Nature Environment and Pollution Technology
An International Quarterly Scientific Journal
p-ISSN: 0972-6268
(Print copies up to 2016)
e-ISSN: 2395-3454
Vol. 23 | No. 4 | pp. 2305-2314 | 2024
Original Research Paper
https://doi.org/10.46488/NEPT.2024.v23i04.034
Open Access Journal

Potential Low-cost Treatment of Tannery Effluents from Industry by Adsorption on Activated Charcoal Derived from Olive Pomace

I. Alouiz, M. Benhadj, D. Elmontassir, M. Sennoune, M.Y. Amarouch and D. Mazouzi†
R.N.E Laboratory, Multidisciplinary Faculty of Taza, University Sidi Mohamed Ben Abdellah, Fez, Morocco
†Corresponding author: D. Mazouzi; driss.mazouzi@usmba.ac.ma

Nat. Env. & Poll. Tech.
Website: www.neptjournal.com

Received: 28-02-2024
Revised: 26-03-2024
Accepted: 11-04-2024

Key Words:
Tannery effluent
Toxicity
Activated charcoal
Adsorption
Treatment
Chromium

ABSTRACT

Tannery wastewater contains a significant amount of chemical compounds, including toxic substances. Due to the toxicity and negative environmental effects of these tannery effluents, mandatory treatment is necessary. The main objective of this study was to treat effluent from an artisanal tannery in the city of Fez (Morocco) using the adsorption process with activated charcoal derived from olive pomace. The physicochemical characterization of tanning water included several parameters, such as chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN), suspended solids (SS), sulfate ions (SO_4^{2-}), nitrate, and chromium Cr(VI). The analyses show that the adsorption process reduced nitrate by 57.54%, sulfate by 94.08%, TKN by 74.84%, COD by 68.18%, Cr by 91.27%, and Cr (VI) by 89.78%. The activated charcoal was characterized before and after tannery effluent treatment using various techniques, including FT-IR, SEM, and EDX. From the above, it can be inferred that using activated carbon made from olive pomace has the potential to reduce tannery effluent pollution parameters. This innovative approach demonstrates that competitive results can be achieved without sacrificing economic viability, thereby promoting sustainable practices in the treatment of industrial liquid waste and wastewater treatment plants.

INTRODUCTION

Environmental pollution is a global issue that is on the rise due to human activities such as urbanization and industrialization (Tadesse et al. 2017, Deghles et al. 2016). Industrial activities disrupt the natural flow of materials and introduce new chemicals into the environment, including bodies of water, soil, plants, vegetables, humans, and other living organisms (Islam et al. 2013, Shaibur et al. 2022). In this sense, water pollution is a significant global issue, primarily caused by the increase in industrialization (Asaduzzaman et al. 2016, Hassan et al. 2020). Indeed, industries produce toxic organic and inorganic substances that lower treatment performance and make reuse impossible (Naushad 2018, Linares-Hernández et al. 2009). Therefore, rational management of water resources become a major challenge worldwide, and wastewater treatment and reuse are considered the best solutions for coping with water scarcity.

Tanneries, or leather manufacturing industries, play a significant role in the economy by generating income and creating jobs. Despite their positive impacts, these industries have a negative image due to the pollution they produce (Elkarrach et al. 2018). In this sense, tanneries are perceived as resource-intensive and polluting. Indeed, during the process of transforming hides into leather goods, several operations generate a considerable amount of waste (Elmagd et al. 2014). At different stages of processing, liquid and solid pollutants are produced (Patel et al. 2021 & Leta et al. 2003). The extent of pollution caused by tanning depends on the methods used. Chromium tanning is the most commonly used method in modern tanneries worldwide (Onukak et al. 2017, Dargo et al. 2014). It is used to enhance the leather's water resistance, flexibility, and high shrinkage temperature. However, the chromium salts are not entirely fixed by the hides, and 70% of them join the spent tanning liquor (Mella et al. 2015, Cooman et al. 2003). Tannery effluents are also known for their high production of wastewater. Processing one ton of raw hide produces 200 kg of final leather product, along with 250 kg of untanned waste, 200 kg of tanned waste (containing 3 kg of chromium), and 50,000 kg of wastewater (containing 5 kg of chromium) (Mella et al. 2017, Sundar et al. 2022). This means that only 20% of the raw material's weight is converted into leather (Tahiri et al. 2009).

During the tanning process, chromium salts produce hexavalent chromium and trivalent chromium. Hexavalent chromium is a well-known toxic substance that can cause teratogenic, carcinogenic, and mutagenic effects on living organisms, even at low concentrations. This is why many countries have designated it as a priority contaminant (Elmagd et al. 2014, Harboul et al. 2022, Sandana Mala et al. 2015). Cr (III) is an essential component of human metabolism and homeostasis. It has low mobility and toxicity and is insoluble in water (Shaibur et al. 2022, Chojnacka et al. 2010, Wang et al. 2020). Cr (III) can be oxidized to Cr (VI) under uncontrollable conditions (Popiolski et al. 2022). The removal of Cr (VI) from industrial wastewater is a long-standing scientific and technological problem. The rapid pace of industrialization has led to an expansion in manufacturing and environmental contamination, mainly by heavy metals, particularly in developing countries (Sandhya et al. 2016). Therefore, it is crucial to note that the process of tanning requires a significant amount of water (Popiolski et al. 2022). As a result, the leftover tanned leather and effluent can be categorized as hazardous waste, posing a significant technological and environmental challenge that necessitates proper treatment and disposal in an industrial landfill.

According to recent literature on tannery wastewater treatment, a variety of physical-chemical, biological, and combined treatment processes have been studied for the treatment of these effluents. These processes include chemical precipitation (Sun et al. 2007, Xu et al. 2011), ion exchange (Pakzadeh & Batista 2011), reverse osmosis (Ranganathan et al. 2011), electrodialysis (Deghles et al. 2016), membrane filtration, photocatalysis (Elahi et al. 2020), and adsorption (Pradhan et al. 2017, Tahir et al. 2007), and ultrafiltration, microfiltration, nanofiltration (Kanamarlapudi et al. 2018), flotation, coagulation/flocculation (Cheballah et al. 2015, Espinoza-Quiñones et al. 2009), methanation (Mekonnen et al. 2016), the combination of ozone oxidation and membrane bioreactor (Di Iaconi et al. 2002), and the sequential batch reactor (Elkarrach et al. 2020). The performance of each process is highly dependent on the nature of the effluent, the flow rate to be treated, and the treatment objective. Physicochemical treatments are known for their high performance, but they are very expensive and can generate other, more serious pollution. Biological treatments are also effective and ecological, but the presence of toxic substances, such as heavy metals like chromium, is one of their major constraints (Mella et al. 2017). The challenge is to select a treatment process that is environmentally friendly, efficient, and economical while providing sustainable waste management. To this end, the current study aims to find an effective, ecological, and low-cost treatment for tannery effluents.

Therefore, the present study aims to investigate the effectiveness of our recently prepared olive pomace-derived activated charcoal for the treatment of tannery effluents in Fez. The activated charcoal is synthesized by a simple, efficient, and economical process using H_3PO_4 as the activating agent, followed by calcination under the atmosphere at 500°C to develop the porous structure (Alouiz et al. 2022). The analyses indicate that the adsorption process achieved significant reductions in nitrate (57.54%), sulfate (94.08%), TKN (74.84%), COD (68.18%), Cr (91.27%), and Cr (VI) (89.78%). The activated carbon was characterized before and after effluent treatment using various techniques, including FT-IR, SEM, and EDX. This study aims to demonstrate that activated carbon derived from olive pomace can be a sustainable, viable, and environmentally friendly solution for mitigating the adverse consequences and reducing the pollution parameters of tannery effluents.

MATERIALS AND METHODS

Synthesis of Activated Charcoal ACp

The preparation of activated charcoal (ACp) from olive pomace (OP) was carried out in two steps: chemical activation of olive pomace followed by calcination of impregnated OP (Fig. 1). Olive pomace was crushed and washed to remove the adhering impurities, then oven-dried at 100°C, followed by chemical activation with H_3PO_4 as the activating agent (22 vol%) for 2h. Finally, the chemically activated OP was heat-treated in the air at temperatures ranging from room temperature to 500°C using a programmable muffle furnace with a calcination time set within 1h, as described by Alouiz et al. (2022). The main physical and chemical properties of the activated carbon are summarized in Table 1.

Sampling of Tannery Effluent

Tannery effluent samples were collected aseptically from the Ain Nokbi industrial zone in the city of Fez-Morocco (Fig. 1), located at 34.0659915 Lat. North and -4.950160 West-Morocco, in March 2022. Samples were transported to the laboratory in a cool box at 4°C. Sampling and storage were carried out by ISO 5667-2 (Rodier et al. 2009).

Physico-chemical Characterization of Tannery Effluent

The collected tannery effluent samples were analyzed to

Table 1: The main physical and chemical properties of the ACp adsorbent.

ACp properties	
Moisture [%]	1.71
Ash [%]	4.15
Fixed carbon [%]	87.77
Density [$g.cm^{-3}$]	1.768
Iodine number [$mg.g^{-1}$]	923
SBET [$m^2 \cdot g^{-1}$]	1400
pH_{pzc}	8.8

Table 2: Analytical methods for physico-chemical parameters of tannery effluents.

Parameters	Analytical methods and equipment	Unit	Standard
pH	Measured by a multi-parameter (type CONSORT C535, Turnhout, Belgium)	1-12	
EC	Measured by a multi-parameter (type CONSORT C535, Turnhout, Belgium)	$\mu S.cm^{-1}$	
SS	Filtration of a volume of effluent on a 0.45 µm membrane	$mg.L^{-1}$	Standard NF T90.105
COD	Acid oxidation by excess potassium dichromate in the presence of ammonium iron sulfate at 148°C	mg of $O_2.L^{-1}$	AFNOR T90-101
SO_4^{2-}	Precipitation of sulfates in hydrochloric acid in the form of barium sulfates. Colorimetric determination by spectrophotometry. (Specuvisi UV/VIS Spectrophotometer, n° RE1701008)	$mg.L^{-1}$	Standard NF T 60-203
NO_3^-	Sodium salicylate. Colorimetric determination by spectrophotometry (Specuvisi UV/VIS Spectrophotometer, n° RE1701008)	$mg.L^{-1}$	AFNOR T90-012, T90-015
TKN	Measured by mineralization followed by distillation	$mg.L^{-1}$	AFNOR T90-110
Cr (VI)	DPC colorimetric method, Spectrophotometric assay (Specuvisi UV/VIS Spectrophotometer, No. RE1701008)	$mg.L^{-1}$	AFNOR NF T 90-043
Metallic elements	Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES)	$mg.L^{-1}$	

determine the intensity and degree of organic and inorganic pollution. Several physicochemical parameters were measured: pH, electrical conductivity (EC), suspended solids (SS), chemical oxygen demand (COD), sulfate (SO_4^{2-}), nitrate (NO_3^-), and Kjeldahl nitrogen (TKN). Concentrations of metallic elements were analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using Jobin-Yvon-Horriba spectroscopy. Table 2 summarizes the analytical methods and equipment used in these measurements according to the protocols described by Rodier (2009). These parameters were measured before and after treatment of the effluent with activated charcoal ACp derived from olive pomace.

Description of Tannery Effluent Treatment Protocol

To evaluate the efficacy of ACp-activated charcoal, 2 g of charcoal was added to 500 mL of tannery effluent contaminated with 50 mg/L Cr (VI). The mixture was stirred at room temperature for up to 48 hours. It was then centrifuged at 6500 rpm for 15 minutes (Fig. 1). The concentration of hexavalent chromium (Cr (VI)) in the filtrate was measured according to AFNOR standard NF T 90-043, using a spectrophotometer colorimetric assay method. Cr (VI) ions were complexed with 1-5 diphenyl carbazide in an acidic medium, forming a complex that could be quantified using a UV-visible spectrophotometer (Specuvisi UV/VIS Spectrophotometer, RE1701008) at a wavelength of 540

Fig. 1: Set-up of treatment of tannery effluents process.

nm. The removal efficiency of Cr (VI), COD, and TKN by ACp-activated charcoal was calculated from the following equation:

$$R(\%) = \frac{C_i - C}{C_i} \times 100 \quad \ldots(1)$$

Ci: initial Cr (VI) concentration in mg/L

C: after-treatment Cr (VI) concentration in mg/L

Materials Characterizations

Determination of the functional groups present in the activated charcoal surface before and after Fourier carried out tannery effluent treatment transform infrared spectroscopy (FT-IR), using an FTIR spectrum recorded with a resolution of 1 cm^{-1} and 10 scans between 400 and 4000 cm^{-1} using an FTR-Vertex 70-Bruker spectrometer. The morphology of the activated charcoal obtained from olive pomace was studied using a JEOL model SEM, JEOL-IT500HR, equipped with an EDX analyzer with an acceleration voltage of 15 kV in high vacuum mode.

RESULTS AND DISCUSSION

Characterization of the Adsorbents

Scanning electron microscopy SEM and EDX analysis: The morphological characteristics of the samples were analyzed using the SEM technique. Fig. 2 shows the different morphologies and microscopic appearance of ACp-activated carbon before and after tannery effluent treatment. The surface morphology of ACp before treatment showed a large number of irregular voids and fine open pores (Fig. 2a). The high porosity resulted in a large surface area (Solgi et al. 2017), which was also confirmed by iodine number analysis (greater than 923 $mg.g^{-1}$) and BET specific surface area (greater than 1400 $m^2.g^{-1}$). Regarding the ACp-Tan sample after the adsorption process and treatment of tannery rejects, the morphology of the carbon surface was significantly modified after the adsorption process due to the precipitation of Cr (VI) on the adsorbent surface (Fig. 2b). The absence of pores on the surface can also be observed, indicating that the Cr adheres to the pore hole and cavity. Consequently, the image of the ACp-Tan surface after treatment indicates the effectiveness of the adsorption process and also confirms the very high values obtained for the de-pollution of tannery effluents. Similar results have been obtained by other researchers using different precursors to show the adsorbent surface modification after chromium adsorption (Benmahdi et al. 2022, Fito et al. 2023). In addition, Fig. 2c.d shows EDX spectra showing that activated carbon is a carbon-enriched material containing about 88.33% carbon. After the wastewater treatment, the carbon content decreased, and the oxygen content increased, resulting in the appearance of a new Cr peak in the ACp-Tan surface (Fig. 2d). Overall, these results confirm the good treatment of tannery effluents by activated carbon.

FT-IR spectroscopy: The surface chemistry of the adsorbent and its effect on the adsorption process is usually studied by Fourier transform infrared spectroscopy (FTIR). The prepared activated carbon had a high carbon content and a low oxygen content. The functional groups on ACp are determined by pHpzc, which was measured at 8.8 (Table 1). However, FTIR analysis provides more information about the nature of these functional groups. The IR spectra of activated carbon before and after treatment of tannery rejects are shown in Fig. 3. The spectra show the shift of some peaks and the appearance of others. The spectrum of activated carbon before ACp treatment (in black) shows the following bands: A band around 1580 cm^{-1} attributed to the stretching vibration of the lactone C=O and carbonyl groups by the C=C groups conjugated to the aromatic rings. The band observed between 1100-1180 cm^{-1} is generally found with oxidized carbons and has been attributed to C-O stretching in acids or ester groups (Yakout et al. 2016, Ozbay et al. 2016). The bands between 1250 and 1300 cm^{-1} may be related to angular deformation in the plane of C-H bonds of aromatic rings.

After treatment, analysis of the FTIR spectrum of ACp-Tan shows changes in the intensity and position of peaks and the appearance of others. A more intense band appears in the region of 3200-3600 cm^{-1}, corresponding to O-H (hydroxyl group) stretching vibrations in alcohols, phenols, and carboxylic acids (Solgi et al. 2017). The peak at 2900 cm^{-1} has been attributed to asymmetric (C-H) stretching vibrations of the methyl group (Fito et al. 2023, Labied et al. 2018). The peaks at 1615 and 1430 cm^{-1} represent the presence of an average stretching vibration C=C and C=O carbonyl group (Abatan et al. 2020). The peak intensity increases from 1000 to 1180 cm^{-1}, corresponding to C-O stretching vibrations (Pradhan et al. 2017, Rahman et al. 2017). Finally, the 700-900 cm^{-1} peaks became more prominent, attributed to C-H stretching vibrations for out-of-plane aromatic deformations (Shakya et al. 2019, Dhanakumar et al. 2007). The different peaks observed before and after wastewater treatment could be due to the presence of different functional groups. The binding of Cr ions in the activated carbon site could be the reason for the increased peaks in the FT-IR spectrum. The adsorption of Cr-O ions in activated carbon derived from olive pomace indicates that ACp has the potential to interact with other metal elements present in tannery rejects (Fito et al. 2023, Abatan et al. 2020). Similar results have been found in previous studies with biochar based on pine apple peels, rapeseed stalks, and medlar seeds (Solgi et al. 2017, Shakya et al. 2019, Zhao et al. 2018).

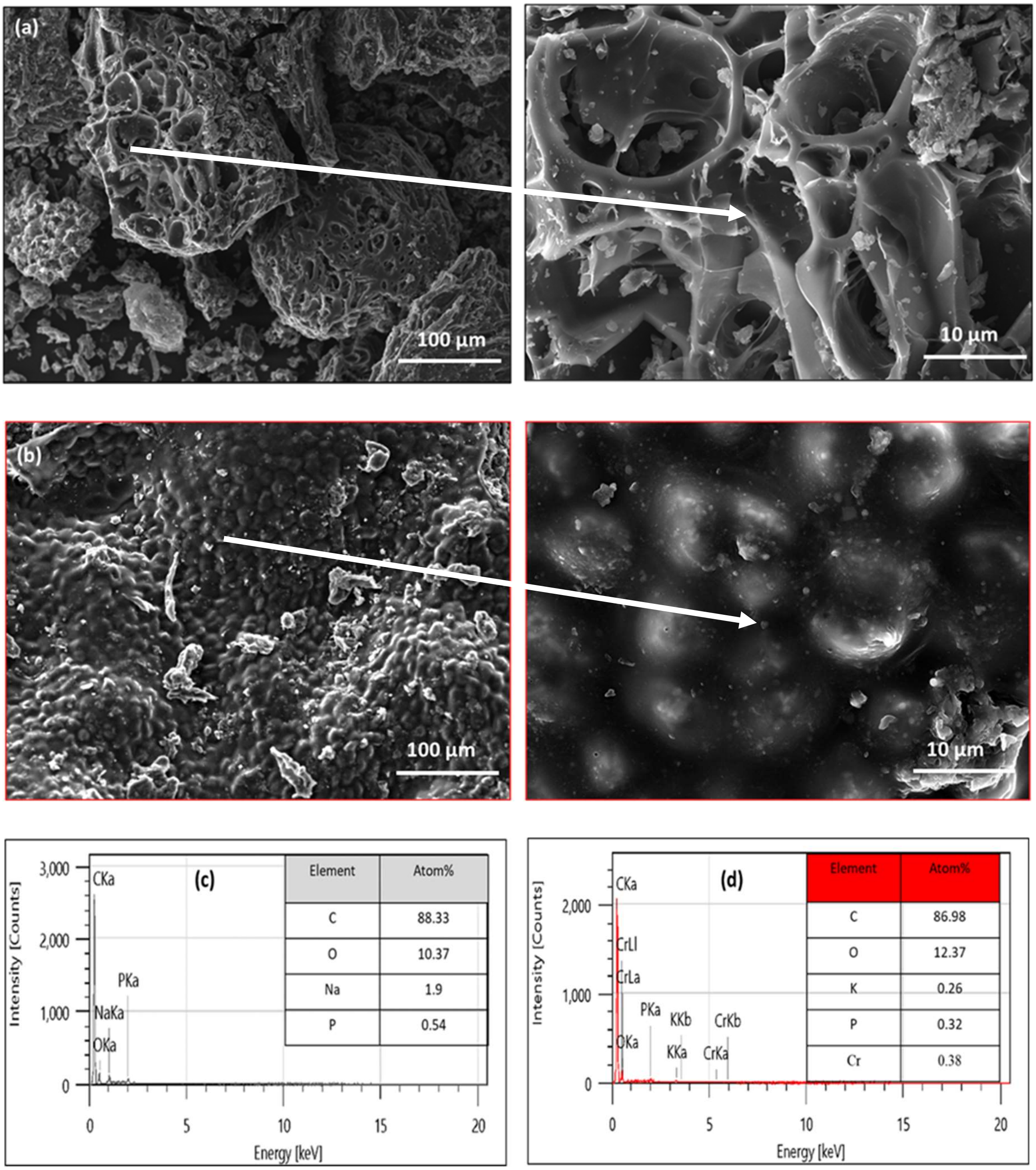

Fig. 2: SEM images of activated charcoal before (a) and after (b) the tannery effluent treatment process, (c) EDX before and (d) EDX after treatment.

Physico-chemical characterization of tannery effluent: To evaluate the physicochemical and metallic quality of the studied tannery effluent, we analyzed the pollution indicator parameters. The results presented in Table 3 show that this effluent is highly polluted and does not meet the Moroccan discharge standard for several parameters, including pH, electrical conductivity, COD, TKN, sulfate ions, suspended solids, chromium, and other metallic elements.

According to Table 3, the pH of this effluent is basic due to the use of sodium carbonate and sodium bicarbonate in the tanning process. These neutralize the sulfides and sulfuric acid used, thus increasing the pH of the effluent. The literature has shown that this parameter is influenced by the type of process used in each tannery. Moreover, the pH value obtained is consistent with that found in other studies by Elkarrach et al. (2021). Other studies, such as those of

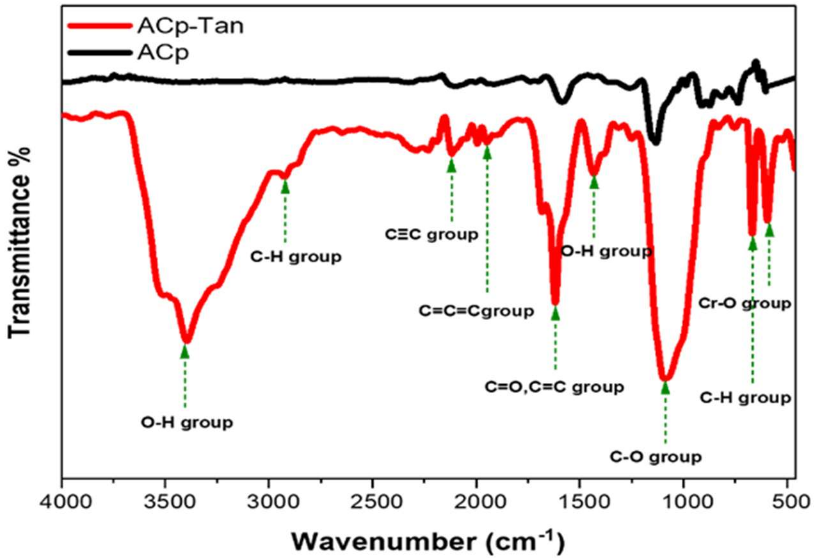

Fig. 3: FT-IR spectrum of activated charcoal before (black-ACp) and after (red-ACp-Tan) the treatment of tannery effluent.

Kurdekar et al. (2015), find a value of pH=2.7 acid. The electrical conductivity, which reflects the ionic concentration of the medium, is in the order of mS/cm for the raw effluent and exceeds the norm with a concentration of about 11.24 mS/cm. This high conductivity is mainly due to the natural salt content of the hides and the preservative salts used by the tanners before tanning (Cooman et al. 2003). Research has shown that high conductivity above 3000 µS/cm can upset the ecological balance and inhibit microbial growth (Merimi et al. 2017).

COD, SS, and sulfate ions are also present in very high concentrations, far from the values set by the Moroccan discharge standards, with values around 14065.92 mg $O_2.L^{-1}$, 5280 $mg.L^{-1}$ and 4919.06 mg/L, respectively. These high concentrations are due to the amount of chemicals used in the tanning process (Leta et al. 2003). TKN is also far from the norm. The TKN concentration is high at 162.624 $mg.L^{-1}$. This concentration represents the amount of organic and ammoniacal nitrogen present in this tannery effluent. As for the analysis of metallic elements, chromium reached a high concentration of 127.04 $mg.L^{-1}$; this high amount was found to be due to the chromium used in the leather manufacturing process (Sundar et al. 2022). The other elements, Al, Fe, and Zn, are present in low concentrations (Table 3). Consequently, the results of the physicochemical characterization of the tannery effluents show that all the parameters analyzed far exceed the discharge standards established in Morocco. This situation is because workers do not use adequate quantities of products and the quality of the hides processed. Chemicals are used excessively to ensure their penetration into the hides (Scholz et al. 2003). Consequently, it is imperative to pre-treat these tannic effluents before discharging them into the environment to comply with current environmental regulations.

Performance of the ACp Tannery Effluent Treatment Process

To evaluate the effectiveness of activated charcoal derived

Table 3: Physicochemical characterization before and after treatment of tannery effluent.

Parameters	Values		
	Raw effluent	Treated effluent	Moroccan Standards of Rejects
Color	Dark blue	-	-
pH	8.67	8.91	5.5-9.5
EC [$mS.cm^{-1}$]	11.24	5.86	2.7
SS [$mg.L^{-1}$]	5280	-	30
NO_3^- [$mg.L^{-1}$]	19.69	8.36	40
SO_4^{2-} [$mg.L^{-1}$]	4919.06	290.81	600
TKN [$mg.L^{-1}$]	162.62	41.74	40
COD [$mg.L^{-1}$]	14065.92	4479.59	500
Ca [$mg.L^{-1}$]	211.08	213.39	-
K [$mg.L^{-1}$]	56.514	56.33	-
Mg [$mg.L^{-1}$]	171.05	56.53	-
Na [$mg.L^{-1}$]	705.72	718.74	-
Zn [$mg.L^{-1}$]	0.880	0.924	5
Fe [$mg.L^{-1}$]	< 0.01	< 0.01	5
Al [$mg.L^{-1}$]	3.13	< 0.01	10
Cr [$mg.L^{-1}$]	127.04	11.08	2
Cr (VI) [$mg.L^{-1}$]	50	5.11	0.2

from olive pomace for the treatment of tannery effluents, physicochemical analyses were carried out on the raw effluent and after charcoal treatment, as shown in Table 3. The reduction rates were then calculated for each parameter after 48 h of treatment. The results of the physicochemical analyses showed a significant reduction in conductivity from 11.24 to 3.86 $mS.cm^{-1}$. In addition, the reduction rate was about 66%. In terms of pH, a stabilization was observed at 8.91 in the basic medium, which was attributed to the pHpzc of the carbon, which is intrinsically basic. This result is in agreement with that obtained by EL Fadel et al. (2013), who attributed the increase in pH to the basicity of the ash used as an adsorbent. The final levels of sulfate and nitrate were less than 290.812 and 8.36 $mg.L^{-1}$, respectively. The treated effluent more than met the Moroccan discharge standards with a sulfate removal efficiency of 94.08%. This removal efficiency is higher than those found by Omor et al., who used the precipitation process (Omor et al. 2017), and Elkarrach et al. (2018), who used a process combining precipitation and a sequential batch reactor to treat tannery effluent. Fig. 4, which illustrates the evolution of COD and TKN over time, shows a decrease in both tannery effluent pollutants during the first 30 h. After this period, COD and TKN concentrations remained constant. COD finally reached a concentration of 4479 mg $O_2.L^{-1}$ and the treated effluent did not comply with the Moroccan discharge standards. On the other hand, the TKN concentration decreased from 163 $mg.L^{-1}$ to 41 $mg.L^{-1}$, giving a reduction rate of 74.84%. This reduction in TKN is also accompanied by a reduction in nitrates. The effluent treatment thus enabled compliance with Moroccan effluent standards. Comparatively, our removal rates exceed those obtained by the activated carbon adsorption process of Kanawade et al. (2014) and are in line with those obtained by Song et al. (2004) on the physicochemical treatment of tannery effluents by the chemical coagulation process. Thus, it appears that biomass-based activated carbon is very efficient and can replace more costly techniques. The results of metal analysis after treatment with ACp are presented in Table 3. Aluminum, iron, and zinc were reduced so that the treated effluent met the Moroccan discharge standards. The evolution and monitoring of hexavalent chromium (Cr (VI)) is shown in Fig. 4. During the treatment, a decrease in Cr (VI) content was observed. This decrease reached up to 5.11 $mg.L^{-1}$ after 48 h of tannery effluent treatment.

The efficiency of activated carbon produced from olive pomace for the treatment of tannery effluents and the reduction of pollutant parameters in these effluents are shown in Fig. 5. We can see that the removal rates for nitrate, sulfate, TKN, COD, total Cr, and Cr (VI) were 57.54%, 94.08%, 74.84%, 68.18%, 91.27%, and 89.78%, respectively. These results indicate that activated carbon from olive pomace effectively reduces several pollutant parameters in tannery effluents. This suggests that this treatment method can significantly contribute to the improvement of tannery effluent quality.

Comparison of Results with Previous Studies

Table 4 compares the results obtained in our study with the literature, highlighting the remarkable performance of our tannery effluent treatment process using olive pomace-derived activated carbon. Our results show that our activated carbon has a good abatement and reduction rate for tannery effluent pollution parameters such as chemical oxygen demand (COD), TKN, sulfate, nitrate, and hexavalent chromium. What sets our approach apart is the simplicity and effectiveness of our method, which uses only activated carbon derived from olive pomace, a locally available biomass, without the need for complex

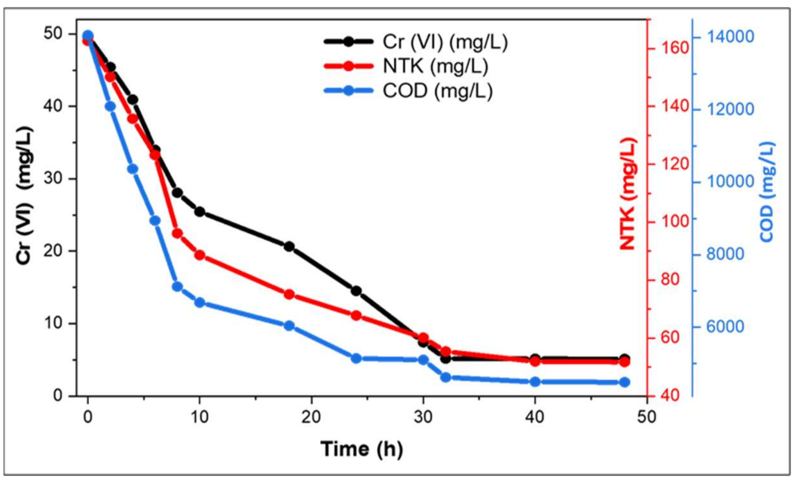

Fig. 4: Evolution of COD, TKN, and Cr (VI) during tannery effluent treatment with ACp.

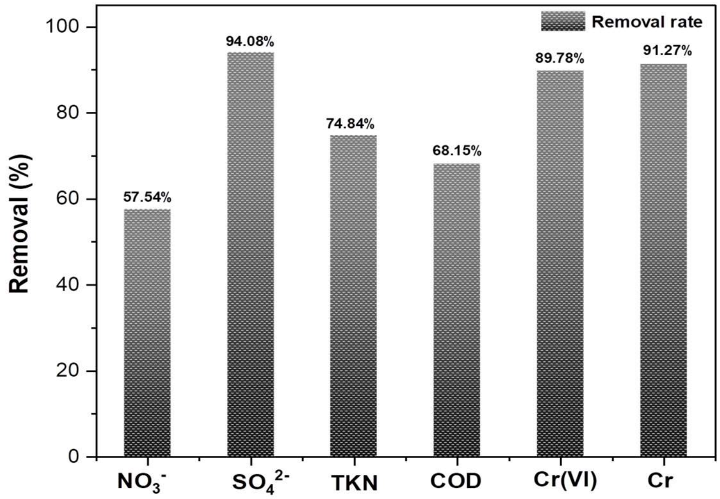

Fig. 5: Activated charcoal abatement rates for different tannery effluent pollution parameters.

Table 4: Comparison of AC_P results with other previous studies.

EC	SO_4^-	TKN	COD	Cr (VI)	Process used	Ref
NR	78	21	49	NR	Membrane filtration	Scholz et al. (2003)
36 %	57%	NR	71%	99.7%	Coagulation and adsorption	Song et al. (2004)
NR	98.5%	66.6%	64.3%	80.7%	Treatment anaerobic and reactor.	Ayoub et al. (2011)
48%	NR	NR	40%	74.4%	Coagulation and adsorption	Kanawade (2014)
82%	99.57%	95.45%	98.17%	96.1%	Precipitation and the sequential batch reactor	Elkarrach et al. (2021)
NR	NR	NR	60.9	99.4%	Chemically enhanced primary treatment	Roš et al. (1998)
66%	94.08%	74.84%	66.18%	89.79 %	Adsorption	present study

NR: not reported

processes or additional costs. Compared to other research studies, some of which are close to our removal rates and others that have achieved better results, it is important to note that these improved performances were often the result of the joint use of two separate processes (Song et al. 2004, Ayoub et al. 2011). This approach, while potentially efficient, is associated with higher processing costs (Scholz et al. 2003), which underscores the economics of our method. The main advantage of our method is its simplicity and accessibility. By focusing solely on the use of activated charcoal derived from olive pomace, we have developed a sustainable and economical solution for the treatment of tannery effluent that meets environmental standards while minimizing the environmental footprint. This innovative approach demonstrates the possibility of achieving competitive results without sacrificing economic viability, thus contributing to the promotion of sustainable practices in the field of industrial liquid effluent treatment.

CONCLUSIONS

This study highlights the importance of treating tannery effluents through the innovative use of activated carbon derived from olive pomace. The results show that this approach is highly effective in reducing effluent pollution parameters, particularly nitrate, sulfate, TKN, COD, Cr, and hexavalent chromium (Cr (VI)). The effectiveness demonstrated by activated carbon in adsorbing and reducing these pollutants is remarkable, achieving competitive removal rates while highlighting the simplicity and accessibility of this treatment method. The in-depth physico-chemical characterization of the tanning water has allowed us to understand the composition of the effluents, underlining the crucial importance of such a step in the environmental management of industrial waste. In addition, the economic advantage of our method is characterized by the use of an adsorbent derived from locally available biomass. This approach offers a promising perspective for the sustainable management of tannery effluents.

ACKNOWLEDGEMENT

The work was financially supported by the VGOLIVES Project, the authors would like to thank the support from the Ministry of Energy, Mining, Water and Environment, Morocco. The findings achieved herein are solely the responsibility of the authors.

REFERENCES

Abatan, O.G., Alaba, P.A., Oni, B.A., Akpojevwe, K., Efeovbokhan, V. and Abnisa, F., 2020. Performance of eggshells powder as an adsorbent for adsorption of hexavalent chromium and cadmium from wastewater. *SN Applied Sciences*, 2, pp.1996.

Alouiz, I., Amarouch, M.Y. and Mazouzi, D., 2022. Process for the elaboration of porous activated carbon reinforced with a fibrous texture from olive pomace. *Morocco Patent*, 55, p.339.

Asaduzzaman, M., Hasan, I., Rajia, S., Khan, N. and Kabir, K.A., 2016. Impact of tannery effluents on the aquatic environment of the Buriganga River in Dhaka, Bangladesh. *Toxicology and Industrial Health*, 32(6), pp.1106–1113.

Ayoub, G.M., Hamzeh, A. and Semerjian, L., 2011. Post treatment of tannery wastewater using lime/bittern coagulation and activated carbon adsorption. *Desalination*, 273(2–3), pp.359–365.

Benmahdi, F., Khettaf, S. and Kolli, M., 2022. Efficient removal of Cr(VI) from aqueous solution using activated carbon synthesized from silver berry seeds: Modeling and optimization using central composite design. *Biomass Conversion and Biorefinery,* 11, p.545.

Cheballah, K., Sahmoune, A., Messaoudi, K., Drouiche, N. and Lounici, H., 2011. Utilization of natural materials for the removal of chromium from tannery wastewater. *Desalination and Water Treatment*, 27, pp.1–8.

Chojnacka, K., 2010. Biosorption and bioaccumulation-the prospects for practical applications. *Environmental International*, 36(3), pp.299–307.

Cooman, K., Gajardo, M., Nieto, J., Bornhardt, C. and Vidal, G., 2003. Tannery wastewater characterization and toxicity effects on *Daphnia spp*. *Environmental Toxicology*, 18(1), pp.45–51.

Dargo, H. and Ayalew, A., 2014. Tannery wastewater treatment: A review. *International Journal of Emerging Trends in Science and Technology*, 1(9), pp.1488–1494.

Deghles, A. and Kurt, U., 2016. Treatment of tannery wastewater by a hybrid electrocoagulation/electrodialysis process. *Chemical Engineering & Processing: Process Intensification*, 104, pp.43–50.

Dhanakumar, S., Solaraj, G., Mohanraj, R. and Pattabhi, S., 2007. Removal of Cr (VI) from aqueous solution by adsorption using cooked tea dust. *Indian Journal of Science and Technology*, 1(2), pp.1–6.

Di Iaconi, C., Lopez, A., Ramadori, R., Di Pinto, A.C. and Passino, R., 2002. Combined chemical and biological degradation of tannery wastewater by a periodic submerged filter (SBBR). *Water Research*, 36(9), pp.2205–2214.

El Fadel, H., Merzouki, M., Faouzi, M., Laamayem, A., Najem, M. and Benlemlih, M., 2013. Purification performance of filtration process for leachate in Morocco by marine sands, clays, and fly ash. *Journal of Biotechnology Letters*, 4(1), pp.51–59.

Elahi, A., Arooj, I., Bukhari, D.A. and Rehman, A., 2020. Successive use of microorganisms to remove chromium from wastewater. *Applied Microbiology and Biotechnology*, 104(9), pp.3729–3743.

Elkarrach, K., Merzouki, M., Laidi, O., Biyada, S., Omor, A. and Benlemlih, M., 2020. Sequencing batch reactor: Inexpensive and efficient treatment for tannery effluents of Fez city in Morocco. *Desalination and Water Treatment*, 202, pp.71–77.

Elkarrach, K., Merzouki, M., Laidi, O., Omor, A. and Benlemlih, M., 2018. Treatment of tannery effluents of Fez City by the sequential batch reactor. *European Journal of Scientific Research*, 150(3), pp.334–348.

Elkarrach, K., Merzouki, M., Laidi, O., Omor, A., Biyada, S. and Benlemlih, M., 2021. Combination of chemical and biological processes for the treatment of tannery effluent of Fez city in Morocco. *Desalination and Water Treatment*, 220(12), pp.109–115.

Elmagd, A.M.A. and Mahmoud, M.S., 2014. Tannery wastewater treatment using activated sludge process system (Lab scale modeling). *International Journal of Engineering Technology Research*, 2(5), pp.21–28.

Espinoza-Quiñones, F.R., Fornari, M.M.T., Módenes, A.N., Palácio, S. M., da Silva, F.G., Szymanski, N., Kroumov, A.D. and Trigueros, D.E.G., 2009. Pollutant removal from tannery effluent by electrocoagulation. *Chemical Engineering Journal*, 151(1–3), pp.59–65.

Fito, J., Tibebu, S. and Nkambule, T.T.I., 2023. Optimization of Cr (VI) removal from aqueous solution with activated carbon derived from *Eichhornia crassipes* under response surface methodology. *BMC Chemistry*, 17(1), pp.1–20.

Harboul, K., Alouiz, I., Hammani, J. and El-Karkouri, A., 2022. Isotherm and kinetics modeling of biosorption and bioreduction of Cr(VI) by *Brachybacterium paraconglomeratum* ER41. *Extremophiles*, 26(3), pp.30.

Hassan, E.S.R.E., Rostom, M., Farghaly, F.E. and Abdel Khalek, M.A., 2020. Bio-sorption for tannery effluent treatment using eggshell wastes, kinetics, isotherm, and thermodynamic study. *Egyptian Journal of Petroleum*, 29(4), pp.273–278.

Islam, S., Islam, F., Bakar, M.A., Das, S. and Bhuiyan, H.R., 2013. Heavy metals concentration at different tannery wastewater canals of Chittagong city in Bangladesh. *International Journal of Agriculture and Environmental Biotechnology*, 6(3), pp.355.

Kanamarlapudi, S., Chintalpudi, V.K. and Muddada, S., 2018. Application of biosorption for the removal of heavy metals from wastewater. *Biosorption*, 18(69), pp.70–116.

Kanawade, S.M., 2014. Treatment of dye industrial wastewater by using adsorption. *International Journal of Chemical and Material Sciences*, 2(3), pp.059–067.

Kurdekar, P. and Shivayogimath, C., 2015. Treatment of tannery effluent using electrocoagulation. *International Journal of Innovative Research in Science, Engineering and Technology*, 4(7), pp.6554–6560.

Labied, R., Benturki, O. and Hamitouche, A.Y.E., Donnot, A., 2018. Adsorption of hexavalent chromium by activated carbon obtained from a waste lignocellulosic material (Ziziphus jujuba cores): Kinetic, equilibrium, and thermodynamic study. *Adsorption Science & Technology*, 36(3–4), pp.1066–1099.

Leta, S., Assefa, F. and Dalhammar, G., 2003. Characterization of tannery wastewater and assessment of downstream pollution profiles along Modjo River in Ethiopia. *Ethiopian Journal of Biological Sciences*, 2(2), pp.157–168.

Linares-Hernández, I., Barrera-Díaz, C., Roa-Morales, G., Bilyeu, B. and Ureña-Núñez, F., 2009. Influence of the anodic material on electrocoagulation performance. *Chemical Engineering Journal*, 148(1), pp.97–105.

Mekonnen, A., Leta, S. and Njau, K.N., 2016. Co-digestion of tannery wastewater and *Phragmites karka* using a laboratory scale anaerobic sequencing batch reactor. *Modern Applied Science*, 9(1), pp.9–14, doi: 10.7537/marsnys09011602.

Mella, B., Glanert, A. C. and Gutterres, M., 2015. Removal of chromium from tanning wastewater and its reuse. *Proceedings of the Institution of Mechanical Engineers, Part B: Journal of Engineering Manufacture*, 95, pp.195–201.

Mella, B., Puchana-Rosero, M.J., Costa, D.E.S. and Gutterres, M., 2017. Utilization of tannery solid waste as an alternative biosorbent for acid dyes in wastewater treatment. *Journal of Molecular Liquids*, 242, pp.137–145.

Merimi, I., Oudda, H. and Hammouti, B., 2017. Characterization of the quality of the polluting load of an industrial zone. *Journal of Chemical and Pharmaceutical Research*, 9(4), pp.165–170.

Naushad, M., 2018. A new generation material graphene: Applications in water technology. *Springer International Publishing*.

Omor, A., Rais, Z., El Rhazi, K., Merzouki, M., El Karrach, K., Elallaoui, N. and Taleb, M., 2017. Optimization of the method wastewater treatment of unit bovine hides' unhairing liming. *Journal of Materials and Environmental Science*, 8(4), pp.1235–1246.

Onukak, I.E., Mohammed-Dabo, I.A., Ameh, A.O., Okoduwa, S.I.R. and Fasanya, O.O., 2017. Production and characterization of biomass briquettes from tannery solid waste. *Recycling*, 2, pp.17.

Ozbay, N. and Yargic, A.S., 2016. Comparison of surface and structural properties of carbonaceous materials prepared by chemical activation of tomato paste waste: The effects of activator type and impregnation ratio. *Journal of Applied Chemistry*, 16(3), pp.1–10.

Pakzadeh, B. and Batista, J.R., 2011. Chromium removal from ion-exchange waste brines with calcium polysulfide. *Water Research*, 45, pp.3055–3064.

Patel, N., Shahane, S., Chauhan, D., Rai, D., Khan, Z.A. and Bhunia, M.B., 2021. Environmental impact and treatment of tannery waste. *Water Pollution and Remediation: Organic Pollutants*, 54, pp.577–592.

Popiolski, A.S., Demaman Oro, C.E., Dallago, R.M., Steffens, J., Bizzi, C.A., Santos, D., Alessio, K.O., Flores, E.M. and Duarte, F. A., 2022. Microwave-assisted extraction of Cr from residual tanned leather: A promising alternative for waste treatment from tannery industry. *Journal of Environmental Chemical Engineering*, 10(1), pp.6–11.

Pradhan, D., Sukla, L.B., Sawyer, M. and Rahman, P.K.S.M., 2017. Recent bioreduction of hexavalent chromium in wastewater treatment: A review. *Journal of Industrial and Engineering Chemistry*, 55, pp.1–20.

Rahman, M.W., Ali, M.Y., Saha, I., Al Raihan, M., Moniruzzaman, M., Alam, M.J. and Deb, A., Khan, M.M.R., 2017. Date palm fiber as a potential low-cost adsorbent to uptake chromium (VI) from industrial wastewater. *Desalination and Water Treatment*, 88(11), pp.169–178.

Ranganathan, K. and Kabadgi, S.D., 2011. Studies on the feasibility of reverse osmosis (membrane) technology for treatment of tannery wastewater. *Journal of Environmental Protection (Irvine, Calif.)*, 2(1), pp.37–46.

Rodier, J., 2009. *Analysis of Water – Fresh Water, Wastewater, Seawater*. Dunod, pp.1475.

Roš, M. and Gantar, A., 1998. Possibilities of reduction of recipient loading of tannery wastewater in Slovenia. *Water Science and Technology*, 37(8), pp.45–52

Sandana Mala, J. G., Sujatha, D. and Rose, C., 2015. Inducible chromate reductase exhibiting extracellular activity in *Bacillus methylotrophicus* for chromium bioremediation. *Microbiological Research*, 170, pp.235–241.

Sandhya, M. and Bharagava, R.N., 2016. Toxic and genotoxic effects of hexavalent chromium in the environment and its bioremediation strategies. *Journal of Environmental Science and Health, Part C*, 34(1), pp.1–32.

Scholz, W. and Lucas, M., 2003. Techno-economic evaluation of membrane filtration for the recovery and re-use of tanning chemicals. *Water Research*, 37(8), pp.1859–1867.

Shaibur, M.R., Tanzia, F.K.S., Nishi, S., Nahar, N., Parvin, S. and Adjadeh, T.A., 2022. Removal of Cr (VI) and Cu (II) from tannery effluent with water hyacinth and arum shoot powders: A study from Jashore, Bangladesh. *Journal of Hazardous Materials Advances*, 7(2), pp.100102.

Shakya, A. and Agarwal, T., 2019. Removal of Cr(VI) from water using pineapple peel derived biochars: Adsorption potential and re-usability assessment. *Journal of Molecular Liquids*, 293, pp.111497.

Solgi, M., Najib, T., Ahmadnejad, S. and Nasernejad, B., 2017. Synthesis and characterization of novel activated carbon from Medlar seed for chromium removal: Experimental analysis and modeling with artificial neural network and support vector regression. *Resources Technology*, 3(3), pp.236–248.

Song, Z., Williams, C.J. and Edyvean, R.G.J., 2004. Treatment of tannery wastewater by chemical coagulation. *Desalination*, 164(3), pp.249–259.

Sun, J.M., Chang, S.Y., Li, R. and Huang, J.C., 2007. Factors affecting co-removal of chromium through copper precipitation. *Separation and Purification Technology*, 56(1), pp.57–62.

Sundar, V.J., Rao, J.R. and Muralidharan, C., 2022. Cleaner chrome tanning emerging options. *Journal of Cleaner Production*, 10, pp.69–74.

Tadesse, G.L. and Kasa, T.G., 2017. Impacts of tannery effluent on environments and human health. *Journal of Environmental and Earth Sciences*, 7(3), pp.88–97.

Tahir, S.S. and Naseem, R., 2007. Removal of Cr(III) from tannery wastewater by adsorption onto bentonite clay. *Separation and Purification Technology*, 53(3), pp.312–321.

Tahiri, S. and Miguel, D., 2009. Treatment and valorization of leather industry solid wastes: A review. *Journal of the American Leather Chemists Association*, 104(2), pp.52–67.

Wang, Q., Zhou, C., Kuang, Y.J., Jiang, Z.H. and Yang, M., 2020. Removal of hexavalent chromium in aquatic solutions by pomelo peel. *Water Science and Engineering*, 13(1), pp.65–73.

Xu, X., Gao, B. Y., Tan, X., Yue, Q.Y., Zhong, Q. and Li, Q., 2011. Characteristics of amine-crosslinked wheat straw and its adsorption mechanisms for phosphate and chromium (VI) removal from aqueous solution. *Carbohydrate Polymers*, 84(3), pp.1054–1060.

Yakout, S.M. and Sharaf El-Deen, G., 2016. Characterization of activated carbon prepared by phosphoric acid activation of olive stones. *Arabian Journal of Chemistry*, 9, pp.S1155–S1162.

Zhao, B., O'Connor, D., Zhang, J., Peng, T., Shen, Z., Tsang, D.C.W. and Hou, D., 2018. Effect of pyrolysis temperature, heating rate, and residence time on rapeseed stem derived biochar. *Journal of Cleaner Production*, 174, pp.977–987.