Al-Sibd Center
for Research and Scholarly Publishing

Iraqi Journal of Natural Sciences
and Nanotechnology IJNSN

Journal Homepage : https://publications.srp-center.iq/index.php/ijn

Synthesis, Characterization and Properties of Polyacrylonitrile (PAN) Fibers

Mahr A. Athal, [1*] Ali Q. Abdullah, [2] W.S. Hanoosh [3]

[1] College of Eudcation in Qurna, University of Basrah, Basra, Iraq
[2] Department of Physics, College of Science, University of Basrah, Basra, Iraq
[3] Department of Chemistry, College of Science, University of Basrah, Basra, Iraq

Corresponding Author: mahr.athal@uobasrah.edu.iq

Keywords:

PAN powder; PAN fiber; Tensile strength; TGA; DSC.

Abstract

From polyacrylonitrile (PAN)-based fiber, carbon fiber is usually made by going through three controlled processes: stabilization, carbonization, and graphitization. In this study, polyacrylonitrile was synthesized by a free radical polymerization at room temperature and characterized by FTIR, and the viscosity average molecular weight was calculated. Then PAN powder was converted to fibers by the electrospinning process, and heat treatment of PAN fiber was done at 280 °C under atmospheric air and at 800 °C under nitrogen atmosphere. The result showed that the stabilized PAN fibers (SPAN) changed in color and the mechanical strength was greater than that of unstabilized PAN fibers (30.4 °C for SPAN and 26.6 °C for unstabilized PAN). The thermal study evaluation was achieved by using TGA and DSC techniques, and the results showed that the SPAN was more thermally stable than PAN fiber. Also, the DSC study has shown that the PAN fiber was melted at 337 °C, while the SPAN was not melted.

Introduction

It is well acknowledged that the currently utilized carbon fibres are exclusively derived from polyacrylonitrile (PAN) precursors. PAN is a polymer with a chain of carbon atoms held together by a covalent bond (see figure 1). It is hard, non-soluble, and melts quickly [1, 2]. Carbon fibers derived from polyacrylonitrile (PAN) are more durable than those produced from alternative precursor materials [3, 4]. Polyacrylonitrile (PAN) fiber is responsible for approximately 90% of global carbon fibre production. Manufacturing PAN-based carbon fibres requires three distinct stages: electrospinning, stabilization, and carbonization [5]. PAN is very cohesive because the presence of a nitrile group results in strong dipole-dipole interaction. Most synthetic fibres are used in textile manufacturing, particularly in the creation of garments and technical textiles.

In recent years, there has been a growing interest in exploring novel fiber features, such as antibacterial and photocatalytic properties and electrical conductivity. Some polymer fibers, like polyaniline, polypyrrole, and polythiophene, have sensing properties but weak mechanical properties [6]. Thus, one of the solutions is to combine some of these polymers with other polymers, especially PAN, to increase their mechanical properties, facilitate their processing [7], and boost the PAN chain's stiffness, leading to increased tensile strength [8, 9]. During stabilization, PAN precursors arrange themselves into a ladder-like structure that improves thermal stability and carbon yield [10]. Electrospinning is a process that resembles the act of drawing, albeit with the notable distinction of use electrical force. An extremely powerful electrostatic field is used in the process of electrospinning to rapidly draw polymeric solutions into extremely fine fibers [11]. Polyacrylonitrile is commercially obtained by suspension polymerization in the presence of catalysts, such as ferric cation-anion persulfate and bisulfite [12] or by adding free radicals and anionic polymerization [13]. Low-temperature treatment of PAN results in carbon fiber with a high carbon yield and a molecular structure that is both thermally stable and well orientated [14]. Due to their exceptional physical and mechanical characteristics, these materials have garnered significant attention for their potential application in aerospace technology's high-performance composites [15].

Experimental procedure

1. Materials

Acrylonitrile monomer (high purity), ethyl methyl ketone peroxide (initiator), and DMF were obtained from Fluka Company, while acetone and tin octanoate catalysts were supplied from Merck Company.

2. Instrument

2.1. Fourier Transform Infrared (FTIR)

The FTIR spectra of PAN fiber were acquired using Shimadzu FTIR-8400s instruments. A disc composed of potassium bromide was employed to record the spectra within the 400 to 4000 cm-1 range. In order to mitigate the effects of water, the potassium bromide (KBr) was subjected to a drying process in an oven set at a temperature of 300 degrees Celsius.

2.2. Thermal Analysis (TGA and DSC)

The thermogravimetric analysis (TGA) findings of TGAQ50U20-13 Build 39 were subjected to analysis. The dynamic scan was conducted within a nitrogen atmosphere with a 30 mL/min flow rate.

The scan was performed over a 25-700 Co temperature range, using heating rates of 20, 30, and 40 mL/min. Differential scanning calorimetry (DSC) was conducted using a Shimadzu DSC-60 instrument to perform dynamic scans within a temperature range of 25-350°C. We scanned at a constant heating rate of ten°C/min in a nitrogen atmosphere with a nitrogen flux of 20 ml/min

2.3. Scanning Electron Microscope (SEM)

The surface morphology of the prepared polymer fibers was studied by SEM on JEOL Model JSMT300 equipment operating at 20 kV. The samples underwent a gold-sputtering process prior to the measurements. The readings were obtained by using an HP4192A impedance analyzer.

2.4. Atomic Force Microscopy (AFM)

To image the morphology and microstructures of polymer fibers, a dimension of 3100 AFM was used. The optical images were acquired using the optical microscope integrated into the AFM instrument. The system was operated using the tapping mode technique, employing a readily accessible silicon probe.

3. Synthesis

3.1. Synthesis of PAN

The sample material for PAN was prepared, as the general procedure for polymer preparation, 10 ml of acrylonitrile (AN) and 1.5% of ethyl methyl ketone peroxide as polymerization initiator [16] were intensively mixed, and then 0.25% of tin octanoate as co-catalyst was added to promote the polymerization reaction. Nitrogen gas was poured into the flask for about 1 hour to prevent oxygen. Then, the mixture was heated at 40–45 C^o in a closed flask (to avoid liquid evaporation) for 24 hours to polymerize the AN, followed by treatment at 110 C^o for 15 minutes. Then, the white powder polymer was washed several times with warm water to remove unpolymerized AN and residue of initiator and co-catalyst, filtered, and dried again at 110 C^o for 1 hour. FTIR characterized the polymer, and its viscosity and average molecular weight were determined.

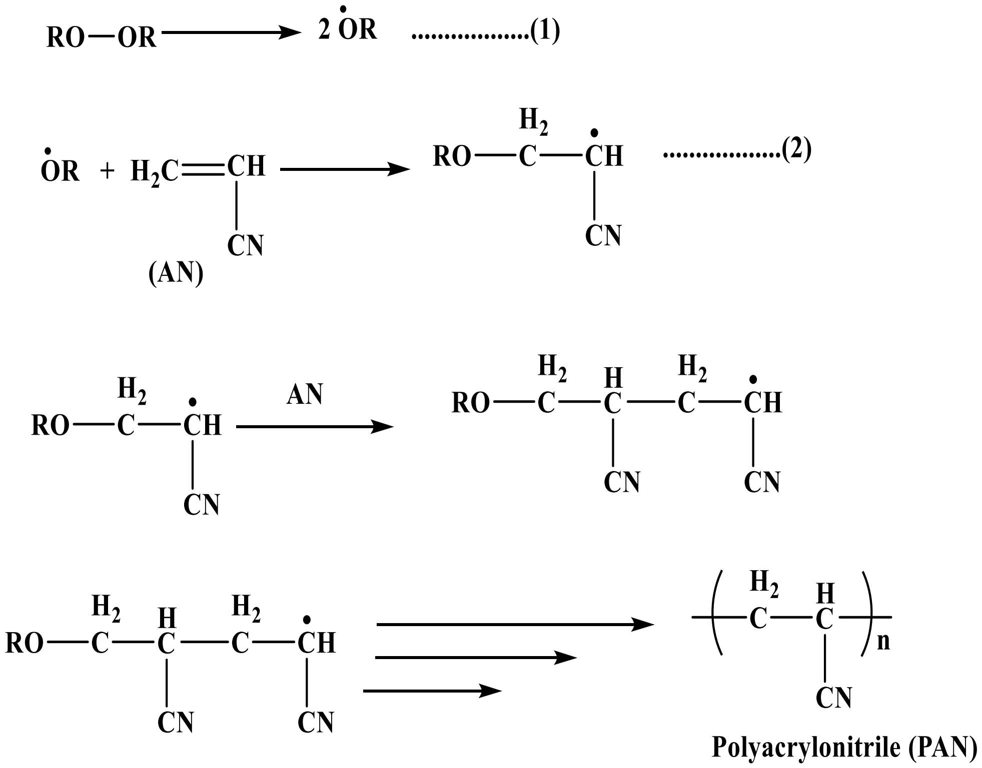
3.2. Electrospinning of PAN

Polyacrylonitrile (PAN) preparation for the electrospinning process entailed the dissolution of 0.3 grams of the polymer in a 10 mL volume of dimethylformamide (DMF) solvent. After being stirred at ambient temperature for roughly 24 hours, the solution was subsequently transferred to a 5ml plastic syringe with a 23-gauge needle to achieve uniformity. The syringe needle was positioned at a distance of 10 cm from the target. An electrical potential of 10 KV was applied using a copper electrode connected to the needle. The feed rate of the solution was set at 0.5 ml/h. All of the testing was conducted in an outdoor, real-world setting. Figure 2 shows a schematic of electrospinning.

Results and discussion

1. Synthesis and Electrospinning of PAN

PAN is a homopolymer of the acrylonitrile monomer and features polar, pendent nitrile groups that interact strongly via electrostatic forces. Several methods exist for polymerizing a monomer, such as bulk polymerization, solution polymerization, or heterogeneous free radical polymerization, which includes processes like suspension, emulsion, and aqueous dispersion polymerization [17, 18]. In this study, bulk polymerization was achieved by using a free radical initiator (ethyl methyl ketone peroxide and tin octanoates as co-catalysts). Scheme 1 shows the polymerization route.



Scheme 1. Polymerization route of acrylonitrile monomer

The PAN fibers were characterized using FTIR, viscosity average molecular weight (Mv). Figure 1 shows the FTIR spectrum of PAN fibers. The complete range of absorption bands exhibited by PAN was observed at wavenumbers of 3445, 2926, 2423, 1731, 1615, 1453, and 1250 cm^{-1}. The absorption band observed in the polymer structure can be attributed to several factors, including the bending of the C-H bond in CH2 and the stretching of N-H and C-H bonds. Additionally, the stretching of C=O and C=C bonds and the stretching of C=N and C=O bonds contribute to the observed absorption band [19]. The polymer's intrinsic viscosity [h] was measured by heating a solution of DMF in a water bath to a consistent temperature of 35°C using an uncalibrated viscometer, as outlined in the study conducted by Kashyap [20]. By utilizing the equation provided in reference [21], we successfully ascertained the mean molecular weight of the viscosity.

$$[\eta]=2.8\text{x}10^{-4}M_v^{0.76}$$

Where 2.78 and 0.76 were K and a of PAN at 35 oC in DMF solvent, and from the result, the Mv was 18320 g/mol. On the other hand, the electrospinning process was conducted in an ambient atmosphere. Figure 2 illustrates the electrospinning diagram.

Co

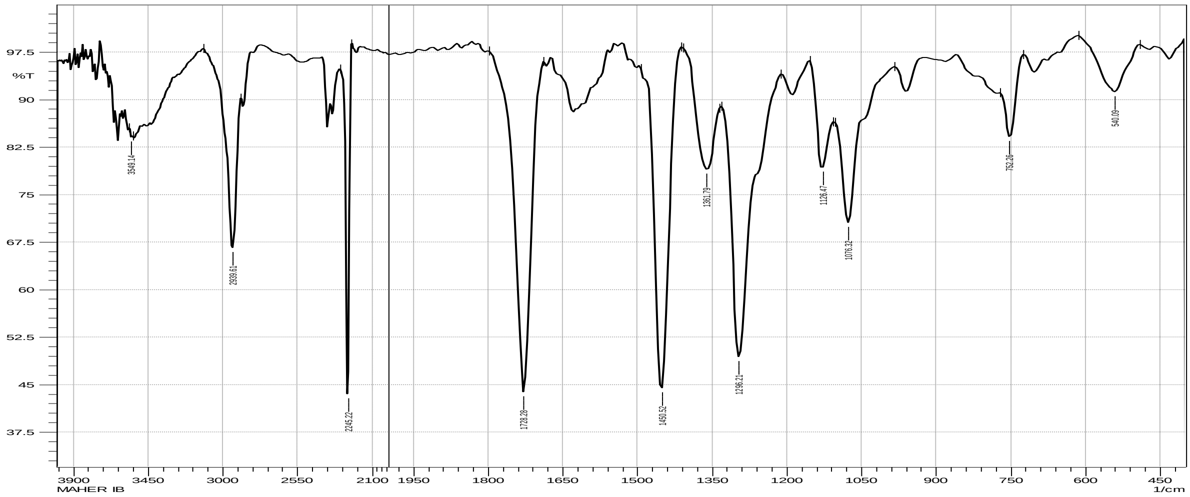


Figure 1. FTIR spectrum of PAN fiber.

Figure 2. Electrospinning diagram

2. TGA Analysis

Thermogravimetry is the preferred method for determining a material's resistance to heat because it only needs a small sample and can be finished in a matter of hours [22]. The thermal stability of PAN and SPAN fibers was assessed by subjecting them to dynamic thermogravimetric analysis (TGA) under a nitrogen atmosphere. Two distinct heating rates, namely 20-30 °C/min are observed. Figure 3-8 presents the Thermogravimetric Analysis (TGA) thermograms. According to the obtained results, the optimum decomposition temperature (top) and the char residue of SPAN fiber are higher than PAN fiber due to the formation of cyclic structure PAN through heat treatment of PAN fiber, which leads to more thermal resistance. On the other hand, the degree of conversion was determined for both PAN and SPAN fiber, and the result is shown in figures 9–11, while table 1 shows some thermal parameters obtained from TGA thermograms

The batch experiments' findings showed that several factors had a major impact on the chromium ions' interactions with the ACDP to achieve the highest removal percentage. These factors involved the beginning pollutant concentration, the initial pH, the dose of the sorbent, the rate of agitation, and the sorbent's particle size corresponding to 25 mg/l, 6, 2 g ACPD per 100 ml,250 rpm, and 250 μm respectively to remove 95% of Cr(III). Multiple types of sorption isotherm calculations were used to match the kinetic measurements for the sorption of chromium ions onto ACDP, the SIPS sorption isotherm proved to most closely approximate the data via a coefficient of determination (R2) of 0.996. Due to the good agreement between the fitted and experimental results, the data for the sorption of Cr (III) onto ACDP were found to obey the pseudo-second-order model, the most dominant mechanism in the sorption process was chemisorption.

References

[1] N. Sezgin, N. Balkaya, Adsorption of heavy metals from industrial wastewater by using polyacrylic acid hydrogel, Desal. Water. Treat., 57 (2016) 2466–2480.

[2] S. Ba, K. Ennaciri, A. Yaacoubi, A. Alagui, and A. Bacaoui, “Activated carbon from olive wastes as an adsorbent for chromium ions removal,” *Iran. J. Chem. Chem. Eng.*, vol. 37, no. 6, pp. 107–123, 2018.

[3] Nieboer E.,.Shaw S.L., “Mutagenic and other Genotoxic Effects of Chromoim Compounds, in Chromium in the Natural and Human Environments”, Eds Nriagu J.O., Nieboer E., (Wiley, New York), Chap. 16: 399-442 (1988).

[4] World Health Organization, Chromium Environmental Health Criteria 61. Geneva, Switzerland (1988).

[5] Gopi Krishna P., Mary Gladis J., Rambabu U., Prasada Rao T., Naidu G.R.K., Preconcentrative Separation of Chromium(VI) Species from Chromium(III) by Coprecipitation of its Ethyl Xanthate Complex onto Naphthalene, Talanta, 63: 541-546 (2004).

[6] Kongsricharoern N., Polprasert C., Chromium Removal by a Bipolar Electro-Chemical Precipitation Process, Water Sci. Technol., 34(9): 109-116 (1996).

[7] Ghanbari Pakdehi S., Adsorption of Cr(III) and Mg(II) from Hydrogen Peroxide Aqueous Solution by Amberlite IR-120 Synthetic Resin, Iran. J. Chem. Chem. Eng. (IJCCE), 32(2): 49-55 (2013).

[8] Ghanbari Pakdehi S., Adsorptive Removal of Al, Zn, Fe, Cr and Pb from Hydrogen Peroxide Solution by IR-120 Cation Exchange Resin, Iran. J. Chem. Chem. Eng. (IJCCE), 35(1): 75-84 (2016)

[9] Das C., Patel P., De S., DasGupta S., Treatment of Tanning Effluent Using Nanofiltration Followed by Reverse Osmosis, Sep. Purif. Technol., 50: 291- 299 (2006).

[10] Parinejad M., Yaftian M.R., A Study on the Removal of Chromium(VI) Oxanions from Acid Solutions by Using Oxonium Ion-Crown Ether Complexes as Mobile Carrier Agents, Iran. J. Chem. Chem. Eng. (IJCCE), 26(4): 19-27 (2007).

[11] Gaikwad M.S., Balomajumder C., Removal of Cr(VI) and Fluoride by Membrane Capacitive Deionization with Nanoporous and Microporous Limonia Acidissima (Wood Apple) Shell Activated Carbon Electrode, Sep. Purif. Technol., 195: 305-313 (2018).

[12] Liu J., Wang C., Shi J., Liu H., Tong Y., Aqueous Cr(VI) Reduction by Electrodeposited ZeroValent Iron at Neutral pH: Acceleration by Organic Matters, J. Hazard. Mater., 163: 370-375 (2009).

[13] Meunier N., Drogui P., Montane C., Hausler R., Mercier G., Blais J.F. Comparison between Electrocoagulation and Chemical Precipitation for Metals Removal from Acidic Soils Leachate, J. Hazard. Mater., 137: 581–590 (2006).

[14] Wang F., Xie Z., Xie L., Preparation of Polyamide Microcapscules and their Application Treating Industrial Wastewater Containing Cr6+ , Chem. Res., 13: 36–38 (2002).

[15] Abdel-Halim E.S., Al-Deyab S.S., Hydrogel from Cross Linked Polyacrylamide/guar Gum Graft Copolymer for Sorption of Hexavalent Chromium Ion, Carbohydr. Polym., 86(3): 1306-1312 (2011).

[16] Samani M.R., Borghei S.M., Olad A., Chaichi M.J., Influence of Polyaniline Synthesis Conditions on its Capability for Removal and Recovery of Chromium from Aqueous Solution, Iran. J. Chem. Chem. Eng. (IJCCE), 30 (3): 97-100 (2011).

[17] Arfaoui S., Frini-Srasra N., Srasra E., Modelling of the Adsorption of the Chromium Ion by Modified Clays, Desalination, 222: 474–481 (2008).

[18] Benhammou A., Yaacoubi A., Nibou L., Tanouti B., Chromium(VI) Adsorption from Aqueous Solution onto Moroccan Al-Pillared and Cationic Surfactant Stevensite, J. Hazard. Mater., 140: 104–109 (2007).

[19] Yavuz A.G., Dincturk-Atalay E., Uygun A., Gode F., Aslan E., A Comparison Study of Adsorption of Cr(VI) from Aqueous Solutions Onto AlkylSubstituted Polyaniline/Chitosan Composites, Desalination, 279: 325–331 (2011).

[20] Gupta V.K., Rastogi A., Nayak A., Adsorption Studies on the Removal of Hexavalent Chromium from Aqueous Solution Using a Low Cost Fertilizer Industry Waste Material, J. Colloid Interf. Sci. 342: 135–141 (2010).

[21] Jung C., Heo J., Han J., Her N., Lee S.J, Ohd J., Ryud J., Yoon Y., Hexavalent Chromium Removal by Various Adsorbents: Powdered Activated Carbon, Chitosan, and Single/Multi-Walled Carbon Nanotubes, Sep. Purif. Technol., 106: 63–71 (2013).

[22] Uysal M., Ar I., Removal of Cr(VI) from Industrial Wastewaters by Adsorption Part I: Determination of Optimum Conditions, J. Hazard. Mater., 149: 482– 491 (2007).

[23] Di Natale F., Lancia A., Molino A., Musmarra D., Removal of Chromium Ions form Aqueous Solutions by Adsorption on Activated Carbon and Char, J. Hazard. Mater., 145: 381–390 (2007).

[24] González Bermúdeza Y., Ricoa I.L.R., Guibal E., Calero de Hocesc M., Martín-Larac M.Á., Biosorption of Hexavalent Chromium from Aqueous Solution by Sargassum muticum Brown Alga. Application of Statistical Design for Process Optimization, Chem. Eng. J., 183: 68–76 (2012).

[25] Faghihian H., Rasekh M., Removal of Chromate from Aqueous Solution by a Novel Clinoptilolite Polyanillin Composite, Iran. J. Chem. Chem. Eng. (IJCCE), 33 (1): 45-51 (2014).

[26] Owlad M., Aroua M.K., Wan Daud W.M.A., Hexavalent Chromium Adsorption on Impregnated Palm Shell Activated Carbon with Polyethyleneimine, Bioresour. Technol. 101: 5098–5103 (2010).

[27] Zhang H., Tang Y., Cai D., Liu X., Wang X., Huang Q., Yu Z., Hexavalent Chromium Removal from Aqueous Solution by Algal Bloom Residue Derived Activated Carbon: Equilibrium and Kinetic Studies, J. Hazard. Mater., 181: 801–808 (2010).

[28] Gupta V.K., Nayak A., Agarwal S., Bioadsorbents for Remediation of Heavy Metals: Current Status and Their Future Prospects, Review Article, Environ. Eng. Res., 20(1): 001-018 (2015).

[29] Duran U., Coronado-Apodaca K.G., Meza-Escalante E.R., Ulloa-Mercado G., Serrano D., Two Combined Mechanisms Responsible to Hexavalent Chromium Removal on Active Anaerobic Granular Consortium, Chemosphere, 198: 191-197 (2018).

[30] Rosales E., Meijide J., Pazos M., Sanromán M. A., Challenges and Recent Advances in Biochar as Low-Cost Biosorbent: From Batch Assays to Continuous-Flow Systems, Bioresour. Technol, 246: 176–192 (2017).

[31] Zhang X., Zhang L., Li A., Eucalyptus Sawdust Derived Biochar Generated by Combining the Hydrothermal Carbonization and Low Concentration KOH Modification for Hexavalent Chromium Removal, J Environ Manage., 206: 989- 998 (2018).

[32] Su H., Chong Y., Wang J., Long D., Qiao W., Ling L., Nanocrystalline Celluloses-Assisted Preparation of Hierarchical Carbon Monoliths for Hexavalent Chromium Removal, J. Colloid Interface Sci., 510: 77–85 (2018).

[33] Burakov A.E., Galunin E.V., Burakova I.V., Kucherova A.E., Agarwal S., Tkachev A.G., Gupta V.K., Adsorption of Heavy Metals on Conventional and Nanostructured Materials for Wastewater Treatment Purposes: A Review, Ecotoxicol Environ Saf., 148: 702–712 (2018).

[34] E. Vunain, J. B. Njewa, T. T. Biswick, and A. K. Ipadeola, "Adsorption of chromium ions from tannery effluents onto activated carbon prepared from rice husk and potato peel by H3PO4 activation," *Appl. Water Sci.*, vol. 11, no. 9, pp. 1–14, 2021, doi: 10.1007/s13201-021-01477-3.

[35] H. M. Rashid and A. A. H. Faisal, "Removal of Dissolved Trivalent Chromium Ions from Contaminated Wastewater using Locally Available Raw Scrap Iron-Aluminum Waste," *Al-Khwarizmi Eng. J.*, vol. 15, no. 1, pp. 134–143, 2019, doi: 10.22153/kej.2019.06.005

[36] K. K. Wong, C. K. Lee, K. S. Low, and M. J. Haron, “Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solutions,” *Chemosphere*, vol. 50, no. 1, pp. 23–28, 2003, doi: 10.1016/S00456535(02)00598-2.

[37] Z. S. Nassir, “RTIFICIAL NEURAL NETWORK (ANN) APPROACH FOR MODELING OF HEAVY METALS ADSORPTION FROM AQUEOUS SOLUTION BY LOW COST ADSORBENTS”, M.S.thesis ,Univ.of Baghdad ,Baghdad ,Iraq ,2016.

[38] P. V Nidheesh, G. Divyapriya, F. E. Titchou, and M. Hamdani, “Treatment of textile wastewater by sulfate radical based advanced oxidation processes,” *Sep. Purif. Technol.*, vol. 293, p. 121115, 2022.

[39] A. H. Sadek and M. K. Mostafa, “Preparation of nano zero-valent aluminum for one-step removal of methylene blue from aqueous solutions: cost analysis for scaling-up and artificial intelligence,” *Appl. WaterSci.*, vol. 13, no. 2, pp. 1–23, 2023, doi: 10.1007/s13201-022-01837-7.

[40] M. Azam, S. M. Wabaidur, M. R. Khan, M. S. Islam, and S. I. Al-Resayes, “Removal of chromium(III) andc admium(II) heavy metal ions from aqueous solutions using treated date seeds: An eco-friendly method,” *Molecules*, vol. 26, no. 12, 2021, doi: 10.3390/molecules26123718.

[41] M. F. F. Sze and G. McKay, “An adsorption diffusion model for removal of para-chlorophenol by activated carbon derived from bituminous coal,” *Environ. Pollut.*, vol. 158, no. 5, pp. 1669–1674, 2010, doi: 10.1016/j.envpol.2009.12.003.

[42] J. W. Brault, “New approach to high-precision Fourier transform spectrometer design,” *Appl. Opt.*, vol. 35, no. 16, pp. 2891–2896, 1996.

[43] K. Mahmoudi, K. Hosni, N. Hamdi, and E. Srasra, “Kinetics and equilibrium studies on removal of methylene blue and methyl orange by adsorption onto activated carbon prepared from date pits-A comparative study,” *Korean J. Chem. Eng.*, vol. 32, no. 2, pp. 274–283, 2015.

[44] I. M. Iloamaeke and C. O. Julius, “Treatment of Pharmaceutical Effluent Using seed of Phoenix Dactylifera as a Natural Coagulant,” *J. Basic Phys. Res.*, vol. 9, no. 1, pp. 91–100, 2019.

[45] A. Benbiyi, M. El Guendouzi, S. Kouniba, and A. Zourif, “Response Surface Modeling for Malachite Green Removal Using the Box-Behnken Experimental Design,” *Environ. Ecol. Res.*, vol. 10, no. 6, pp. 830–838, 2022, doi: 10.13189/eer.2022.100617.

[46] J. M. Salman and F. M. Abid, “Preparation of mesoporous activated carbon from palm-date pits: optimization study on removal of bentazon, carbofuran, and 2, 4-D using response surface methodology,” Water Sci. Technol., vol. 68, no. 7, pp. 1503–1511, 2013.

[47] M. A. Islam, I. A. W. Tan, A. Benhouria, M. Asif, and B. H. Hameed, “Mesoporous and adsorptive properties of palm date seed activated carbon prepared via sequential hydrothermal carbonization and sodium hydroxide activation,” Chem. Eng. J., vol. 270, pp. 187–195, 2015.

[48] Y. Shu *et al.*, “Almond shell-derived, biochar-supported, nano-zero-valent iron composite for aqueous hexavalent chromium removal: performance and mechanisms,” *Nanomaterials*, vol. 10, no. 2, p. 198, 2020.

[49] S. J. Mohammed, M. J. M-Ridha, K. M. Abed, and A. A. M. Elgharbawy, “Removal of levofloxacin and ciprofloxacin from aqueous solutions and an economic evaluation using the electrocoagulation process,” Int. J. Environ. Anal. Chem., vol. 00, no. 00, pp. 1–19, 2021, doi: 10.1080/03067319.2021.1913733.

[50] H. S. Alhares et al., “Sunflower Husks Coated with Copper Oxide Nanoparticles for Reactive Blue 49 and Reactive Red 195 Removals: Adsorption Mechanisms, Thermodynamic, Kinetic, and Isotherm Studies,” Water. Air. Soil Pollut., vol. 234, no. 1, 2023, doi: 10.1007/s11270-022-06033-6.

[51] Y.A. Ouaissa, M. Chabani, A. Amrane and A. Bensmaili, J. Environ. Chem. Eng. 2 (1), 177 (2014). doi:10.1016/j.jece.2013.12.009

[52] M. Al-Shannag, Z. Al-Qodah, K. Bani-Melhem, M. R. Qtaishat, and M. Alkasrawi, “Heavy metal ions removal from metal plating wastewater using electrocoagulation: Kinetic study and process performance,” *Chem. Eng. J.*, vol. 260, pp. 749–756, 2015, doi: 10.1016/j.cej.2014.09.035

[53] S. T. Akar, A. Gorgulu, Z. Kaynak, B. Anilan, and T. Akar, “Biosorption of Reactive Blue 49 dye under batch and continuous mode using a mixed biosorbent of macro-fungus Agaricus bisporus and Thuja orientalis cones,” *Chem. Eng. J.*, vol. 148, no. 1, pp. 26–34, 2009, doi: 10.1016/j.cej.2008.07.027.

[54] M. Asgher and H. N. Bhatti, “Removal of reactive blue 19 and reactive blue 49 textile dyes by citrus waste biomass from aqueous solution: Equilibrium and kinetic study,” *Can. J. Chem. Eng.*, vol. 90, no. 2, pp. 412–419, 2012, doi: 10.1002/cjce.20531.

[55] M. Salman, H. Alhares, Q. Ali, M. M-Ridha, S. Mohammed, and K. M. Abed, “Cladophora Algae Modified with CuO Nanoparticles for Tetracycline Removal from Aqueous Solutions,” *Water, Air, Soil Pollut.*, vol. 233, Aug. 2022, doi: 10.1007/s11270-022-05813-

[56] Z. Belala, M. Jeguirim, M. Belhachemi, F. Addoun, and G. Trouvé, “Biosorption of basic dye from aqueous solutions by Date Stones and Palm-Trees Waste: Kinetic, equilibrium and thermodynamic studies,” *Desalination*, vol. 271, no. 1–3, pp. 80–87, 2011, doi: 10.1016/j.desal.2010.12.009.

[57] M-Ridha, M.J., Faeq Ali, M., Hussein Taly, A., Abed, K.M., Mohammed, S.J., Muhamad, M.H., Abu Hasan, H., 2022. Subsurface Flow Phytoremediation Using Barley Plants for Water Recovery from Kerosene-Contaminated Water: Effect of Kerosene Concentration and Removal Kinetics. Water 14, 687. https://doi.org/10.3390/w14050687