

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

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

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

**Background & Aims of the Study:** A high nitrate and arsenic concentration in water resources represents 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 was 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, initial concentration were studied as variables.

**Results:** The effective pH for adsorption onto activated carbon was 6.5. The results indicate that 70 s and 3 mins was sufficient time to attain equilibrium for a maximum removal efficiency of 78.44% and 98% respectively for nitrate and arsenic. 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 show 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 m<sup>2</sup>g<sup>-1</sup> and decreased the mean pore size from 3.28 to 2.08 nm. The characterization results show the major reasons of adsorption could be structure, size and distributions of pores, high surface area and chemical bonds.

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## Background

Nitrate ions (NO<sub>3</sub><sup>-</sup>) are a stable form of nitrogen that naturally Emerge in the N-cycle for oxygenated systems and are of 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 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 NO<sub>3</sub><sup>-</sup> waste streams that do not reduce the excess NO<sub>3</sub><sup>-</sup> 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 cause Long-term exposure through drinking water. Arsenic has been determined to be a class a human carcinogen by the US EPA and World Health Organization. Therefore, 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 operate, design and 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 sorption of  $\text{NO}_3^-$  by adsorption method, but it shows poor adsorption and requires a lengthy time interval for nitrate pollutants. In the last two decades adsorption with iron oxide, activated carbon and etc., has been identified as one of the most important processes 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 micropores 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 and, 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 chemically 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 and 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  $\text{N}_2$  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 and then crushed and washed to remove the impurities. The material was then dried overnight in an oven at  $110^\circ\text{C}$ . The material was loaded into an electric furnace and the temperature was ramped up from room temperature to  $600^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ . To activate the samples, samples 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 produced was stored safe 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. The chemo-physical AC was then washed with hot ultra-pure water until the pH of the filtrating solution became neutral. Next, the samples were dried overnight at 120°C and then placed in a dry place.

## Results

The maximum nitrate and arsenic removal occurs 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 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  $\mu$ g arsenic/gr adsorbent as the concentration are 120 mg/l nitrate with removal percentage was 78.44% and 120  $\mu$ g/l arsenic with removal percentage was 98%.

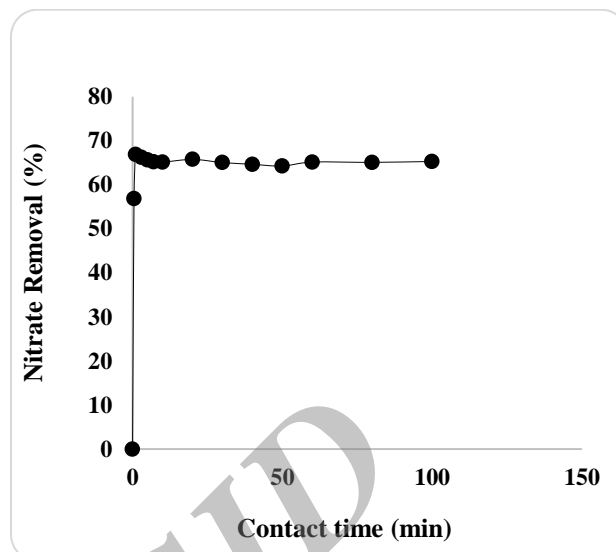


Figure 1) Effect of contact time on nitrate adsorption

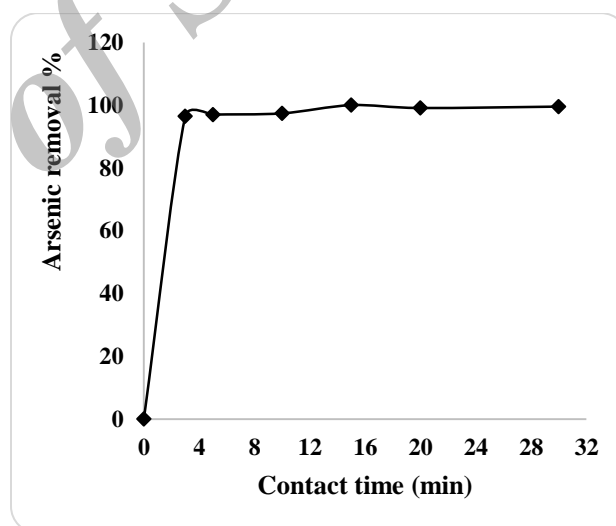


Figure 2) Effect of contact time on arsenic adsorption

## Adsorption Equilibrium

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

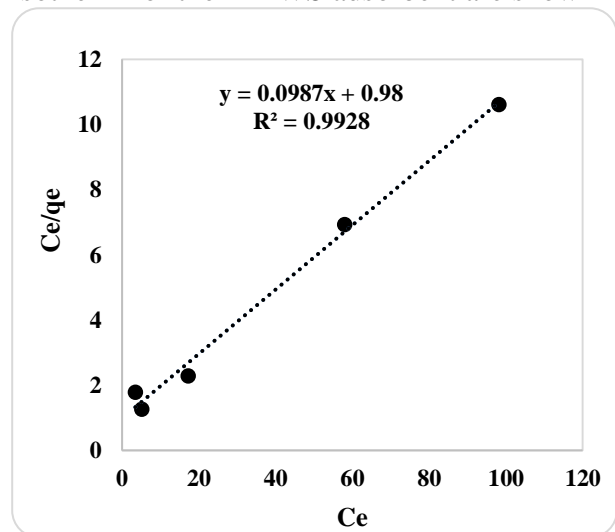


Figure 3 and 4. The linear plot of the equation isotherm shows that the adsorption obeyed the Langmuir model (Table 1).

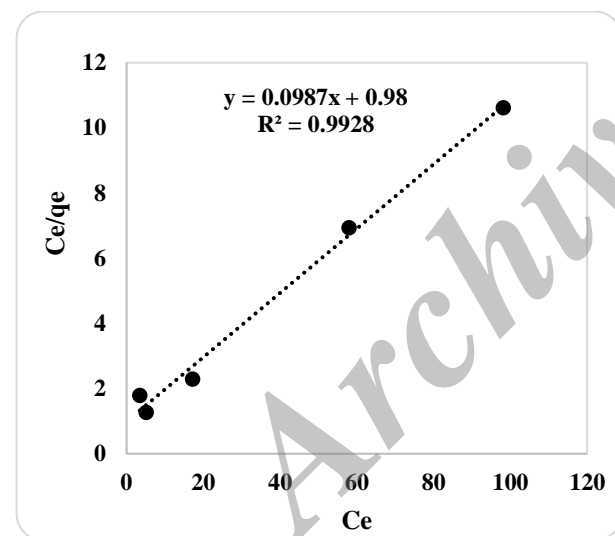


Figure 3) Langmuir isotherm of nitrate adsorption.

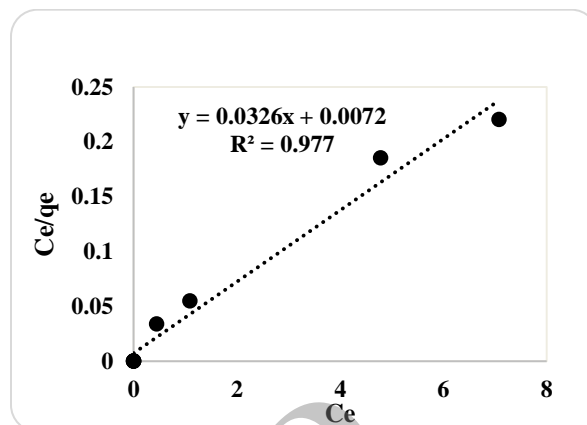


Figure 4) Langmuir isotherm of arsenic adsorption.

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 Fig 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.

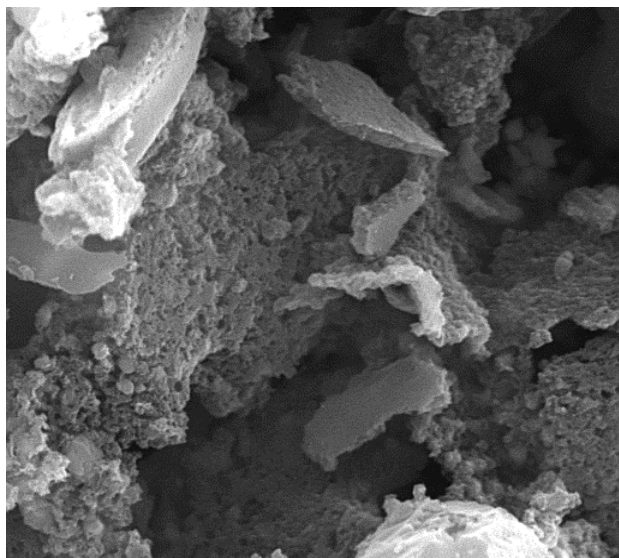


Figure 5) Scanning Electron Micrographs (SEM) of the PAWS adsorbent

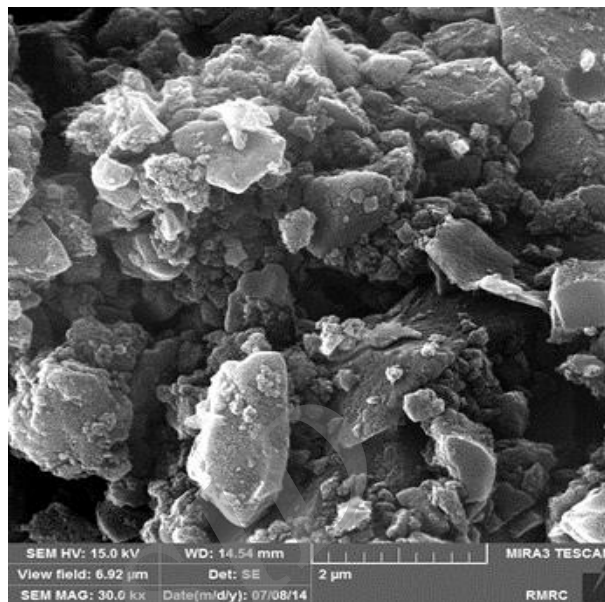


Figure 6) Scanning Electron Micrographs (SEM) of the MAWS adsorbent

Table 2) Surface Area Analysis of MAWS and PAWS adsorbents

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

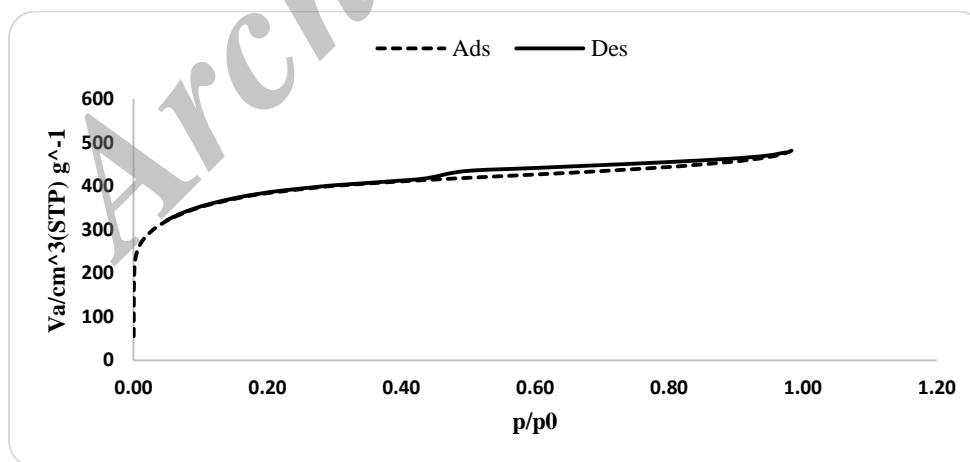


Figure 7) Nitrogen adsorption/desorption isotherm for activated carbon



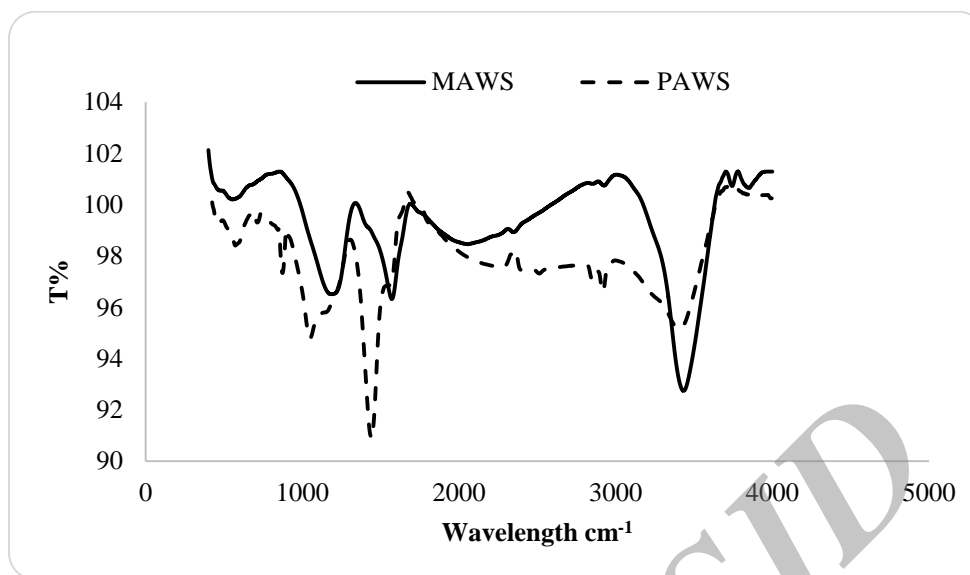


Figure 8) FT-IR spectra of MAWS and PAWS adsorbent samples

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  $\text{cm}^{-1}$  using KBr pellets. FT-IR spectroscopy is very sensitive to 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 and less of reported results. Surface charge is an important factor for the adsorption phenomena on activated carbon, and surface charge 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 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 indicative of the simultaneous presence of micropores and mesopores as demonstrated by Prahas *et al.* (21) (Figure 2.)

An evident decrease was observed in the C–O stretching vibrations ( $\sim 1200\text{ cm}^{-1}$ ), such as those for ether, phenol and hydroxyl groups, and the (N–H) band at about  $1600\text{ cm}^{-1}$ . 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 electrostatic attraction between the (N–H) and C–O bonds

with  $\text{NO}_3^-$  and As. Sharp decreases at about  $1200$  and  $1600\text{ cm}^{-1}$  and increases at  $3430$  to  $3440\text{ cm}^{-1}$  after acidification. As the hydroxyl increased, nitrate and arsenic was adsorbed onto the surface adsorbent by electrostatic attraction and ion exchange (12,23).

Table 3 and 4 compares the results of the present study with those from previous studies and indicates that nitrate and arsenic removal efficiency was 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	$\sim 7$	70secs	this study
$\text{H}_2\text{SO}_4$ treated carbon cloth	2.03mmol/g	25	115	7	1hr	(24)
$\text{ZnCl}_2$ treated coconut	10.2 mg/g	25	5–200	$\sim 5.5$	2hrs	(19)
Powdered activated carbon	10 mmol /g	25	5–100	$< 5.0$	1hr	(25)
$\text{ZnCl}_2$ 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
Walnutshell	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 2.08 nm. Equilibrium and kinetic studies show 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  $\text{H}_3\text{PO}_4$ . The synthesized adsorbent was characterized by FT-IR, BET analysis and SEM observation. The results show 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.

## References

- WHO. Nitrate and Nitrite in Drinking-water. Geneva. Switzerland: WHO Press; 2011.
- Bryan NS, Loscalzo J. Nitrite and Nitrate in human Health and Disease. Humana Press: Springer; 2011.
- WHO. Guidelines for Drinking water Quality (Forth Edition). Geneva, Switzerland: WHO Press; 2011.
- Mohseni-Bandpi A, Elliott DJ, Zazouli MA. Biological nitrate removal processes from drinking water supply-a review. *J Environ Health Sci Eng* 2013;11-35.
- Mukherjee R, De S. Adsorptive removal of nitrate from aqueous solution by polyacrylonitrile-alumina nanoparticle mixed matrix hollow-fiber membrane. *J Membrane Sci* 2014;466:281-92.
- Bhatnagar A, Sillanpää M. A review of emerging adsorbents for nitrate removal from water. *Chem Eng J* 2011;168(2):493-504.
- Sobhanardakani S ZR, Mohammadi MJ. . Removal of Ni(II) and Zn(II) from Aqueous Solutions Using Chitosan. *Arch Hyg Sci* 2016;5(1):47-55.
- USEPA. IRIS (Integrated Risk Information System) On-line Database Maintained in Toxicology Data Network (TOXNET) by the National Library of Medicine. USEPA (US Environmental Protection Agency). 1997.
- Yazdani MR, Tuutijärvi T, Bhatnagar A, Vahala R. Adsorptive removal of arsenic (V) from aqueous phase by feldspars: Kinetics, mechanism, and thermodynamic aspects of adsorption. *J Mol Liq* 2016;214:149-56.
- Lalley J, Han C, Li X, Dionysiou DD, Nadagouda MN. Phosphate adsorption using modified iron oxide-based sorbents in lake water: Kinetics, equilibrium, and column tests. *Chem Eng J* 2016;284:1386-96.
- Benjwal P, Kar KK. Simultaneous photocatalysis and adsorption based removal of inorganic and organic impurities from water by titania/activated carbon/carbonized epoxy nanocomposite. *J Environ Chem Eng* 2015;3(3):2076-83.
- Cho DW, Chon CM, Kim Y, Jeon BH, Schwartz FW, Lee ES, et al. Adsorption of nitrate and Cr (VI) by cationic polymer-modified granular activated carbon. *Chem Eng J* 2011;175:298-305.
- Wu Q, Shi H, Ma Y, Adams C, Jiang H, Wang J, et al. Removal of N-nitrosamine precursors in drinking



water system using adsorption methods. *Sep Purif Technol* 2015;156(3).

14. Lin K-YA, Liu Y-T, Chen S-Y. Adsorption of fluoride to UiO-66-NH<sub>2</sub> in water: Stability, kinetic, isotherm and thermodynamic studies. *Curr Opin Colloid Interface Sci* 2016;461:79-87.

15. Vitela-Rodriguez AV, Rangel-Mendez JR. Arsenic removal by modified activated carbons with iron hydro(oxide) nanoparticles. *J Environ Manag* 2013;114:225-31.

16. Bogusz A, Oleszczuk P, Dobrowolski R. Application of laboratory prepared and commercially available biochars to adsorption of cadmium, copper and zinc ions from water. *Bioresour Technol* 2015;196:540-9.

17. Hong HJ, Ryu J, Park IS, Ryu T, Chung KS, Kim BG. Investigation of the strontium (Sr(II)) adsorption of an alginate microsphere as a low-cost adsorbent for removal and recovery from seawater. *J Environ Manage* 2016;165:263-70.

18. Mishra T, Mahato DK. A comparative study on enhanced arsenic (V) & (III) removal by iron oxide and manganese oxide pillared clays from ground water. *J Environ Chem Eng* 2016;4(1).

19. Bhatnagar A, Ji M, Choi YH, Jung W, Lee SH, Kim SJ, et al. Removal of nitrate from water by adsorption onto zinc chloride treated activated carbon. *Sep Sci Technol* 2008;43(4):886-907.

20. Saadat S, Karimi-Jashni A. Optimization of Pb(II) adsorption onto modified walnut shells using factorial design and simplex methodologies. *Chem Eng J* 2011;173(3):743-9.

21. Prahas D, Kartika Y, Indraswati N, Ismadji S. Activated carbon from jackfruit peel waste by H<sub>3</sub>PO<sub>4</sub> chemical activation: Pore structure and surface chemistry characterization. *Chem Eng J* 2008;140(1-3):32-42.

22. Silverstein RM, Bassler GC, Morrill TC. Spectrometric identification of organic compounds. New York: Wiley Online Library; 2001.

23. Namasivayam C, Sangeetha D. Removal and recovery of nitrate from water by ZnCl<sub>2</sub> activated carbon from coconut coir pith, an agricultural solid waste. *Indian J Chem Technol* 2005;12(2):512-21.

24. Afkhami A, Madrakian T, Karimi Z. The effect of acid treatment of carbon cloth on the adsorption of nitrite and nitrate ions. *J Hazard Mater* 2007;144(1-2):427-31.

25. Khani A, Mirzaei M. Comparative study of nitrate removal from aqueous solution using powder activated carbon and carbon nanotubes. 2nd International IUPAC Conference on Green Chemistry, Russia; 2008.

26. Demiral H, Gündüzoğlu G. Removal of nitrate from aqueous solutions by activated carbon prepared from sugar beet bagasse. *Bioresour Technol* 2010;101(6):1675-80.

27. Rezaee A, Godini H, Dehestani S, Khavanin A. Application of Impregnated Almond Shell Activated Carbon by Zinc and Zinc Sulphide for Nitrate Removal from Water. *J Environ Health Sci Eng* 2008;5(2):125-30.

28. Mohan D, Pittman CU Jr, Bricka M, Smith F, Yancey B, Mohammad J, et al. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *J Colloid Interface Sci* 2007;310(1):57-73.

29. Thirunavukkarasu OS, Viraraghavan T, Subramanian KS. Arsenic Removal from Drinking Water using Iron Oxide-Coated Sand. *Water Air Soil Pollution* 142(1):95-111.

30. Budinova T, Petrov N, Razvigorova M, Parra J, Galiatsatou P. Removal of arsenic(III) from aqueous solution by activated carbons prepared from solvent extracted olive pulp and olive stones. *Ind Eng Chem Res* 2006;45(6):1896-901.