

Water Pollutants Adsorption through an Enhanced Activated Carbon Derived from Agriculture Waste

Mojtaba Fazeli^a, Mohammad Javad Kazemi Balgeshiri^a, Abolghasem Alighardashi^{*a}

^aDepartment of water and wastewater engineering, School of Water and Environmental Engineering, University of Shahid Beheshti, Tehran, Iran.

*Correspondence should be addressed to Mr. Abolghasem Alighardashi, Email: a_ghardashi@sbu.ac.ir

A-R-T-I-C-L-E-I-N-F-O

Article Notes:

Received: April 19, 2016

Received in revised form:
June 28, 2016

Accepted: Aug 3, 2016

Available Online: Sep 28,
2016

Keywords:

Nitrate
Arsenic
Walnut Shells
Adsorption
Activated Carbon
Agriculture Waste
Iran.

A-B-S-T-R-A-C-T

Background & Aims of the Study: A high nitrate and arsenic concentration in water resources represent a potential risk to the environment and public health. The present work improved a chemo-physically modified activated carbon derived from walnut shells as an adsorbent to improve nitrate and arsenic removal ability from water.

Materials & Methods: To increase removal efficiency, activated carbon surface characteristics were improved by acidification. Chemical activation was achieved when the carbon was mixed with water and 5% (v/v) phosphoric acid. After adsorbent preparation, the contact time, pH and the initial concentration were studied as variables.

Results: The effective pH for adsorption onto activated carbon was 6.5. The results indicated that 70 s and 3 mins was the sufficient time to attain equilibrium for a maximum removal efficiency of 78.44% and 98% for nitrate and arsenic, respectively. The adsorption capacity of the adsorbent was 10.60 mg nitrate/g carbon and 120 µg arsenic/g carbon. Removal obeyed the Langmuir isotherm and pseudo-second-order kinetic model.

Conclusion: The results showed a noticeable improvement in activated walnut-shell carbon absorbance (improvement in crystalline structure, chemical bonds, and morphology of micropores) by chemo-physical activation. Chemo-physical activation increased the surface area of the adsorbent from 1067 to 1437 m²g⁻¹ and decreased the mean pore size from 3.28 to 2.08 nm. The characterization results showed the major reasons of adsorption could be structure, size and distributions of pores, high surface area and chemical bonds.

Please cite this article as: Fazeli M, Kazemi Balgeshiri MJ, Alighardashi A. Water Pollutants Adsorption through an Enhanced Activated Carbon Derived from Agriculture Waste. Arch Hyg Sci 2016;5(4):286-294.

Background

Nitrate ions (NO₃⁻) are stable form of nitrogen that naturally emerge in the N-cycle for oxygenated systems and are considered as prime concerns on a global scale (1). Its high concentration in water resources represents a potential risk to the environment and public health in the form of eutrophication in the bodies of water, Methemoglobinemia, cancer and formation of hazardous nitrosamine chemicals (2). The recommended level in the

recently-revised WHO guidelines for drinking water of 50 mg/l nitrate was derived to protect human health (3). Nitrate can be removed from water by ion-exchange resin, biological and chemical denitrification, chemically by zero-valent iron (ZVI), electrocoagulation, electrodialysis, catalytic denitrification and reverse osmosis (4,5). Each process has its own strength and limitations. Most are expensive and generate additional by-products. These technologies also generate concentrated NO₃⁻ waste streams that do not reduce the excess

NO_3^- in the environment and pose a disposal problem caused by its high saline content (6). Also, heavy metals pollution is an important environmental problem due to its high toxicity and carcinogenicity (7). Health risks like skin conjunctivitis, vascular, reproductive, neurological effects, internal cancers and diabetes can increase the effect of long-term exposure through drinking water. Arsenic has been determined to be a human carcinogen by the US EPA and World Health Organization. Therefore, it has been set-up 0.01 mg/L for drinking water (8). Several methods of arsenic removal are already available including precipitation, adsorption, ion exchange, solvent extraction, nano filtration, foam flotation and biological sequestration (9).

Adsorption is convenient, simple to design and operate; it is considered the best for water treatment (10). It has been found successful for removal/minimizing organic and inorganic pollutants (11) such as nitrate (12), N-nitrosamine (13), phosphate (10), fluoride (14), arsenic (15), cadmium, copper, zinc ions (16), strontium (17) and other heavy metals. Studies have reported adsorption of NO_3^- by adsorption method, but it shows poor adsorption and requires a lengthy interval time for nitrate pollutants. In the last two decades adsorption with iron oxide, activated carbon etc. has been identified as one of the most important processes for controlling arsenic mobility (18). Activated carbon (AC) from agricultural waste has a high adsorption capacity, considerable mechanical strength and low ash content. Attempts have been made to obtain low-cost adsorbent from agricultural waste such as pecan shells, almond shells, peach pits and olive pits (6). Removal of specific types of contaminants could be possible in the future with modification of the surface of the AC (19). AC contains micro pores that improve adsorption efficiency and mass transference (6).

Aims of the study:

Iran ranks fourth in walnut production worldwide, producing about 290000 metric tons

of walnuts per year, consequently, walnut shells as an agricultural by-product (20). In similar studies, the efficiency of nitrate and arsenic removal has been markedly low and the contact time markedly high. The present research puts forward a simple chemo-physically modified AC derived from walnut shells as a readily-available adsorbent material for treatment of nitrate and arsenic contaminated aqueous solutions. The study characterizes the adsorbent, but the effect of contact time, pH, initial nitrate and arsenic concentration were beyond the scope of this essay.

Materials & Methods

Materials and Chemicals

All chemicals were purchased from Merck (Germany). Ultra-pure water was used to prepare and dilute the nitrate and arsenic solutions.

Instruments

The pH values were measured with a Hatch HQ 40d multi-parameter device. Scanning electron microscopy (SEM) was performed, using a Tescan Vega II. The concentration of the nitrate ions and arsenic were measured, using a Metrohm 850 professional IC ion chromatography system and Inductively Coupled Plasma (ICP) Varian-710, respectively. The Brunauer-Emmett-Teller (BET) test was carried out, using a BELsorp mini-II with N_2 gas and 150 mA current sensor. Fourier transform infrared spectrophotometry (FT-IR) was carried out on a Bruker Tensor 27 spectrophotometer.

Preparation and activation of adsorbent

Firstly raw walnut shells were dried in sunlight; then crushed and washed to remove the impurities. The material was dried over the night in an oven at 110°C. The material was loaded into an electric furnace and the temperature was ramped up from temperature room to 600°C at a rate of 10°C/min. To activate the samples, they put into a furnace in a

water stream at 1000°C then sieved with size 50 meshes (0.3 mm). The physically activated walnut shells (PAWS) carbon production was stored safely from moisture. To prepare the modified activated walnut shell (MAWS) carbon, the PAWS carbon was mixed with 5% H_3PO_4 and stirred continuously, using a magnetic stirrer for 30 min. After that, the chemo-physical AC was washed with hot ultra-pure water until the pH of the filtrating solution became neutral. Next, the samples were dried over the night at 120°C and then placed in a dry place.

Results

The maximum of nitrate and arsenic removal occurred in 70 seconds (exceeding 67%) (Fig 1) and 3 minutes (98%) (Fig 2), respectively.

The effect of pH of the solutions with optimal contact times was measured. Maximum nitrate removal was occurred in the pH range 6.5 to 8. The removal efficiency in the range was 83% and the maximum arsenic removal was occurred in the pH range 6 to 6.5. The percent removal in the range was 98%.

The effect of initial concentration on optimum contact time and pH on nitrate and arsenic removal tested. The amount of nitrate and arsenic adsorbed at equilibrium of the adsorption index (q_e) are 7.8 mg nitrate/g adsorbent and 32.2 μg arsenic/gr adsorbent as the concentration are 120 mg/l nitrate with the removal percentage of 78.44% and 120 $\mu\text{g/l}$ arsenic with removal percentage of 98%.

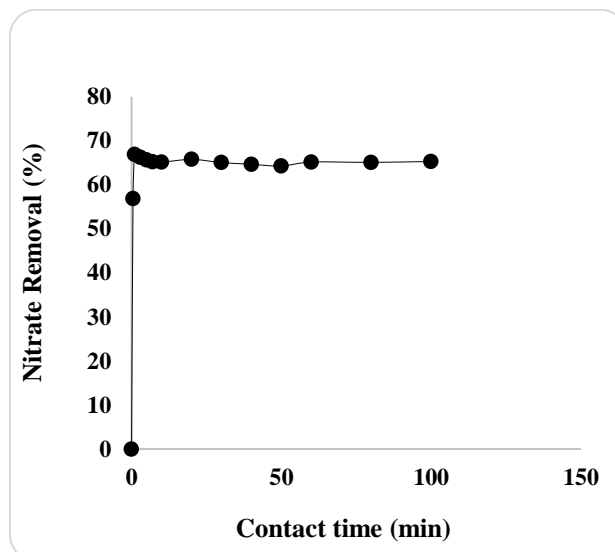


Figure 1) Effect of contact time on nitrate adsorption

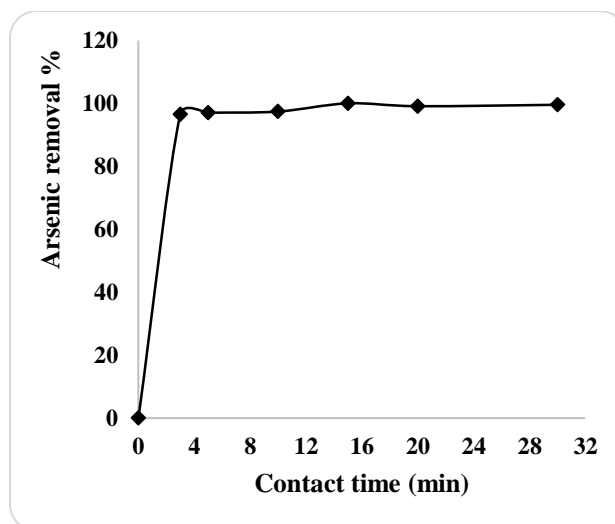


Figure 2) Effect of contact time on arsenic adsorption

Adsorption Equilibrium

The experimental nitrate and arsenic adsorption isotherm for the MAWS adsorbent are shown in

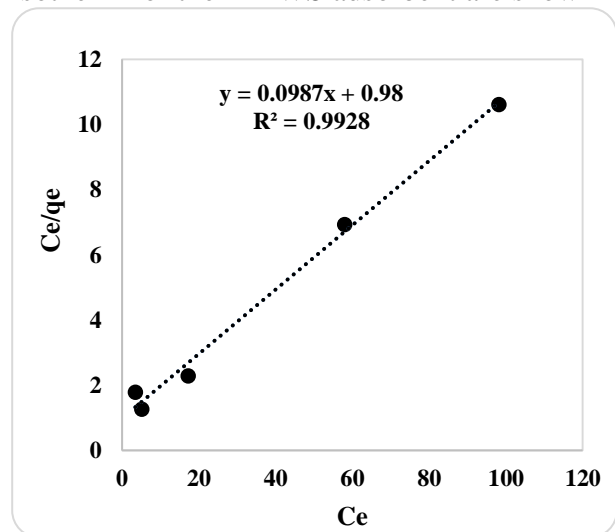


Figure 3 and 4. The linear plot of the equation isotherm shows that the adsorption obeyed the Langmuir model (Table 1).

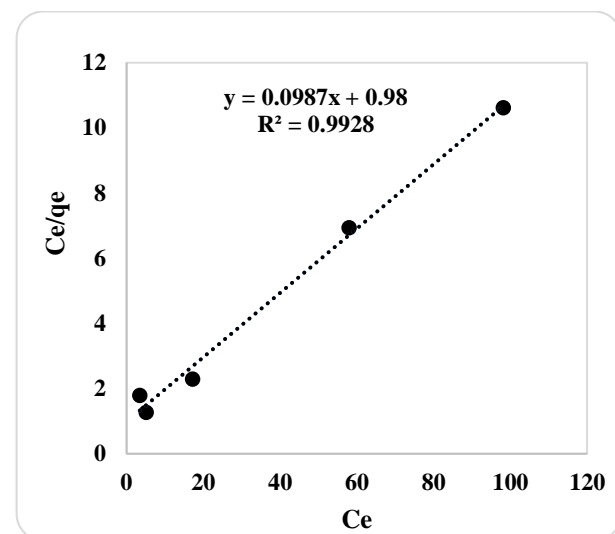


Figure 3) Langmuir isotherm of nitrate adsorption.

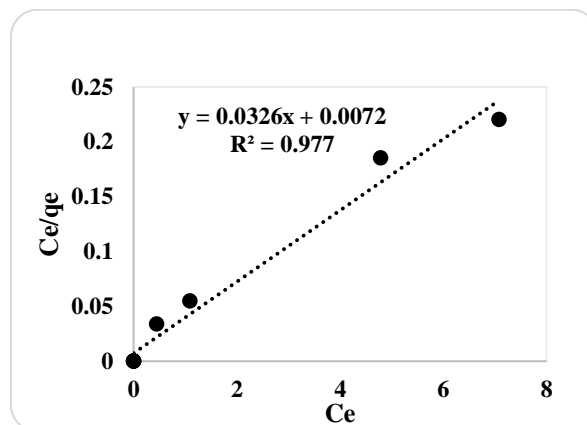


Figure 4) Langmuir isotherm of arsenic adsorption.

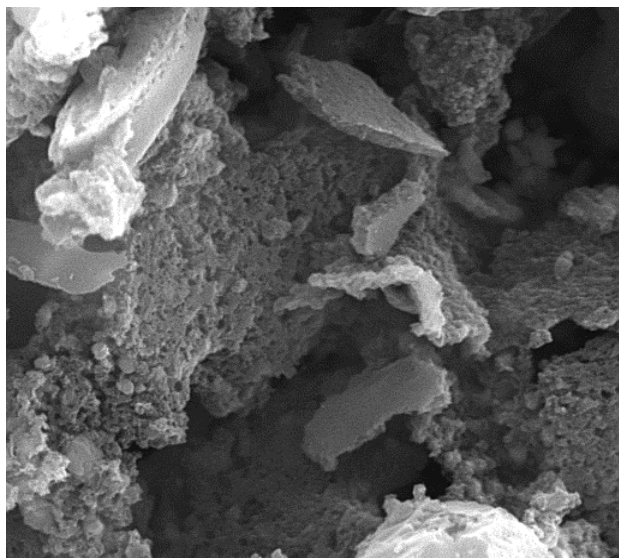
Table 1) Langmuir Isotherm constants for nitrate and arsenic adsorption.

	q_m (mmol/g)	b (L/mmol)	R^2
nitrate	0.1	10.13	0.992
arsenic	4.572	30.674	0.997

Characterization

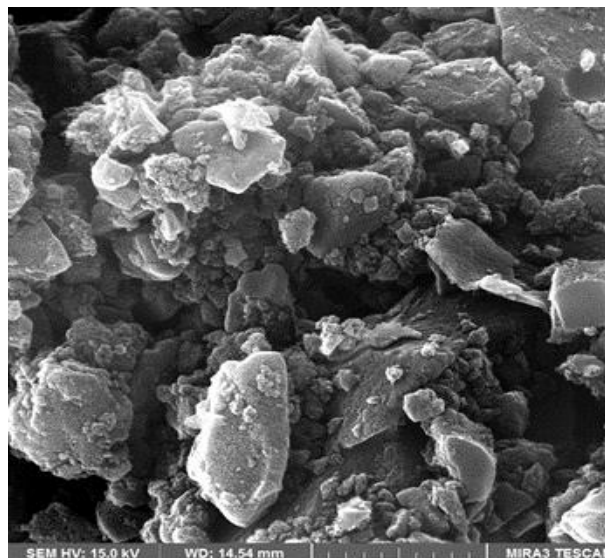
SEM was used to examine the physical morphology of the surface of the activated carbon. SEM images of the chemo-physical activated adsorbent are shown in Figure 5 and 6.

The characteristics of the activated carbon and textural characteristics of the samples were determined. The BET surface area analysis plots are shown in Figure 7 and the data is shown in table 2.



SEM MAG: 15.00 kx Det: SE
SEM HV: 15.00 kV WD: 8.786 mm
Date(m/d/y): 10/31/13 Vac: HiVac
VEGA3 TESCAN
2 µm
RMRC

Figure 5) Scanning Electron Micrographs (SEM) of the PAWS adsorbent



SEM HV: 15.0 kV WD: 14.54 mm
View field: 6.92 µm Det: SE
SEM MAG: 30.0 kx Date(m/d/y): 07/08/14
MIRA3 TESCAN
2 µm
RMRC

Figure 6) Scanning Electron Micrographs (SEM) of the MAWS adsorbent

Table 2) Surface area analysis of MAWS and PAWS adsorbents

Parameter	Specific area (m ² /g)	Max. diameter (mm)	Mean Pore Size diameter (nm)	total pore volume (P/P ₀ =0.990) (cm ³ /g)
MAWS	1434.6	>1.21	2.08	0.747
PAWS	1067.4	1.22<	3.23	0.864

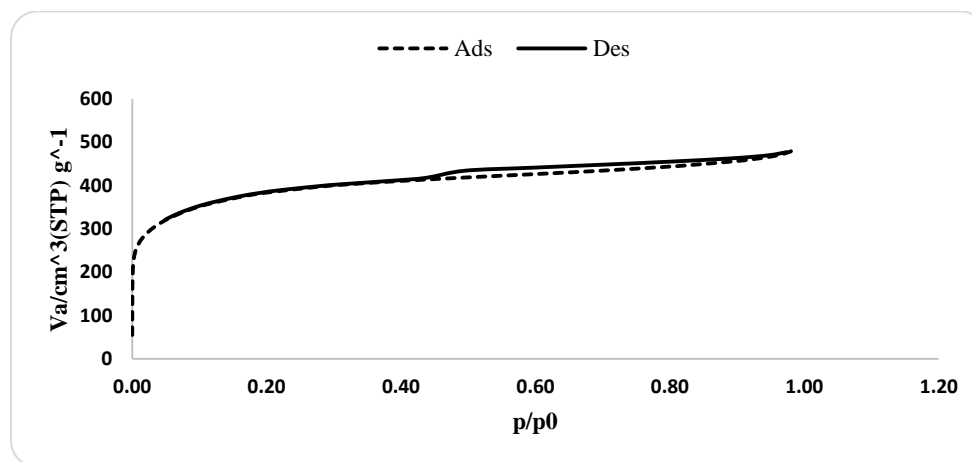


Figure 7) Nitrogen adsorption/desorption isotherm for activated carbon

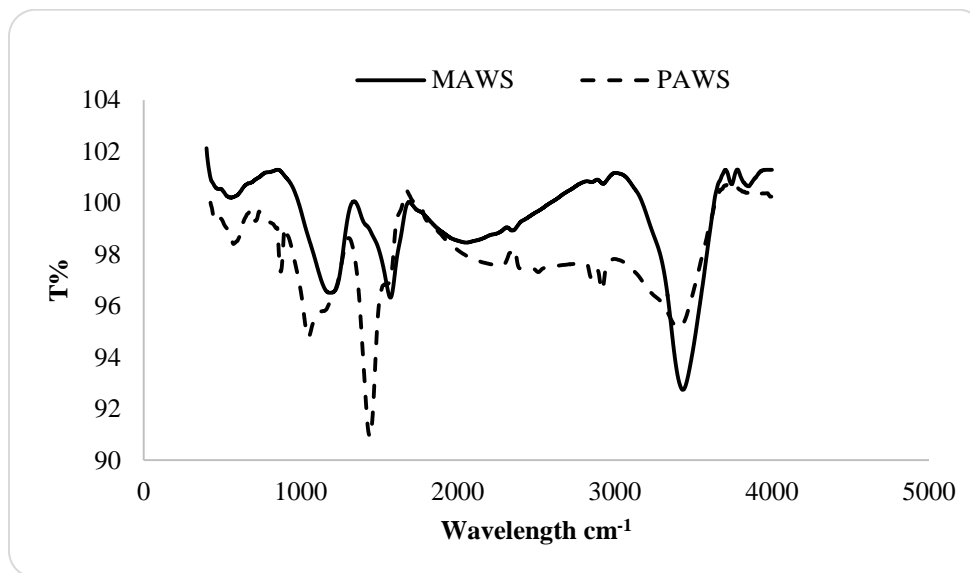


Figure 8) FT-IR spectra of MAWS and PAWS adsorbent samples

FT-IR spectroscopy Figure 8 was carried out to analyze the effect of acid erosion and the changes in the structure of the walnut shells as a result of modification by acid activation. The samples were measured to be 400 to 4000 cm^{-1} , using KBr pellets. FT-IR spectroscopy is very sensitive in the modification of walnut shell structure after acid treatment.

Significant changes were visible in the functional group after acid modification of primary activated carbon.

Discussion

The obtained data of nitrate and arsenic removal have been shown the removal percentage increased directly with an increased contact time. In comparison with similar research works, the optimum contact time with practically removal efficiency is specifically less than reported results. Surface charge is an important factor for the adsorption phenomena on activated carbon and it is very much dependent on the pH of the solution. The results demonstrated that the removal percentage decreased as the solution nitrate concentration increased. At higher concentrations, more nitrate and arsenic ions remained in the

dissolved phase because of the saturation of adsorption sites. Experimental adsorption isotherm obeys the Langmuir model for both of them. The pseudo-second-order kinetic model is explaining the adsorption kinetics of the present adsorption process.

The micrograph shows large cavities and is very irregular, indicating that the porosity of the material was produced by acid erosion during activation. A combination of physical and chemical activation resulted in the creation of more pores and substantial removal of contaminants. The bulk density and apparent density increased with chemo-physical activation.

The pore size distribution (PSD) represent a model of solid's internal structure, which assumes that an equivalent set of non-interacting and regularly shaped model pores can represent the complex void spaces within the real solid. PSD is related to both kinetic and equilibrium properties of porous material and is one of the most important aspects for characteristics of industrial applicable sorbents. Activated carbon possessed a combination of type I and type II adsorption/desorption isotherms (based on IUPAC classification).

This combination is indicated the simultaneous presence of micropores and mesopores as demonstrated by Prahas *et al.* (21) (Fig 2.)

An evident decrease was observed in the C–O stretching vibrations ($\sim 1200\text{ cm}^{-1}$), such as those for phenol and hydroxyl groups and the (N–H) band at about 1600 cm^{-1} . An increase in the hydroxyl (O–H) stretching band at $3400\text{--}3440\text{ cm}^{-1}$ as mentioned (12,22) reflects acidification. When high amounts of free carboxyl groups were introduced, it can be concluded that acid modified primary activated carbon presented adequate physical and chemical properties to adsorb the ions. Fig 3 shows all the sharp peaks after adsorption decreased in, probably as the result of nitrate adsorption onto the adsorbent by an electrostatic attraction between the (N–H) and C–O bonds with NO_3^- and As. Sharp decreases at about 1200 and 1600 cm^{-1} and increases at

3430 to 3440 cm^{-1} after acidification. As the hydroxyl increased, nitrate and arsenic were adsorbed onto the surface adsorbent by electrostatic attraction and ion exchange (12,23).

Table 3 and 4 compare the results of the present study with those from previous studies and indicates that nitrate and arsenic removal efficiency were much higher than for similar works. Despite the comparable nitrate and arsenic removal efficiency of the various types of AC(q in Table 3,4), the MAWS adsorbent required less adsorbent and less contact time for maximum removal efficiency. After chemophysical activation, the surface of the MAWS adsorbent was positively charged and the nitrate and arsenic ions established chemical bonds with it.

Table 3) Comparison of optimum conditions for nitrate removal by three different types of activated carbons

Adsorbent type	capacity	Temperature (°C)	Initial concentration (mg/l)	pH	Contact time	reference
Walnut shell	10.60 mg/g	25	25–200	~7	70secs	this study
H ₂ SO ₄ treated carbon cloth	2.03mmol/g	25	115	7	1hr	(24)
ZnCl ₂ treated coconut	10.2 mg/g	25	5–200	~5.5	2hrs	(19)
Powdered activated carbon	10 mmol /g	25	5–100	<5.0	1hr	(25)
ZnCl ₂ treated sugar beet	9.14 mg/g	25	10–200	3	4hrs	(26)
Almond Shell	16 mg/g	20	100 -500	6.2	45mins	(27)

Table 4) Comparison of optimum conditions for arsenic removal by different types of activated carbons

Adsorbent type	capacity	Temperature (°C)	Initial concentration (mg/l)	pH	Contact time	reference
Walnut shell	120 µg/g.	25	25-200 µg/l	6.5	3 mins	This study
Pine wood char	125 µg/g.	25	1-1000ppb	3.5	24hrs	(28)
Iron oxide coated sand	43µg/L	22	100µg/L	7.6	6hrs	(29)
Activated carbons carbon	18.60 µmol/g.	25	5–20 mg/L	7	40mins	(30)

Conclusion

The surface area of walnut shell activated carbon can increase by chemo-physical activation process $1437 \text{ m}^2\text{g}^{-1}$ and the mean pore size of the adsorbent was 2.08 nm. Equilibrium and kinetic studies showed that the nitrate and arsenic removal process on walnut shell activated carbon obeys Langmuir isotherm and pseudo second order kinetic model. The results of this work demonstrate that walnut shell is an attractive source of raw material for preparing high quality activated carbon chemo-physical activation with H_3PO_4 . The synthesized adsorbent was characterized by FT-IR, BET analysis and SEM observation. The results showed a noticeable improvement in adsorption at minimum contact time by chemo-physical activation e.g. higher surface area, improvement in crystalline structure, chemical bonds and morphology of mesopores.

Footnotes

Conflict of Interest:

The authors declared no conflict of interest.

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