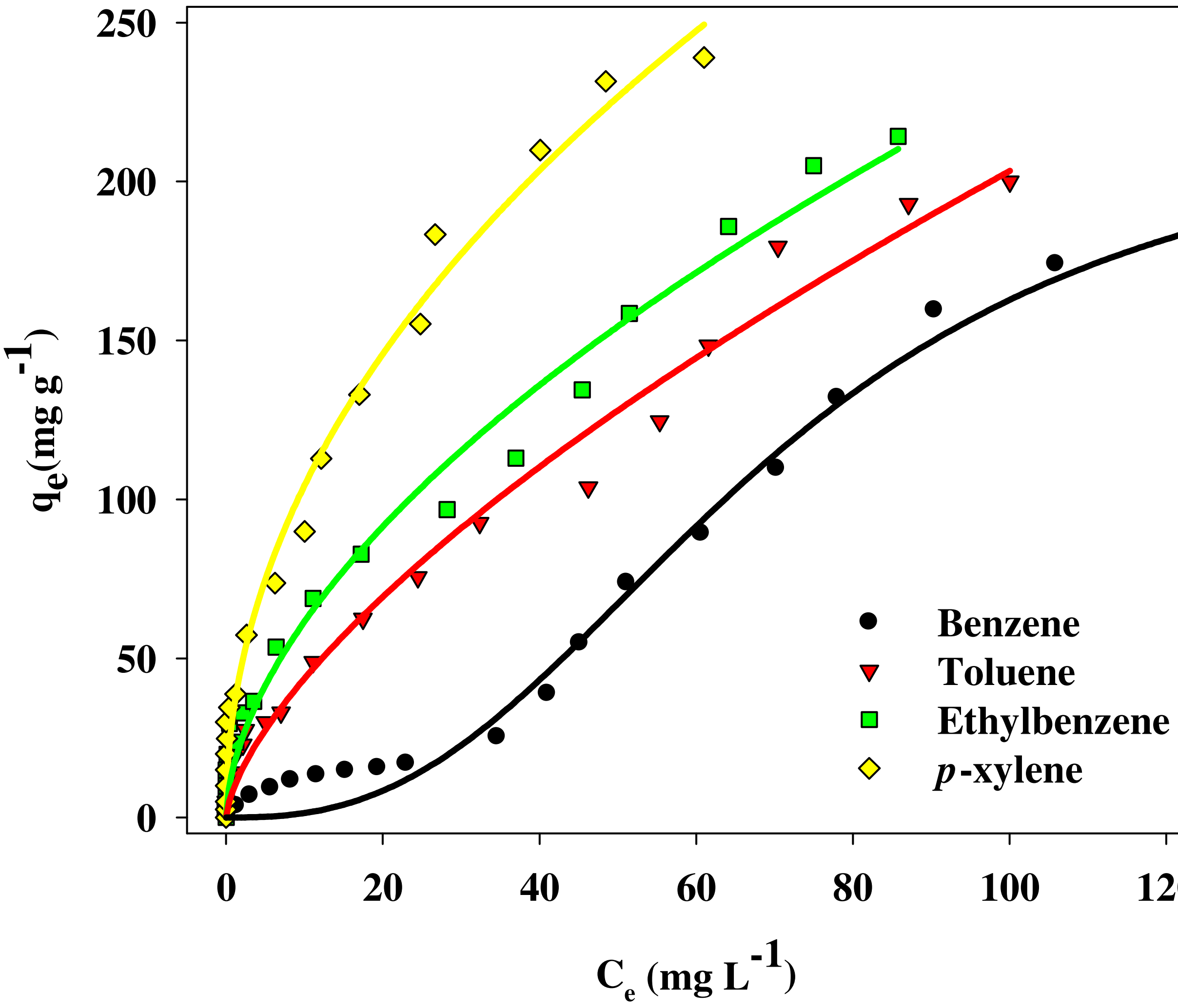


Fig. 8. Equilibrium absorption of BTEX on OBW-NaOH-CA at 25 °C and pH = 7.0.

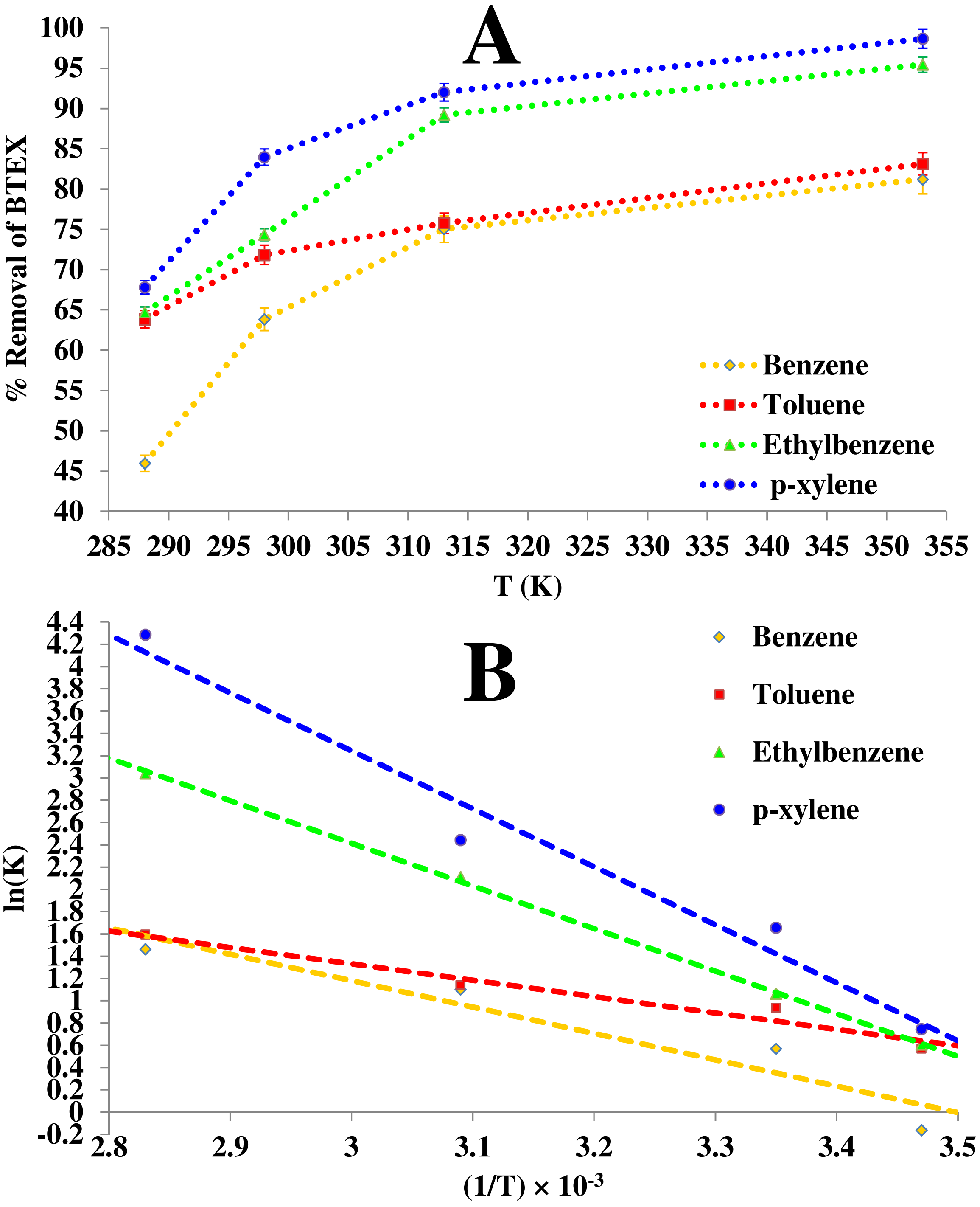


Fig. 9. Effect of temperature (A) and plot of lnK vs. 1/T (B) on the adsorption of BTEX by OBW-NaOH-CA at different initial concentrations.

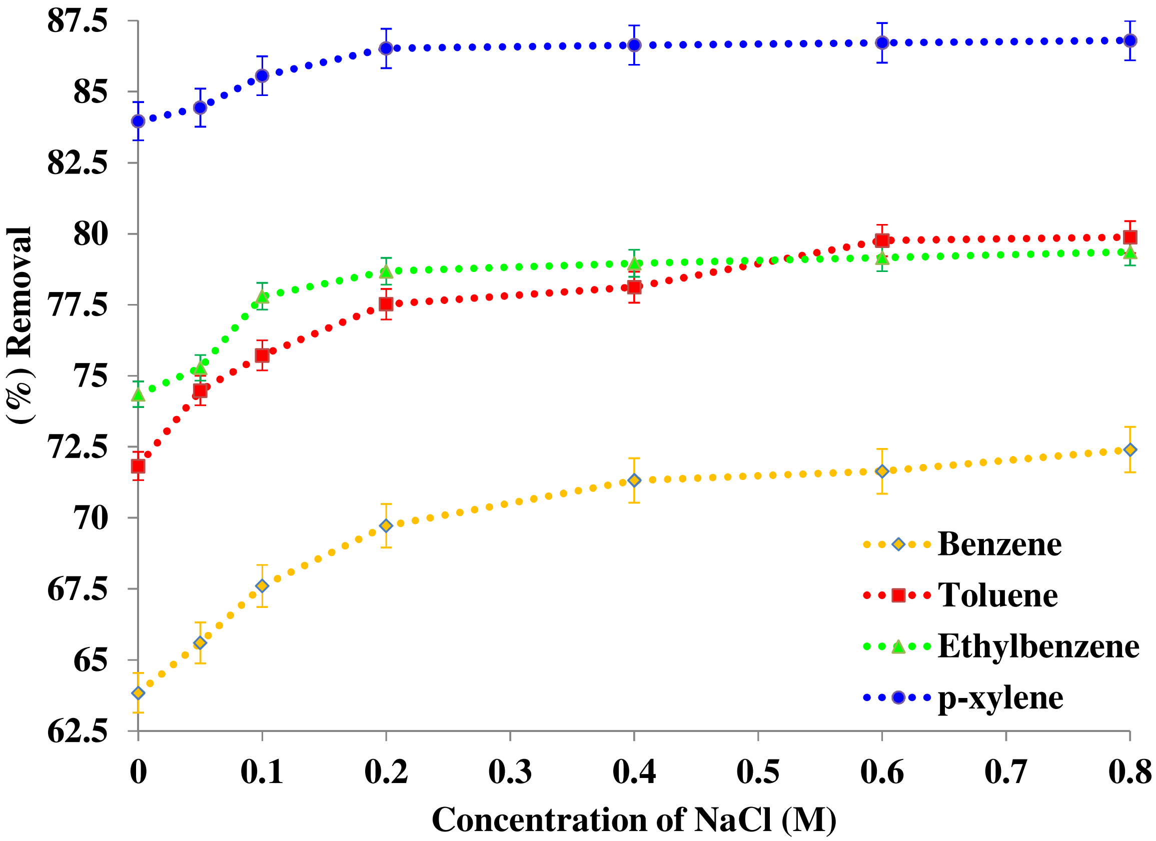


Fig. 10. The effect of chloride ion on the removal of BTEX by OBW-NaOH-CA; pH = 7.0, contact time = 24 h, T = 25 °C.

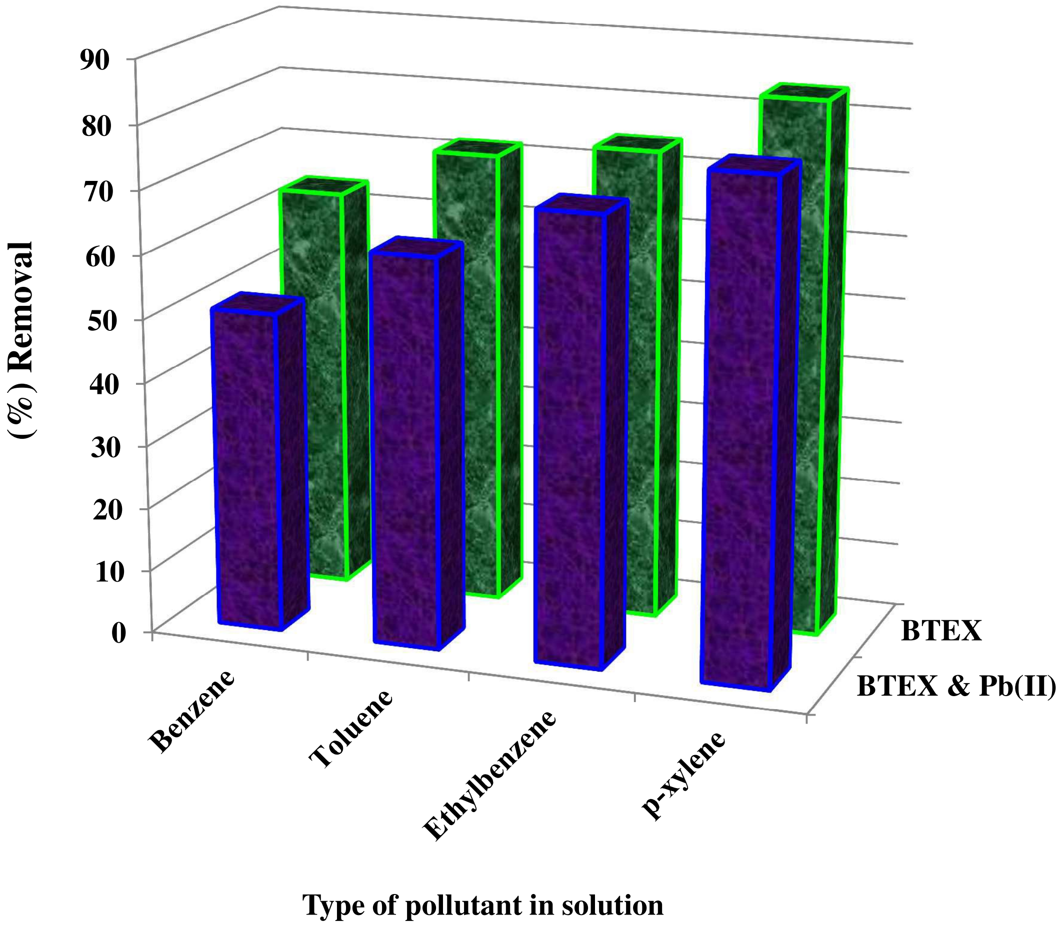


Fig. 11. , Adsorption of Pb(II) and BTEX by OBW-NaOH-CA in a binary solution with initial pH 7.0. Experimental error: ±2%.

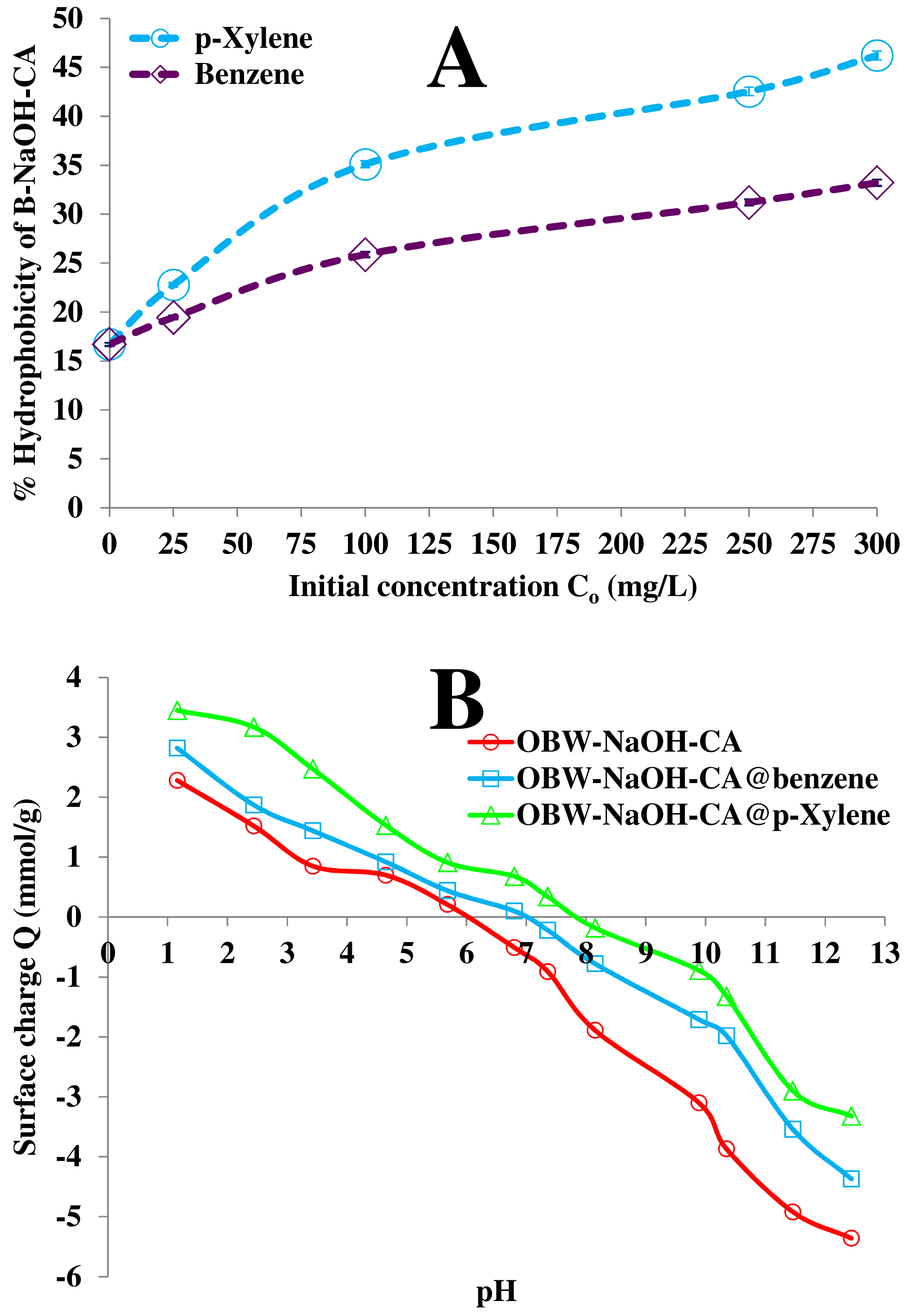


Fig. 12. The % hydrophobicity and Zeta potential of OBW-NaOH-CA after adsorption of benzene and *p*-xylene.

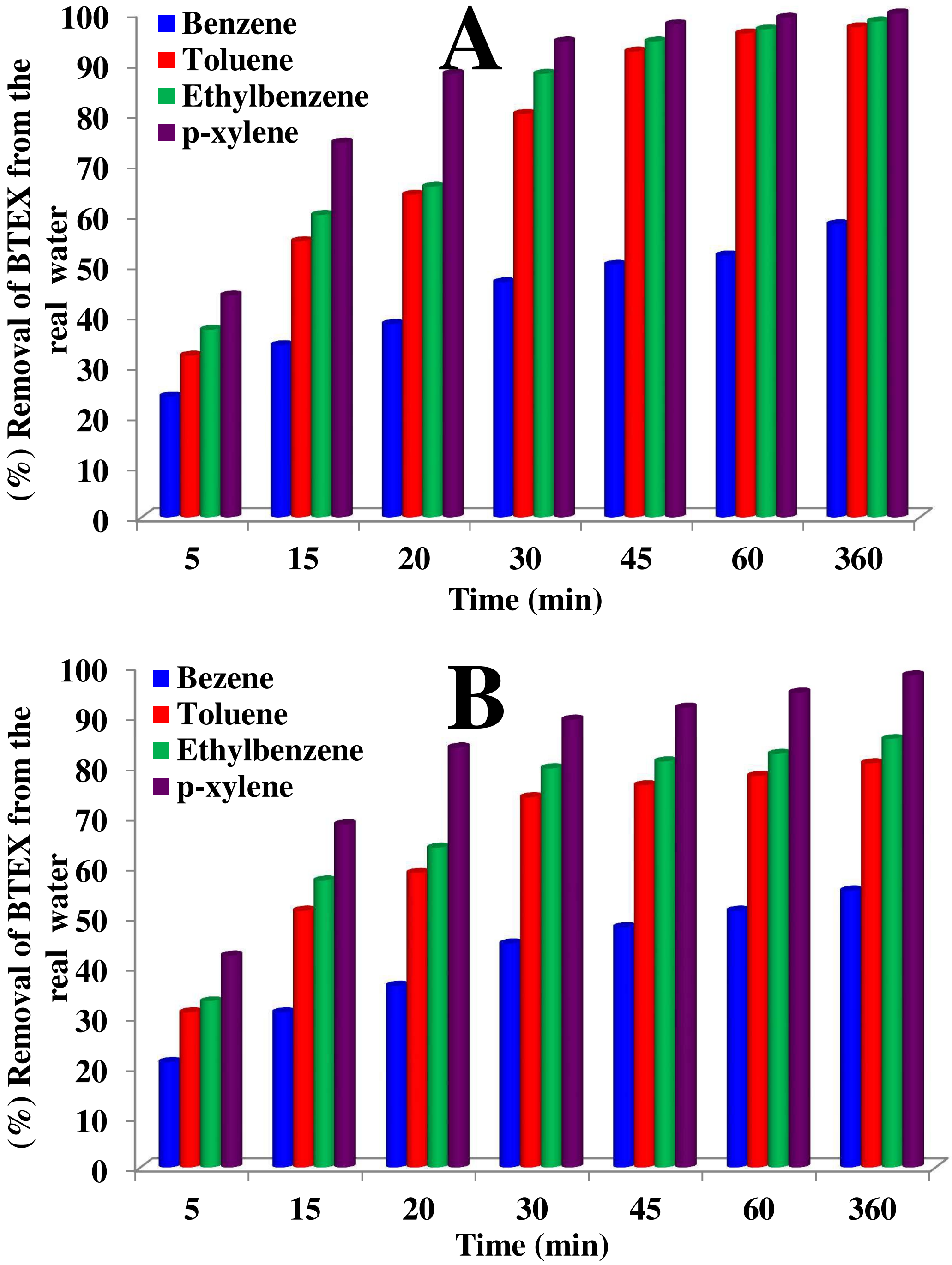


Fig. 13. BTEX removal from Persian Gulf water at initial concentrations of 25 mg/L (A) and 80 mg/L(B) after exposure to OBW-NaOH-CA at varying times. Experimental error: ±2%.

Table

Table 1. The physicochemical properties of the bone samples.

Table 2. The effect of citric acid concentration levels on hydrophobicity percentage and immobilized amount of citric acid on the pristine ostrich bone waste.

Table 3. Kinetic parameters for the adsorption of BTEX by OBW-NaOH-CA.

Table 4. Fitting of the parameters of the experimental results to the Langmuir and Freundlich equation parameters.

Table 5. Thermodynamic parameters for the adsorption of BTEX onto the OBW-NaOH-CA as a function of temperature.

Table 6. Impact of Pb(II) on BTEX adsorption by OBW-NaOH-CA.

Table 7. Comparisons in BTEX adsorption of various adsorbents.

Table 1. The physicochemical properties of the bone samples.

	POBW	OBW-NaOH	OBW-NaOH-CA
Total surface area (m^2/gr)	3.69	14.21 m^2/gr	17.73 m^2/gr
Average pore size[a] (Å)	43.22	63.7	67.43

[a] The pore size calculated using the BJH method.

Table 2. The effect of citric acid concentration levels on hydrophobicity percentage and immobilized amount of citric acid on the pristine ostrich bone waste.

Citric acid (wt. %)	Hydrophobicity of B-NaOH-CA (% weight)	The immobilized amount of citric acid (meq/g)
0	29.8 ± 0.3	0.0
1	27.5 ±0.7	0.051
2	25.6 ±0.4	0.078
4	24.6 ±0.6	0.107
5	21.2 ±0.2	0.135
7	19.5 ±0.4	0.168
8	16.7 ±0.7	0.195
10	15.5 ±0.5	0.222
11	15.1 ±0.4	0.231
12	14.9 ±0.3	0.249
15	13.6 ±0.1	0.258
20	13.2 ±0.5	0.271
25	12.3 ±0.8	0.298
30	12.2 ±0.5	0.320

Table 3. Kinetic parameters for the adsorption of BTEX by OBW-NaOH-CA.

System	First-order model			
	k_1(min^{-1})		q_1 (mg/g)	R^2
Benzene	1.261		130.54	0.9453
Toluene	1.40		131.23	0.8528
Ethylbenzene	1.214		159.23	0.8290
p-xylene	1.480		148.80	0.7375
System	Second-order model			
	k_2 (mg/(g min))	q_2 (mg/g)	h (mg/(g min))	R^2
Benzene	0.0034	168.9	98.03	0.9999
Toluene	0.0018	193.8	69.30	0.9999
Ethylbenzene	0.0017	204.9	73.58	0.9998
p-xylene	0.0011	239.2	67.29	0.9998
System		Inter-particle model		
		K_{int} (mg/(g min$^{1/2}$))		R^2
Benzene		4.309		0.3648
Toluene		5.409		0.4386
Ethylbenzene		5.571		0.4268
p-xylene		7.238		0.5084

Table 4. Fitting of the parameters of the experimental results to the Langmuir and Freundlich equation parameters.

System	q_m	K_L	K_F	n	R^2	Sorption model[a]
OBW-NaOH-CA						
Benzene	297	5.08×10^{-5}			0.9567	L
			0.445	0.295	0.9570	F
Toluene	328	8.91×10^{-3}			0.9726	L
			0.580	0.252	0.9408	F
Ethylbenzene	360	1.57×10^{-2}			0.9562	L
			0.664	0.233	0.9101	F
p-xylene	425.1	4.38×10^{-2}			0.9632	L
			0.951	0.189	0.8187	F
OBW-NaOH						
Benzene	77.6	3.91×10^{-3}			0.9870	L
			0.113	0.657	0.9320	F
Toluene	71.2	7.46×10^{-3}			0.9888	L
			0.133	0.597	0.8711	F
Ethylbenzene	78.8	8.54×10^{-3}			0.9881	L
			0.148	0.560	0.8400	F
p-xylene	100.2	6.96×10^{-3}			0.9909	L
			0.164	0.529	0.8837	F
POBW						
Benzene	1.33	3.66×10^{-3}			0.9913	L
			0.006	1.00	0.9278	F
Toluene	1.37	4.01×10^{-3}			0.9888	L
			0.007	1.00	0.9119	F
Ethylbenzene	1.831	3.11×10^{-3}			0.9900	L
			0.008	1.00	0.9398	F
p-xylene	4.83	3.34×10^{-3}			0.9905	L
				1.00	0.9322	F

[a] Legends: Langmuir; L and Freundlich; F.

Table 5. Thermodynamic parameters for the adsorption of BTEX onto the OBW-NaOH-CA as a function of temperature.

System	ΔH^o (J/mol)	ΔS^o (J/(mol K))	$-\Delta G^o$ (kJ/mol)			
			288	298	312	353
Benzene	19.67	68.83	19.803	20.491	21.455	24.277
Toluene	12.21	47.71	13.728	14.205	14.873	16.829
Ethylbenzene	38.21	134.52	38.703	40.048	41.932	47.447
p-xylene	43.27	156.80	45.115	46.683	48.878	55.307

Table 6. Impact of Pb(II) on BTEX adsorption by OBW-NaOH-CA.

System	Kd(L/kg)	Inhibition (%)
Benzene	1.76	
Benzene & Pb(II)	1.02	42.07
Toluene	2.54	
Toluene & Pb(II)	1.59	37.28
Ethylbenzene	2.89	
Ethylbenzene & Pb(II)	2.34	19.03
p-Xylene	5.23	
p-Xylene & Pb(II)	3.52	32.73

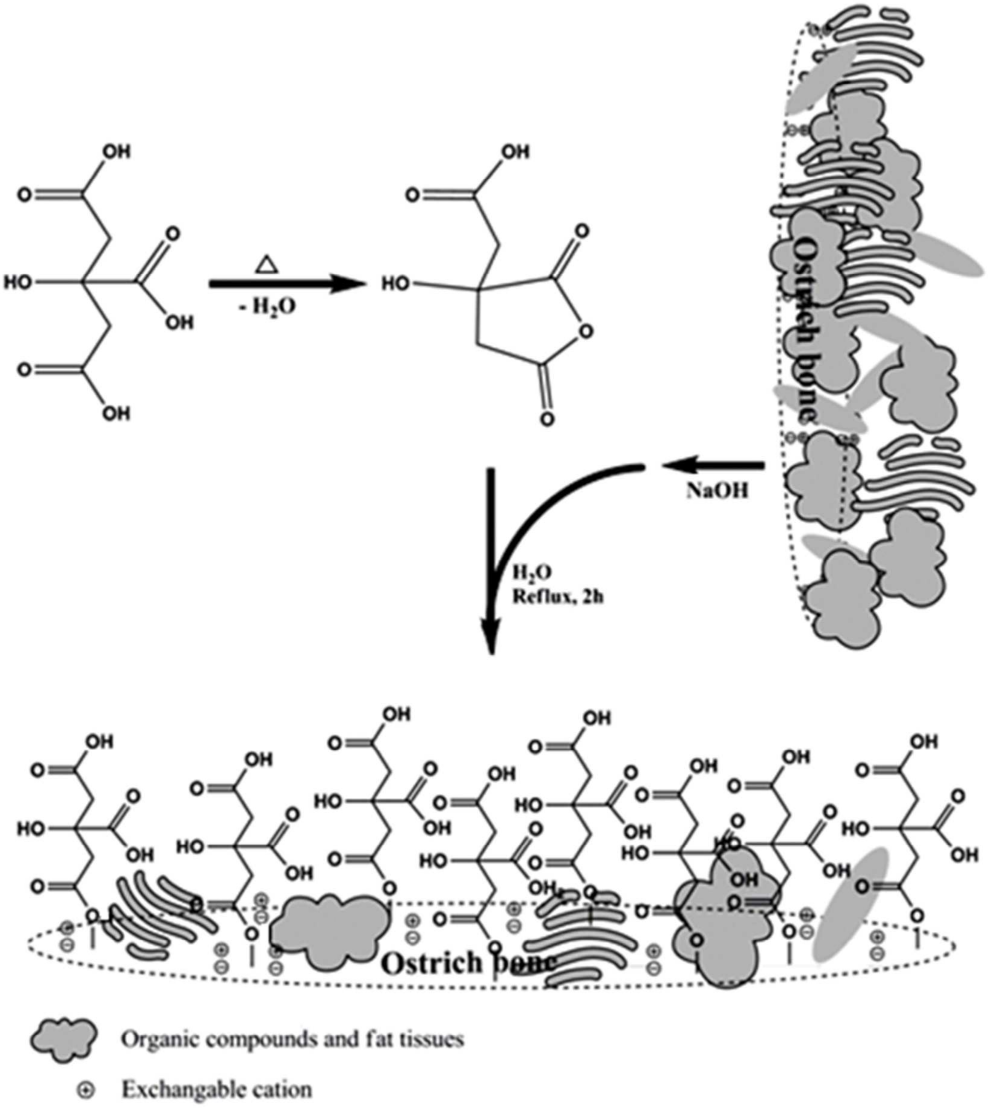
Table 7. Comparisons in BTEX adsorption of various adsorbents

Adsorbents[a]	q_e (mg/g)[b]				Conditions[c]	Refs.
	Benzene	Toluene	Ethylbenzene	p-xylene		
GAC	217.32	221.1	250.6	301.4	pH 7, T: 298	14
CNT(NaOCl)	247.9	279.8	342.7	413.77	pH 7, T: 298	14
SWCNT(NaOCl)	60.1	103.2	-	-	pH: 7, T: 303	26
GAC	183.3	194.1	-	-	pH: 7, T: 303	26
GAC(HNO3)	114.4	122.3	-	-	pH: 7, T: 303	26
ACF	85	237	-	-	pH: 7, T: 303	26
SWCNT	-	-	-	77.5	pH: 5.4, T: 298	31
SWCNT(HNO3)	-	-	-	85.5	pH: 5.4, T: 298	31
CNT	18.1	80.1	81.1	147.8	pH: 7, T: 298	36
CNT(NaOCl)	230.7	252.1	261.2	318.3	pH: 7, T: 298	36
MWCNT(NaOCl)	36.2	-	-	-	pH: 7, T: 298	37
CNTs-KOH	87.12	322.0	-	-	pH 6, T: 293	38
CNTs-3.2%O	-	99.47	115.63	-	pH 7 T: 283	39
OBW-NaOH-CA	297	328	360	425	pH 7, T: 298	This work

[a] SWCNT = single-walled carbon nanotube; MWCNT = multi-walled carbon nanotube;GAC = granular activated carbon; ACF = activated carbon fiber. [b] Maximum adsorption capacity calculated from Langmuir model. [c] T = temperature (K).

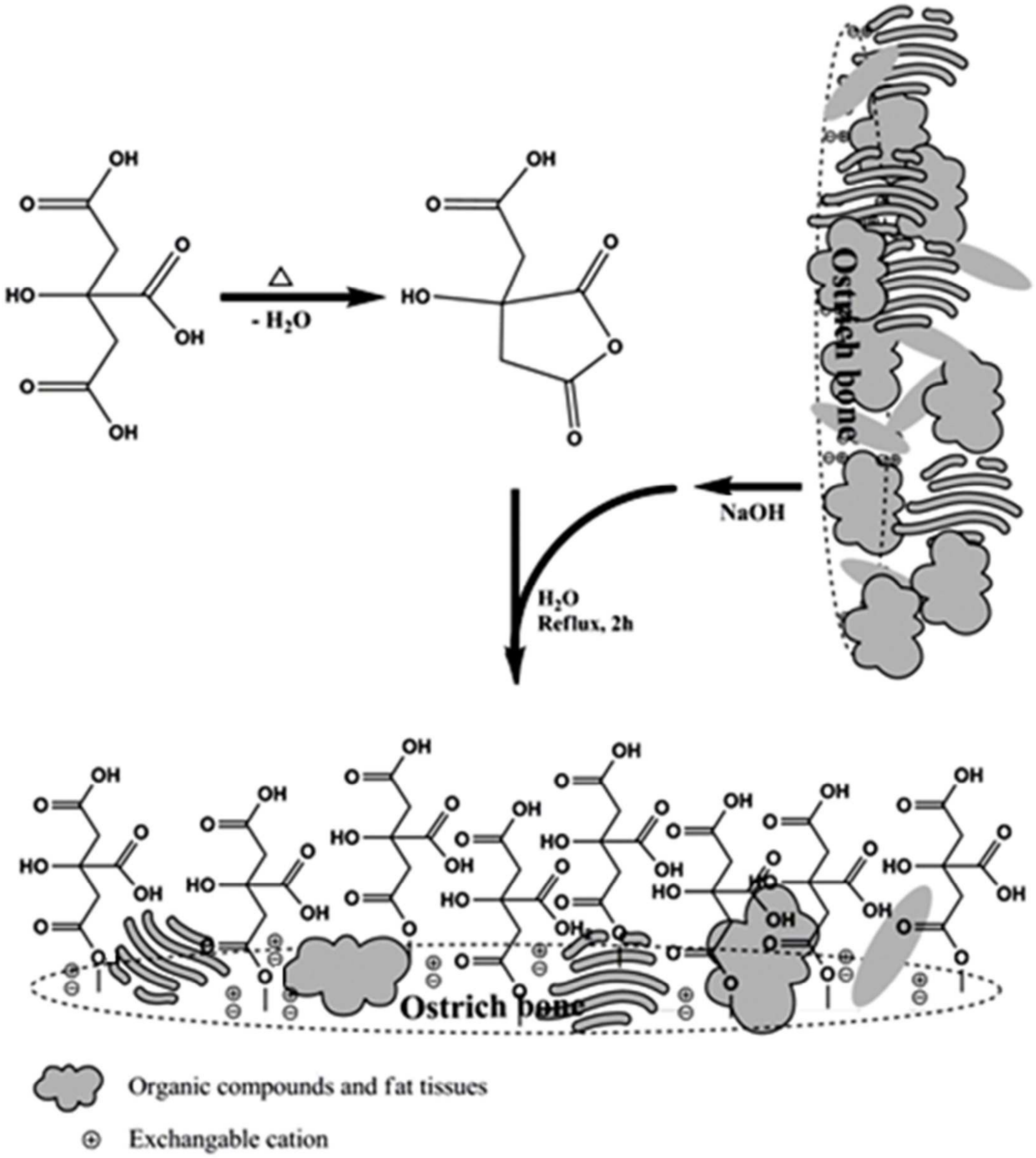
Schemes

Scheme 1.Chemical procedure for the immobilization of CA on OBW.



Scheme 1.Chemical procedure for the immobilization of CA on OBW.

Graphical Abstract



Chemically ostrich bone wastes (OBW) was modified with citric acid as bioadsorbent.

The uptake of benzene, toluene, ethylbenzene, and *p*-xylene (BTEX) were studied.

The immobilized CA on OBW shifted the surface charge towards negative value.

Order of BTEX removal on OBW-NaOH-CA was *p*-xylene > ethylbenzene > toluene > benzene

The adsorption mechanism of BTEX by the green adsorbent (OBW-NaOH-CA) was studied.