

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

**Eco-friendly PVA-LYS fibers for gold nanoparticle recovery from water and their catalytic performance**

**This is the author's manuscript**

*Original Citation:*

*Availability:*

This version is available <http://hdl.handle.net/2318/1902616> since 2023-05-08T13:53:49Z

*Published version:*

DOI:10.1007/s11356-023-26912-7

*Terms of use:*

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

1 This version of the article has been accepted for publication, after peer review (when applicable) and is  
2 subject to Springer Nature's AM terms of use, but is not the Version of Record and does not reflect post-  
3 acceptance improvements, or any corrections. The Version of Record is available online at:

4 <https://doi.org/10.1007/s11356-023-26912-7>  
5

6 Eco-friendly PVA-LYS fibers for gold nanoparticles recovery from water

7 and their catalytic performance

8 Eya Ben Khalifa<sup>a</sup>, Claudio Cecone<sup>a</sup>, Pierangiola Bracco<sup>a</sup>, Mery Malandrino<sup>a</sup>, Maria

9 Cristina Paganini<sup>a</sup>, Giuliana Magnacca<sup>a</sup>

10 <sup>a</sup> Department of Chemistry and NIS Interdepartmental Centre, Torino University, Via P.

11 Giuria 7, 10125 Torino, Italy

12 Corresponding Author: Claudio Cecone, Email: [claudio.cecone@unito.it](mailto:claudio.cecone@unito.it), Tel.

13 +390116707558

14 Abstract

15 In this work, we grafted lysine on PVA electrospun fibers, using a green preparation  
16 technique. The resulting fiber mats were proposed for gold nanoparticles (AuNPs) removal  
17 from water. The efficiency of three fibers with different lysine amounts (10, 20 and 30%)  
18 was investigated. The incorporation of amino groups in PVA fibers was firstly proved by  
19 FTIR, SEM and elemental analysis, confirming the presence of lysine. Among the three  
20 different fibers, PVA-LYS 30% has shown the best removal efficiency, reaching 65%, at pH  
21 equal to 5. Adsorption isotherms were studied and showed that the Langmuir model is the  
22 best model fitting our experimental results, with a maximum adsorption capacity of 20.1 mg  
23 g<sup>-1</sup>. Metal-ligand interactions and electrostatic attraction between protonated amino groups  
24 of lysine on the fibers and negatively charged, citrate capped, AuNPs are the main proposed  
25 mechanisms for AuNPs adsorption on the fibers. Sustainability of AuNPs adsorbed on these  
26 fibers has been checked through their reuse as catalyst for the reduction of 4-nitrophenol to  
27 4-aminophenol. The process was completed within 60 min and their reusability showed more  
28 than 99% efficiency after 5 reduction cycles. Our results prove that green PVA-LYS fibers

29 can extract nanoparticles from water, as low cost effective and eco-friendly adsorbent, and  
30 contribute to the promotion of a circular economy approach, through their reuse as catalyst  
31 in the reduction of pollutants.

32 Keywords: Electrospinning, Polyvinyl alcohol, Lysine, Surface modification, Green  
33 crosslinking, Nanoparticles

34 Abbreviations

35 PVA: Polyvinyl Alcohol

36 LYS: Lysine

37 AuNPs: Gold nanoparticles

38 FTIR: Fourier Transform Infrared Red Spectroscopy

39 CAGR: Compound Annual Growth Rate

40 CIRC: International Center of Research on Cancer

41 SEM: Scanning Electron Microscopy

42 TEM: Transmission Electron microscopy

43 TGA: Thermogravimetric Analysis

44 PVA-CA: Polyvinyl Alcohol -Citric Acid fibers

45 ATR: Attenuated Total Reflectance

46  $pH_{pzc}$ : pH of zero charge

47 ICP-OES: Inductively Coupled Plasma - Optical Emission Spectroscopy

48 U.S.: United States

49 1. Introduction

50 Metallic nanoparticles have received great interest due to their unique optical (Zhang et al.  
51 2013), electrical and magnetic (Rudakov et al. 2019) properties, their high surface to volume  
52 ratio, small size and peculiar, adjustable shapes (Thakur et al. 2022). These properties are  
53 interesting in numerous applications, including cell imaging (Karmakar et al. 2019), sensors

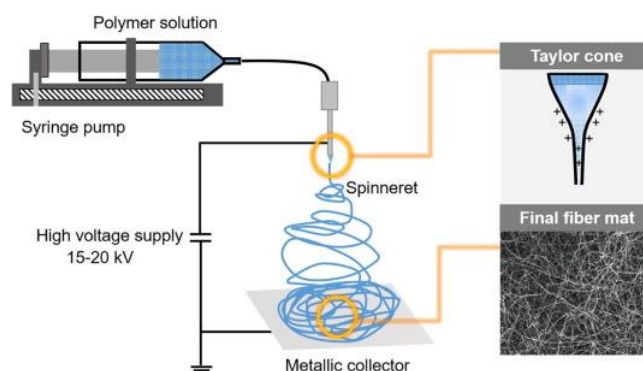
54 (Montes-Garcı et al. 2021), and sunlight energy conversion (Zhang et al. 2022). They are  
55 considered as promising tools for light and magnetic based tumor visualization and guided  
56 drug delivery (Kuchur et al. 2020). Gold nanoparticles (AuNPs) have been used in cancer  
57 remediation in recent years, because of their facile synthesis and surface modification, their  
58 unique surface plasmon resonance, as well as excellent biocompatibility (Huang and El-  
59 Sayed 2010). Applications related to plasmon absorption and scattering of AuNPs are  
60 impressively numerous, ranging from sensing and photothermal effects, to cell imaging  
61 (Amendola et al. 2017). Despite the unique advantages of metallic NPs, their adverse effects,  
62 related to short and long term toxicity are a critical issue. Different studies have been  
63 conducted to explore the dark side of nanotechnology (Grieger et al. 2019; Haase et al. 2012;  
64 Hochella et al. 2019). The nanotoxicity includes cytotoxicity, genotoxicity, production of  
65 reactive oxygen species (ROS), oxidative stress and inflammation, modulation of cell  
66 signaling and cancer (Manuja et al. 2021). The global market for nanotechnology is expected  
67 to grow from \$2.0 billion in 2018 to \$2.1 billion by 2023, at a compound annual growth rate  
68 (CAGR) of 19.4% (BBC research reports 2021). This huge production of nanomaterials will  
69 increase their release in the environment (soil, water, and atmosphere) and cause a higher  
70 risk to the ecosystem and human health (Du et al. 2020; Mao et al. 2018). Therefore, progress  
71 in reducing nanoparticles release of and/or developing efficient removal techniques is  
72 urgently needed. Research studies on their removal from water are at the first stage and  
73 limited investigations are available in the literature. The efficiency of porous melamine-  
74 formaldehyde resin (Li et al. 2021), functionalized carbon spheres (Kumar et al. 2014),  
75 amine-functionalized block copolymers (Querchi et al. 2014) and cellulose based nanofibers  
76 (Mahanta et al. 2012) has been evaluated to reduce the levels of AuNPs in water. The  
77 preparation of the previously mentioned adsorbents was usually done using toxic chemicals  
78 like glutaraldehyde, formaldehyde, and tetrahydrofuran. In contrast, this work focuses on the

79 use of green and ecofriendly crosslinking agent to produce electrospun fibers as AuNPs  
80 adsorbents from aqueous solutions.

81 Green electrospun fibers have shown excellent efficiency in water remediation. Picón et al.  
82 2022 reported a novel immobilized L-cysteine on PVA nanofibers to remove arsenic from  
83 water. PAN fibers have been used by Alarifi et al. 2020 as a filtration membrane to remove  
84 pollutants from municipal wastewater. Wang et al. 2022 prepared an eco-friendly calcium  
85 crosslinked alginate electrospun nanofibers with high adsorption efficiency of copper,  
86 reaching 285.5 mg g<sup>-1</sup>. Moreover, Elkady et al. 2020 fabricated PVA / alginate / chitosan  
87 nanofibers for phenol decontamination. Electrospinning is a promising technique, getting an  
88 increasing interest due to its simplicity, efficiency, low cost, and easy scalability (Zhang et  
89 al. 2022; Omer et al. 2021). This technique is based on flowing a polymer solution through  
90 a syringe, while an electrical field is applied to the polymer droplet. Once the electrostatic  
91 repulsion of the charged polymer liquid becomes higher than the surface tension, a conical  
92 shape, known as Taylor's cone, forms and the jet initiation starts from the cone tip. The  
93 produced fibers are deposited on a metallic collector (Fig. 1). Polyvinyl alcohol (PVA) is a  
94 synthetic polymer, characterized by its non-toxicity, biodegradability, low cost,  
95 biocompatibility, and good mechanical strength (Park et al. 2017; Zhan et al. 2021). It has  
96 been widely used as blending polymer in electrospinning for different applications: tissue  
97 engineering scaffolds (Teixeira et al. 2019), food packaging and water treatment (Zhang et  
98 al. 2019; Zhang et al. 2020). PVA is water-soluble thanks to the presence of hydroxyl groups  
99 (Thong et al. 2016), then PVA nanofibers can be easily obtained from the electrospinning of  
100 aqueous solutions. On the other hand, an appropriate crosslinking step after electrospinning  
101 can guarantee the stability of the fibers in an aqueous environment. Different chemical agents  
102 such as glutaraldehyde (Mansur et al. 2008), glyoxal (Zhang et al. 2010), formaldehyde and  
103 methanol (Franco et al. 2012) were previously used as cross-linkers. However, these agents

104 are highly dangerous for human health and classified as carcinogen by the CIRC (ANSES,  
105 2021). As an alternative, citric acid was added to the polymer blending, as a green and non-  
106 toxic crosslinker, in this work (Cecone et al. 2022). Lysine (2,6-diaminohexanoic acid) is  
107 one of the essential amino acids, containing two amino groups and  $\alpha$ -carboxylic acid group  
108 (Stagi et al. 2022). The presence of these functional groups offers different advantages when  
109 lysine is loaded on PVA electrospun fibers: the amide bond formation between carboxylic  
110 groups of citric acid and amino groups of lysine enhances the grafting of lysine to the  
111 polymer substrate, while the reactivity of the residual amino groups can be exploited as  
112 active sites for metallic nanoparticles adsorption, thanks to their ability to bind to the NPs  
113 (Lapenna et al. 2020; Liguori et al. 2019).

114



115

116

**Fig. 1** Electrospinning set up (Wen et al. 2021)

117 This study investigates the use of lysine grafted PVA fibers, as green adsorbent of AuNPs  
118 from water. To test the efficiency of these fibers, three different amounts of lysine were  
119 added to the PVA polymer mixture. The produced fibers were characterized by  
120 scanning electron microscopy (SEM), Fourier Transform InfraRed spectroscopy (FTIR),  
121 thermogravimetric analysis (TGA), elemental analysis, and pH of zero charge. Batch  
122 adsorption experiments were conducted in a pH range of 5 to 9, with an amount of adsorbent  
123 from 5 to 20 mg and at two concentrations of AuNPs. Adsorption kinetics and isotherms  
124 were studied, and an adsorption mechanism has been proposed. Finally, the catalytic

125 performance of the recovered AuNPs was evaluated through the reduction of 4-nitrophenol  
126 to 4-aminophenol and a reusability test was carried out to check the recyclability of these  
127 fibers after AuNPs adsorption.

## 128 2. Materials and Methods

### 129 2.1. Materials

130 Polyvinyl alcohol (PVA) 99 % hydrolyzed, with an average molecular weight of 89000 -  
131 98000 Da, hydrogen tetrachloroaurate trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ), trisodium citrate  
132 ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ ), sodium hydroxide (NaOH), hydrochloric acid (HCl), Lysine (Lys), sodium  
133 borohydride ( $\text{NaBH}_4$ ), nitric acid ( $\text{HNO}_3$ ) and hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) were purchased  
134 from Sigma Aldrich. 4-Nitrophenol (4-NP) was supplied by Merck. All chemicals were  
135 analytical grade. Deionized water was used to prepare the solutions.

### 136 2.2. AuNPs synthesis

137 AuNPs were prepared using the trisodium citrate reduction method according to the  
138 procedure proposed by Li. et al. (2011). Briefly, 2 mL of chloroauric acid solution (25 mM)  
139 were introduced into a flask, then 6.6 mL of NaOH ( $20 \text{ mmol L}^{-1}$ ) and 11.4 mL of deionized  
140 water were added to reach a final volume of 20 mL. After boiling this mixture for 30 min,  
141 0.6 mL of sodium citrate solution ( $50 \text{ mg mL}^{-1}$ ) was rapidly introduced under vigorous  
142 stirring and kept boiling for 2 min. The solution color changed from yellow to ruby red.  
143 Then, the suspension was cooled and diluted to 100 mL for further uses.

### 144 2.3. Preparation of PVA and LYS blend solution

145 The polymer mixture was prepared by dissolving 1 g of PVA in 10 mL of deionized water  
146 at  $80^\circ\text{C}$  for 4 hours. After cooling, different amounts of lysine were added to the PVA  
147 solution to achieve 10, 20 and 30 %wt. referred to the weight of PVA (Table 1). Citric acid  
148 (CA), used as in-situ crosslinking agent, was added to all blends in a percentage of 15% of

149 the total polymer weight. Prior to use for electrospinning, the mixture was stirred for 1 h to  
150 obtain a homogeneous solution.

151 Pure PVA-CA fibers were also prepared in the same way, without adding lysine to the  
152 mixture.

153

**Tab. 1** Prepared polymer solutions

Sample Name	Amount of lysine in PVA blend (wt %)	Amount citric acid (wt %) **
PVA-CA*	0	
PVA-LYS 10	10	15
PVA-LYS 20	20	
PVA-LYS 30	30	

154 \*PVA-CA: PVA-Citric Acid, \*\*Amount of citric acid is 15 % of total polymer weight

#### 155 2.4. Fabrication of PVA-LYS fibers

156 PVA-LYS fibers were prepared by electrospinning. The setup is composed of a high-voltage  
157 power supply, a syringe pump, and a stainless steel collector. The electrospinning process  
158 was performed using 30 kV field strength, 15 cm tip-to-collector distance and 0.9 mL min<sup>-1</sup>  
159 flow rate. After electrospinning, the fibers were cured by thermal treatment at 180°C for 30  
160 min.

#### 161 2.5. Characterization

162 A Malvern Zetasizer Nano - ZS was used to measure the surface charge of AuNPs. HR-TEM  
163 micrographs of AuNPs were obtained using a JEOL JEM 3010 instrument (300 kV)  
164 equipped with LaB<sub>6</sub> filament. A few drops of nanoparticles suspension were placed on a 200  
165 mesh carbon-coated copper grids and allowed to dry before analysis. Elemental analysis was  
166 conducted by a Thermo Fisher FlashEA 1112 Series elemental analyzer. Fibers morphology



167 was characterized by Zeiss EVO 50 scanning electron micrograph, operating at 10 kV  
168 accelerating voltage. The samples were first coated with gold using a Baltec SCD 050 sputter  
169 coater for 40 seconds at 60 mA. FTIR spectra were obtained using a Perkin Elmer instrument  
170 (Spectrum 100) in attenuated total reflectance (ATR) mode. The spectra were recorded in  
171 the range from 650 to 4000  $\text{cm}^{-1}$ , at 4  $\text{cm}^{-1}$  resolution and 8 scans/spectrum, using a DTGS  
172 detector. Thermogravimetric analysis was performed on a TA instrument SDT Q600, under  
173 a nitrogen gas flow of 100  $\text{ml min}^{-1}$ . About 10 mg of sample were placed in an alumina pan  
174 and heated from 30 to 700°C with a ramp of 10°C  $\text{min}^{-1}$ .

175 The pH of zero charge ( $\text{pH}_{\text{pzc}}$ ) of PVA-LYS fibers was determined using the following  
176 experimental procedure: 30 mg of the material were introduced in six Erlenmeyer flasks  
177 containing 10 mL of NaCl (0.01  $\text{mol L}^{-1}$ ) then the pH was adjusted in the range 2 to 12 with  
178 HCl or NaOH (0.1 and 1  $\text{mol L}^{-1}$ ). The mixtures were maintained under stirring for 24 hours.  
179 Finally, the final pH was measured using a Metrohm pHmeter and the  $\text{pH}_{\text{pzc}}$  was determined  
180 as the intersection of the curve initial pH versus final pH with the bisector (Faria et al. 2004).  
181 The solubility test of PVA-LYS fibers was carried out by introducing 20 mg of each sample  
182 in 5 mL deionized water for 24 hours at room temperature. The soluble fraction was obtained  
183 by measuring the weight loss after drying the membranes, using the equation 1:

$$W_{\text{loss}}(\%) = \frac{(w_0 - w_1)}{w_0} \times 100 \quad \text{Eq.1}$$

184 Where,  $w_0$  is the initial weight (mg) and  $w_1$  is the final weight after drying (mg).

## 185 2.6. Batch adsorption experiments

186 The efficiency of PVA-LYS fibers toward AuNPs removal was evaluated by a batch  
187 adsorption study. Different amounts of PVA-LYS fibers were added to 5 mL of AuNPs  
188 suspension with a concentration of 0.1 mM. The mixtures were kept under stirring (450 rpm)  
189 at room temperature. The residual concentration of AuNPs was determined using a Varian  
190 Cary 300 Scan UV-Visible spectrophotometer, by measuring the absorption at 520 nm.

191 Kinetic studies were conducted at different times, ranging from 30 min to 24 h and for two  
192 concentrations of AuNPs: 0.1 mM and 0.25 mM. The effect of pH on nanoparticle adsorption  
193 was investigated using an initial concentration of 0.1 mM and 10 mg of fibers. The initial  
194 pH was adjusted in the range 5 to 9 using 0.1 M HCl or 0.1 M NaOH.  
195 The removal percentage  $Y$  (%) and the adsorption capacity  $q_e$  ( $\text{mg g}^{-1}$ ) were calculated  
196 according to equations 2 and 3:

$$Y = [(C_0 - C_e)/C_0] \times 100 \quad \text{Eq. 2}$$

$$q_e = (C_0 - C_e) \times V/W \quad \text{Eq. 3}$$

197 where,  $C_0$  ( $\text{mg L}^{-1}$ ) is the initial concentration,  $C_e$  ( $\text{mg L}^{-1}$ ) is the concentration at equilibrium,  
198  $V$  (L) is the solution volume and  $W$  (g) is the adsorbent amount.

199 All adsorption experiments were performed in triplicate. The error was estimated as the  
200 standard deviation of the three measurements.

## 201 2.7. Fibers digestion and analysis by ICP-OES

202 The presence of gold nanoparticles on PVA-LYS fibers after adsorption has been confirmed  
203 through the digestion of dried AuNPs/PVA-LYS fibers, followed by ICP-OES  
204 measurements. The sample was digested by a microwave oven (Milestone-MEGA 1200)  
205 with a mixture of 3 mL of nitric acid and 1 mL of hydrogen peroxide in 100 mL  
206 tetrafluoromethoxyl vessels. The following heating steps were applied consecutively: 5 min  
207 at 250 W, 5 min at 400W, 5 min at 600 W, 5 min at 250 W and finally 30 min of ventilation.  
208 The resulting solutions were filtered on cellulose filters (Whatman Grade 5) to eliminate the  
209 undissolved polymer and diluted to 10 mL with HPW (Milli-Q (Millipore) ultrapure water,  
210 resistivity = 18.2  $\text{M}\Omega \text{ cm}$ ). Au concentration was determined by Inductively Coupled Plasma  
211 Optical Emission Spectroscopy, ICP-OES (PerkinElmer, model Optima 7000 DV) equipped  
212 by a Teflon Mira Mist nebulizer, a cyclonic spray chamber and an Echelle monochromator.  
213 The applied power was 1300 W. Plasma, auxiliary and nebulizer gas flows were 15, 0.2 and

214 0.6 L min<sup>-1</sup> respectively. The signals were measured in triplicate. Au concentration was  
215 measured at 267.595 nm.

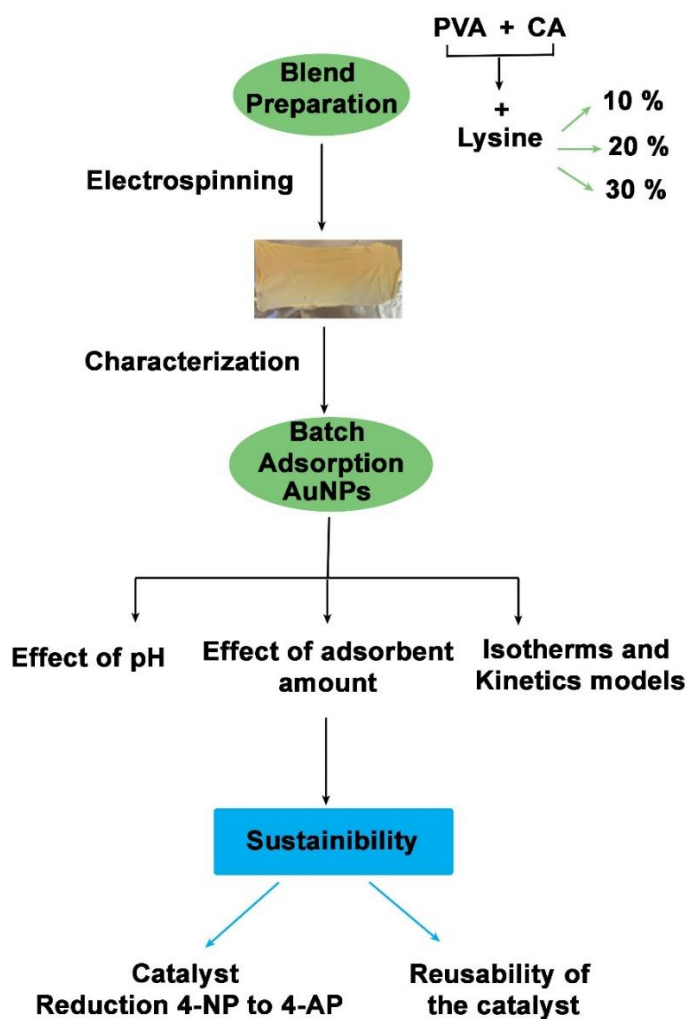
216

217

218 2.8. Catalytic performance of AuNPs/PVA-LYS

219 The catalytic performance of AuNPs adsorbed on PVA-Lys fibers was evaluated by the  
220 reduction of 4-NP in the presence of NaBH<sub>4</sub> as a reducing agent. 30 mg of dried fibers,  
221 recovered from the AuNPs adsorption experiment from water, were added to a solution of  
222 4-NP (1 mM, 5 mL) and a freshly prepared NaBH<sub>4</sub> solution (50 mM, 15 mL) under stirring  
223 (Hashimi et al., 2019). The kinetic of the reaction was monitored by the absorbance of  
224 nitrophenolate ion at the wavelength 400 nm.

225 The following flowchart summarized the methodology used in this work (Scheme 1).



226

227

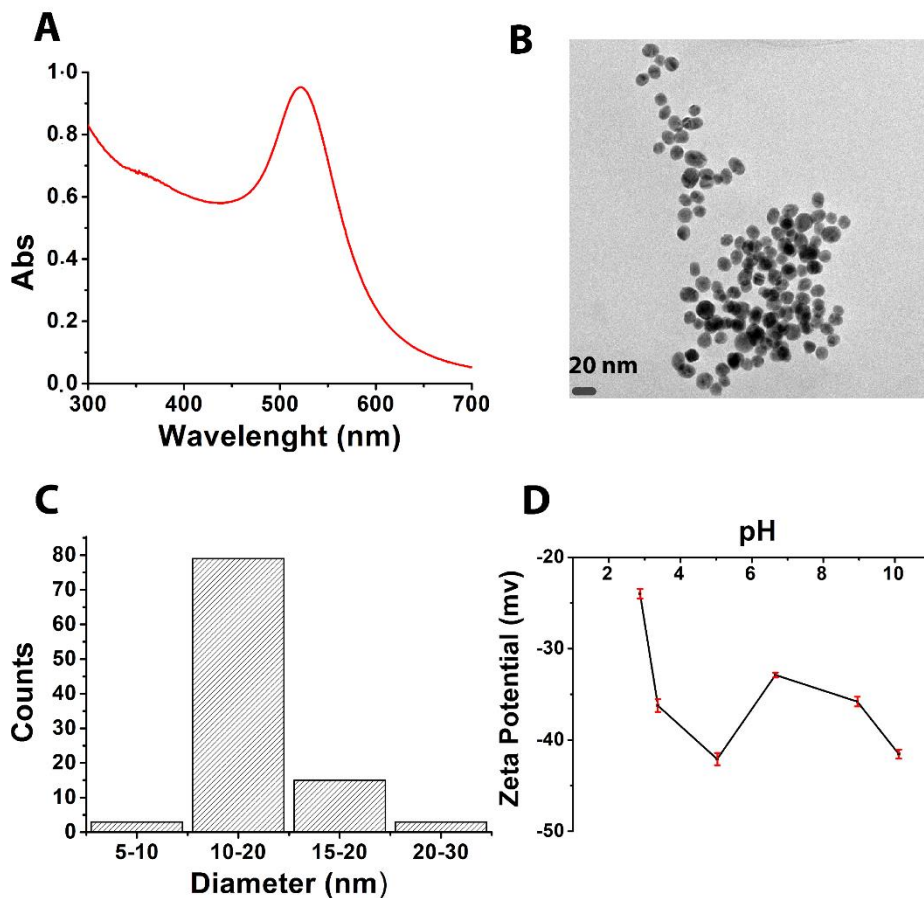
Scheme 1: Flowchart of the methodology

228 3. Results and discussions

229 3.1. Characterization

230 The synthesized AuNPs were characterized using UV-Visible, TEM and Zeta-potential  
 231 techniques. The UV-Visible spectrum (Fig.2A) shows that the surface plasmon resonance  
 232 peak occurs at 520 nm, confirming the successful preparation of AuNPs (Hammami et al.  
 233 2021). TEM images (Fig.2B) reveal that the nanoparticle shape was uniform and  
 234 predominantly spherical. Their average size is equal to  $13.07 \text{ nm} \pm 2.49 \text{ nm}$  (evaluated on a  
 235 sample of 100 particles, Fig.2C). Zeta potential values were negative over all the pH range  
 236 as shown in Fig.2D, indicating a good stability of the suspension. These negative values  
 237 could be associated to the citrate ions adsorbed on the surface of AuNPs (Gicheva et al.

238 2013). Hence, these results confirm the successful synthesis of stable citrate capped AuNPs  
239 with a negatively charged surface.



240

241 **Fig. 2** UV-Visible spectrum of AuNPs (A) TEM image (B) Size distribution of

242 nanoparticles (C) Zeta potential of AuNPs (D)

243 ATR-FTIR spectra of the three PVA-LYS fibers, PVA-CA fibers, pure PVA and Lysine are

244 shown in Fig.3. In the region between  $650\text{ cm}^{-1}$  and  $1500\text{ cm}^{-1}$ , the spectrum of pure PVA

245 crosslinked with citric acid presents the characteristic bands at 840, 1092, 1235 and 1420

246  $\text{cm}^{-1}$ , corresponding to C-C (Santos et al. 2014), C-O (Fu et al. 2019), C-C-O stretching (Park

247 et al. 2017) and C-H bending, respectively. The two peaks appearing at  $2941\text{ cm}^{-1}$  and  $2912$

248  $\text{cm}^{-1}$  are related to the symmetric and asymmetric stretching of -CH (Rosli et al. 2022, Fu et

249 al. 2017).

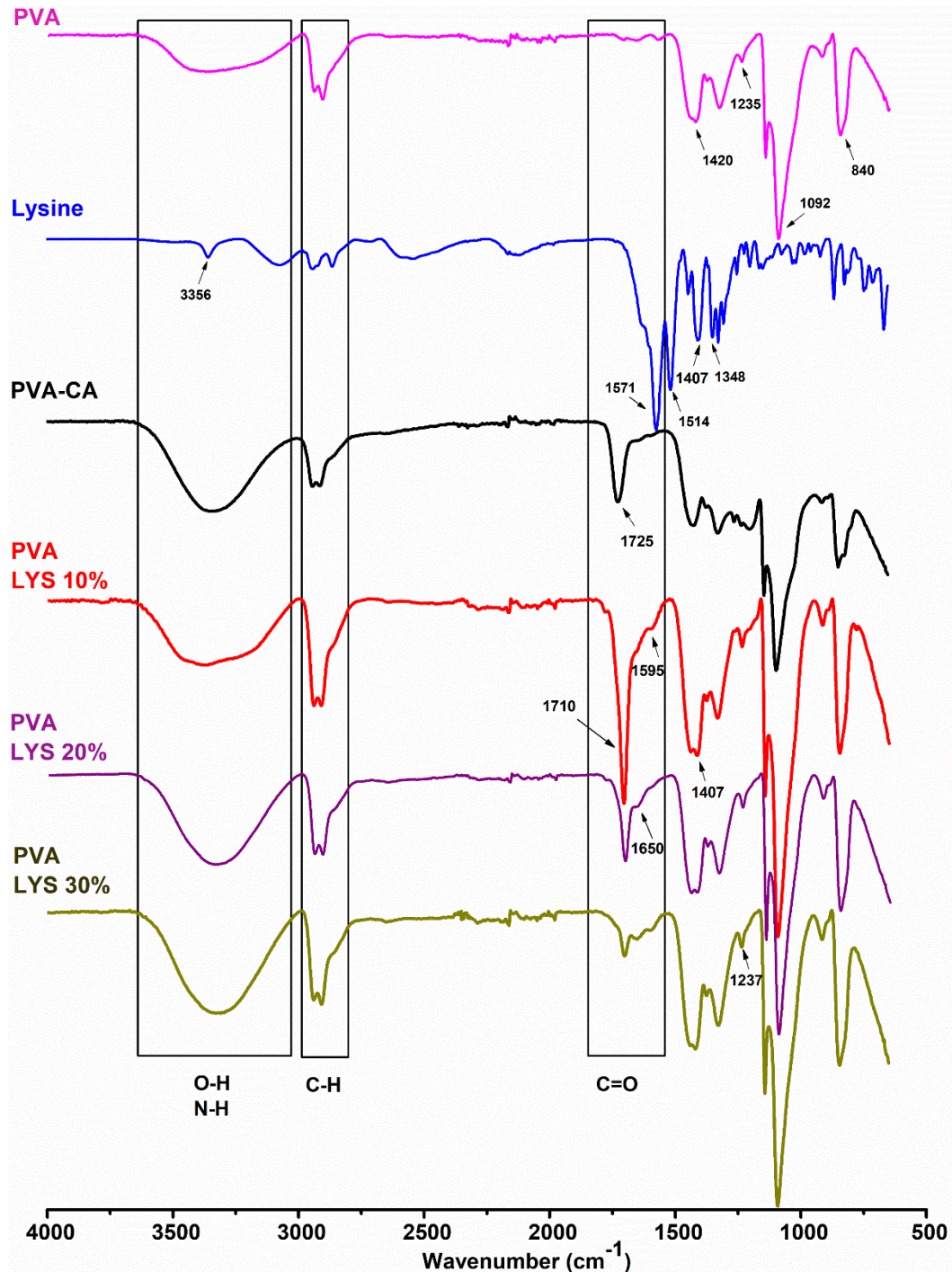
250 Lysine is usually known to exist in the zwitterionic form in both solid and solution  
251 conditions, with the unprotonated carboxyl group ( $-\text{COO}^-$ ) and the protonated amino group  
252 ( $-\text{NH}_3^+$ ). Accordingly, the spectrum of pure lysine shows a distinct absorption at  $3356\text{ cm}^{-1}$ ,  
253 assigned to the asymmetric stretching vibrations of the primary amino group, while the  
254 stretching vibration of the protonated amino group gives several broad bands between 2500  
255 and  $3200\text{ cm}^{-1}$ . The strong bands at  $1571$  and  $1514\text{ cm}^{-1}$  are attributed to the asymmetric  
256 stretching vibration of  $-\text{COO}^-$  and the bending of  $-\text{NH}_3^+$  group, respectively (Yao and Huang  
257 2022).

258 PVA-LYS spectra show: a broad band around  $3300\text{ cm}^{-1}$ , assigned to the overlapping of  
259 stretching vibrations of O-H and N-H groups (Zhang et al. 2020) and two weak absorption  
260 signals at  $1595$  and  $1650\text{ cm}^{-1}$ , attributed to the amidic C=O, resulting from the reaction  
261 between the amino groups of lysine and the carboxylic acid groups of CA, as reported by  
262 Uranga et al. during the preparation of gelatin fibers (Uranga et al. 2016). Low wavenumber  
263 IR signals of these amide groups could be hidden by the intense low-frequency bands of pure  
264 PVA crosslinked fibers (Santiago-Castillo et al. 2021). However, a shoulder at  $1407\text{ cm}^{-1}$ ,  
265 typical of lysine, together with the C-N stretching vibration band at  $1237\text{ cm}^{-1}$  are also  
266 observed.

267 The ester carbonyl stretching signal of pure crosslinked PVA-CA fibers at  $1725\text{ cm}^{-1}$  shifts  
268 to  $1710\text{ cm}^{-1}$  in the PVA-LYS spectra, confirming the change in the chemical environment  
269 due to the presence of lysine in the fibers. This band is assigned to the carbonyl of ester  
270 groups, resulting from the crosslinking reaction between the carboxylic group of citric acid  
271 and hydroxyl group of PVA. In addition, as the amount of lysine in the material increases,  
272 the intensity of this signal decreases, while those at  $1595$  and  $1650\text{ cm}^{-1}$ , attributable to the  
273 amide carbonyl groups increase, as if the presence of amino groups of lysine causes a  
274 competitive reaction with carboxylic groups of citric acid, hindering the formation of ester



275 bonds. In conclusion, the ATR-FTIR spectra suggest that lysine can react with the cross-  
276 linker (citric acid) through the formation of amide groups, guarantying its grafting onto the  
277 PVA fibers.



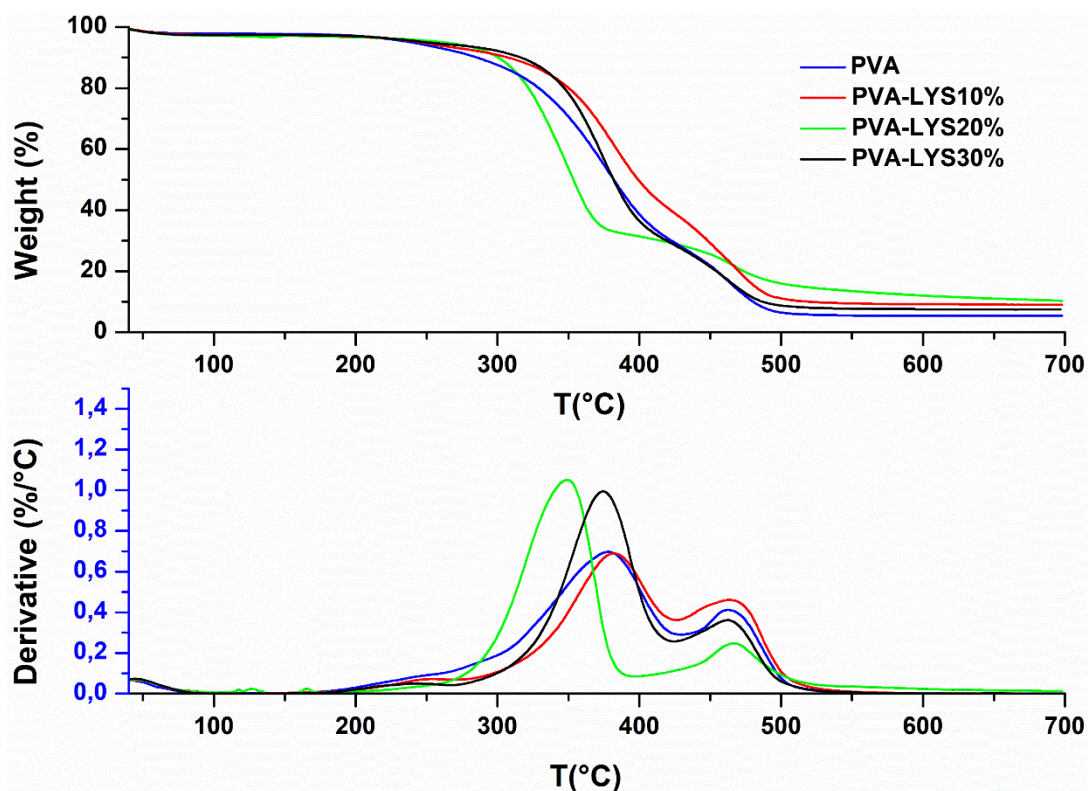
278

279 **Fig. 3** ATR-FTIR spectra of reference PVA, Lysine, PVA-CA, and PVA-LYS fibers

280 The thermal stability of PVA-LYS and PVA was studied through their TGA, shown in Fig.

281 4. The fibers resulted thermally stable up to approximately 200°C. Thermogravimetric

282 profiles were characterized by a first weight loss step, occurring approximately up to 150°C,  
283 which was related to the volatilization of the water adsorbed on the samples or trapped by  
284 the hydrophilic hydroxyl groups in the polymer matrix (El-Sayed et al. 2011; Singh et al.  
285 2022). Between 250°C and 500°C a two-step degradation process was observed, as  
286 evidenced by the derivative curves (Fig. 4), giving a stable carbon residue at 700°C  
287 corresponding approximately to 15% of the initial weight. The first weight loss between  
288 230°C and 350°C might be related to the removal of hydroxyl groups and the formation of  
289 polyene, as mentioned by (Tamer et al. 2021). The following weight loss could also be  
290 attributed to the decomposition of the PVA main chain and the decomposition of citrate and  
291 lysine (Aparecida Toledo Costa et al. 2022; Zhang et al. 2017).



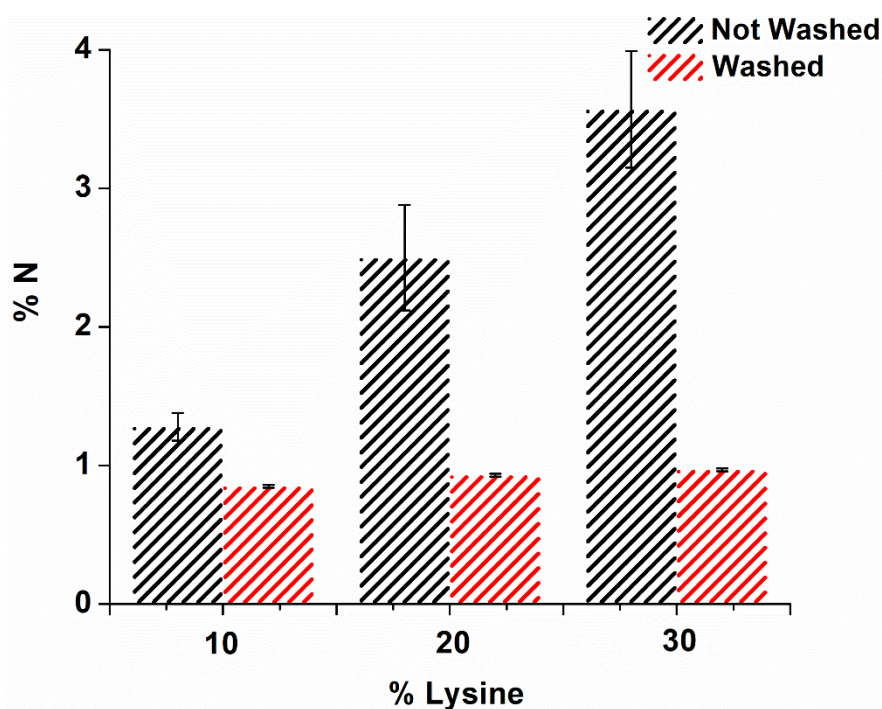
292

293 **Fig. 4** Thermographs of PVA and PVA-LYS fibers

294 Fig. 5 presents the nitrogen content in the PVA-LYS fibers as a function of lysine percentage.  
295 The amount of nitrogen increases from 1.28% to 3.57% with the loaded concentration of  
296 lysine for the unwashed membranes; however, washing the fibers causes a reduction in the



297 lysine content. The amount of N detected after this step, corresponding to less than 1% for  
298 all materials, shows very limited variations from one sample to another. These results  
299 indicate that not all the lysine added to the mixture was chemically bonded to the matrix,  
300 and moreover that the material reaches a maximum possible loading corresponding to about  
301 0.9%. The solubility test shows that more than 75 wt% of the initial material is insoluble, as  
302 the soluble fractions were  $12.5 \pm 1.4$  wt%,  $23.7 \pm 4.2$  wt% and  $27.4 \pm 2.6$  wt%, for PVA-  
303 Lys 10, 20 and 30%, respectively. The observed weight loss can be associated to the  
304 uncrosslinked PVA chains and the released lysine after washing. The results of the elemental  
305 analysis and the soluble fractions values proved that the amino acid has been grafted on the  
306 PVA, which is accordance with the FTIR adsorption bands of PVA-LYS.



307

308

**Fig. 5** Nitrogen content in PVA-LYS fibers

309

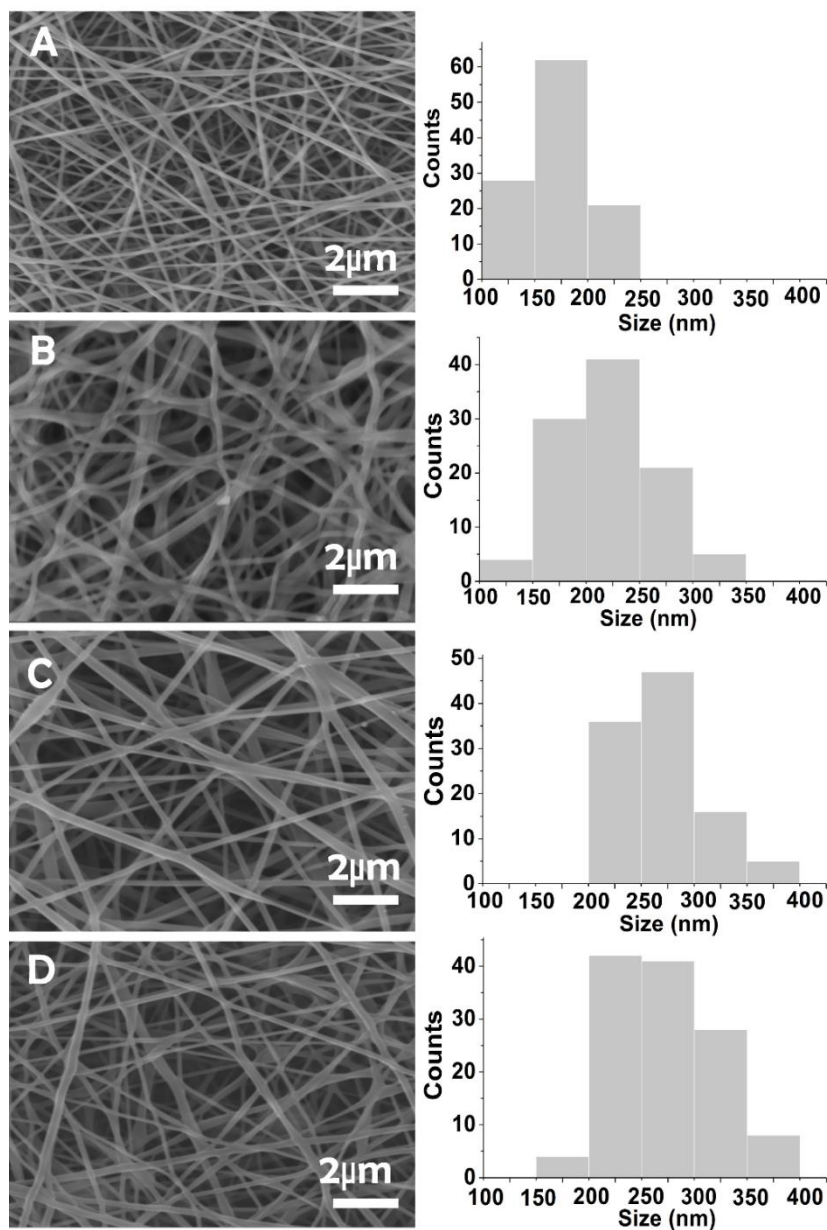
310

311

312

The morphological features of the membranes were studied through SEM, as shown in Fig.6. The PVA fibers (Fig. 6A) showed a circular and smooth surface morphology, without any beads formation, and their average diameter was  $177 \text{ nm} \pm 25 \text{ nm}$ . After the addition of lysine, the morphology of the modified fibers was maintained compared to the PVA fibers.

313 The diameter and morphology of the PVA-LYS fibers were smooth and uniform along the  
 314 fiber axis. The average diameter of the PVA-LYS fibers is presented in Table 2. A  
 315 proportional increase in diameter is observed, with increasing the lysine percentage,  
 316 explained by the increase in the overall blend concentration (Nezarati et al. 2013). This  
 317 increase could also result by the interactions between PVA and CA, as well as between PVA  
 318 and LYS (Zhang et al. 2020).



319  
 320 **Fig. 6** SEM images and size distribution of PVA (A), PVA-LYS 10% (B), PVA-LYS 20%  
 321 (C) and PVA-LYS 30% (D) fibers

322

323

**Tab. 2** Average diameter of PVA and PVA-LYS

fibers

% Lysine	Average Diameter (nm)
0	177 ± 25
10	222 ± 46
20	268 ± 36
30	272 ± 47

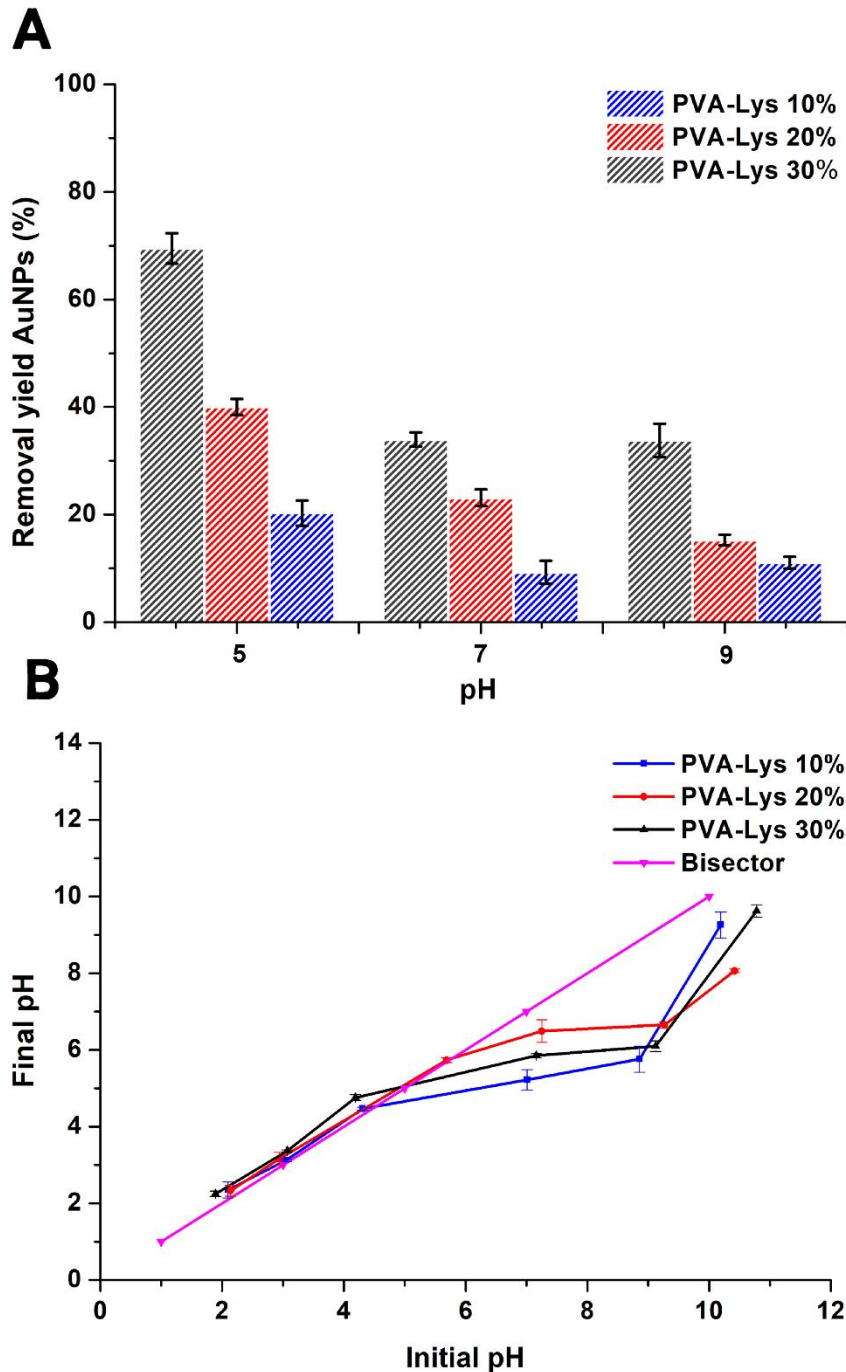
324

### 325 3.2. Efficiency of PVA-LYS fibers in AuNPs extraction

326 The presence of AuNPs on the fibers was first confirmed by the digestion of PVA-LYS  
327 fibers after the adsorption experiment. The concentration of Au on the digested fibers,  
328 measured by ICP-OES, was equal to  $11.31 \pm 0.18 \text{ mg g}^{-1}$ . After confirming the presence of  
329 AuNPs on PVA-LYS fibers, the effect of different parameters, such as pH, amount of fibers  
330 and initial AuNPs concentration are investigated in this section. The effect of pH on the  
331 nanoparticles adsorption is an important key to understand the interaction mechanisms  
332 involved in the adsorption process. The choice of a pH range from 5 to 9 was based on the  
333 region where NPs are stably suspended, to avoid their aggregation and consequent  
334 precipitation that could affect the results (Li et al. 2014). In all these experiments only,  
335 washed fibers were tested. The AuNPs removal percentage decreased with increasing pH, as  
336 shown in Fig.7A. A significant improvement in removal efficiency was observed when  
337 switching from PVA-LYS 10% to PVA-LYS 30%. The AuNPs adsorption percentage  
338 reached 70% at pH 5 for PVA-LYS 30%. The pH effect can be explained in terms of  $\text{pH}_{\text{pzc}}$   
339 of the adsorbent.  $\text{pH}_{\text{pzc}}$  was equal to 4.60, 4.98 and 5.80 for PVA-LYS 10, 20 and 30%,

340 respectively (Fig.7B). The surface of PVA-LYS 30%, and only that, is therefore positively  
341 charged when pH is below 5.80. At pH 5, the electrostatic attraction between the positively  
342 charged surface fiber of PVA-LYS 30% and the negatively charged citrate capped AuNPs  
343 can explain the increase in removal uptake to 65%. However, the electrostatic repulsion  
344 between the carboxylate ions present on the fibers and the nanoparticles could explain the  
345 decreasing of the removal yield for basic pH. Nevertheless, Fig. 7A shows that the removal  
346 percentage for PVA-LYS 30% is around 40%, even for pH above 5, indicating that the  
347 electrostatic interaction is not the only mechanism involved in the adsorption process.  
348 Selvakannan et al. (2003) demonstrated through NMR investigations that gold nanoparticles  
349 can bind to  $\alpha$ -amino groups of lysine. Other phenomena involving the matrix need to be  
350 hypothesized to explain the results observed for AuNPs removal. In fact, washing causes an  
351 important leaching of lysine, as indicated by the N content measurements described in Fig.  
352 5. After washing, all samples contain almost the same amount of lysine, but lysine and matrix  
353 probably interact more intimately in the sample PVA-LYS 20% and 10%, and this  
354 interaction could block part of the amino groups of lysine which are no longer available for  
355 AuNPs removal.

356



357

358 **Fig. 7** Effect of pH on AuNPs adsorption for the PVA-LYS fibers (A)

359 Determination of  $pH_{pzc}$  of PVA-Lys fibers (B) ( $[AuNPs] = 0.1$  mM, suspension

360 volume = 5 mL, time = 24h, 10 mg fibers)

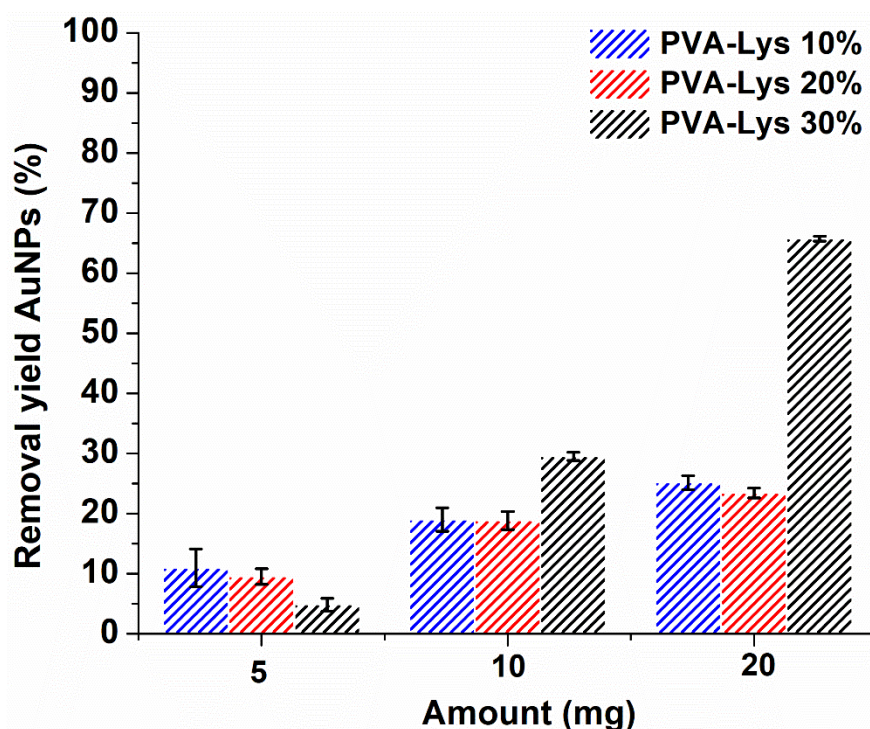
361 Different amounts of PVA-LYS fibers were tested to evaluate their effect on AuNPs

362 removal, as shown in Fig. 8. Increasing the fibers amount from 5 to 20 mg produced a higher

363 removal efficiency, reaching 67% for PVA-LYS 30%, due to the presence of a higher

364 number of functional groups available for interaction with AuNPs (Ahmed et al. 2020).  
365 Fibers with 10 and 20 % lysine content showed a slight increase in the removal yield from 5  
366 to 10 mg, then a non-significant enhancement was observed. The next adsorption  
367 experiments were performed using the PVA-LYS 30 % fibers and the amount of 20 mg of  
368 fibers.

369



370

371 **Fig. 8** Effect of PVA-LYS amount ( $[AuNPs] = 0.25$  mM, suspension volume = 5  
372 mL, time = 24h, pH=7)

373 The kinetics of adsorption of molecules can be determined by their transport toward the  
374 surface by diffusion or by interface attachment. The shape and flexibility of the molecules  
375 may play a role on the timescale of the kinetic process (Alkafeef and Al-Marri 2016). The  
376 kinetic of AuNPs adsorption on PVA-LYS 30% was evaluated at two different AuNPs  
377 concentrations (Fig. 9A). AuNPs adsorption reached the equilibrium within 4 hours, with  
378 removal yields of 94% and 53% for 0.1 and 0.25 mM, respectively. To better investigate the

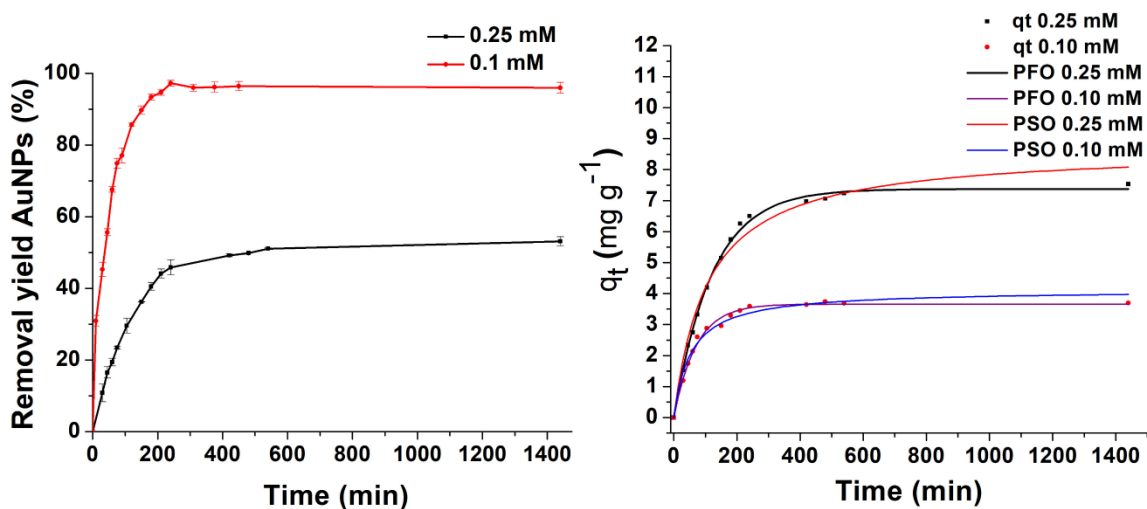
379 adsorption process, the experimental data were fitted with a pseudo first order (Eq.4)  
 380 (Lagergren et al. 1898) and pseudo second order (Eq.5) (Hamoudi et al. 2018) laws:

$$q_t = q_e (1 - \exp(-k_1 t)) \quad \text{Eq.4}$$

$$q_t = \frac{k_2 q_e^2 t}{1 + q_e k_2 t} \quad \text{Eq.5}$$

381 where  $q_t$  is the adsorption capacity at time  $t$ ,  $q_e$  is the adsorption capacity at the equilibrium  
 382 ( $\text{mg g}^{-1}$ ),  $k_1$  is the pseudo first order rate constant in  $\text{min}^{-1}$ ,  $k_2$  describes the adsorption rate of  
 383 the pseudo second order model, expressed in  $\text{g mg}^{-1} \text{min}^{-1}$ .

384 Kinetic parameters are summarized in Table 3 and the non-linear fitting plots are presented  
 385 in Fig. 9B. The highest values of correlation coefficient (0.997) and lowest Reduced Chi  
 386 Square (0.015) were obtained in the pseudo first order model, as shown in Table 3, which  
 387 best represents the interaction mechanism. Also, the calculated values  $q_{e, \text{cal}}$ , determined by  
 388 the pseudo-first order model, are in accordance with the experimental data:  
 389  $q_{e, \text{cal}}=7.38 \text{ mg g}^{-1}$ ,  $q_{e, \text{exp}}=7.40 \text{ mg g}^{-1}$ , for an initial concentration of 0.25 mM and  
 390  $q_{e, \text{cal}}=3.68 \text{ mg g}^{-1}$ ,  $q_{e, \text{exp}}=3.69 \text{ mg g}^{-1}$ , for an initial concentration of 0.1 mM. This model  
 391 indicates that the external diffusion and internal diffusion are the rate controlling steps in the  
 392 adsorption process of gold nanoparticles (Wang and Guo. 2020a).



393

394 **Fig. 9** Effect of contact time for PVA-LYS 30% (A) Kinetic models (B)

395 ([AuNPs] = 0.1 mM and 0.25 mM, 20 mg fibers, suspension volume = 5 mL, pH=7)

396

397

Tab.3 Kinetic parameters of Pseudo first order and Pseudo second order models for AuNPs adsorption on PVA-LYS 30%

[AuNPs] (mM)	Pseudo first order				Pseudo second order			
	q <sub>e</sub> (mg g <sup>-1</sup> )	k <sub>1</sub> (h <sup>-1</sup> )	χ <sup>2</sup> *	r <sup>2</sup>	q <sub>e</sub> (mg g <sup>-1</sup> )	k <sub>2</sub> (g mg <sup>-1</sup> h <sup>-1</sup> )	χ <sup>2</sup> *	r <sup>2</sup>
0.10	3.68	0.021	0.022	0.982	4.06	0.008	0.023	0.981
0.25	7.38	0.008	0.015	0.997	8.68	0.001	0.109	0.981

398 \* χ<sup>2</sup>: Reduced Chi Square

399 Adsorption isotherms describe the distribution of the adsorbate between the liquid and solid  
400 phase and its interaction with the adsorbent surface (Al-Ghouti and Da'ana 2020).

401 The experimental data were correlated to the Langmuir and Freundlich models. The  
402 Langmuir isotherm model assumes a monolayer adsorption of the molecules (Fu et al. 2021).

403 The equation (Eq.6) is defined as (Mozaffari et al. 2022):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad \text{Eq. 6}$$

404 where, q<sub>e</sub> (mg g<sup>-1</sup>) is adsorption capacity at equilibrium, C<sub>e</sub> (mg L<sup>-1</sup>) is equilibrium  
405 concentration, K<sub>L</sub> is the Langmuir equilibrium constant related to the affinity of binding sites  
406 (L g<sup>-1</sup>) and q<sub>m</sub> (mg g<sup>-1</sup>) represents the maximum adsorption capacity.

407 Freundlich isotherm model is applied to represent the multi-layer adsorption on  
408 heterogeneous surfaces (Wang and Guo 2020b). The non-linear form is described by the  
409 following equation (Eq.7):

$$q_e = K_F C_e^{1/n} \quad \text{Eq. 7}$$

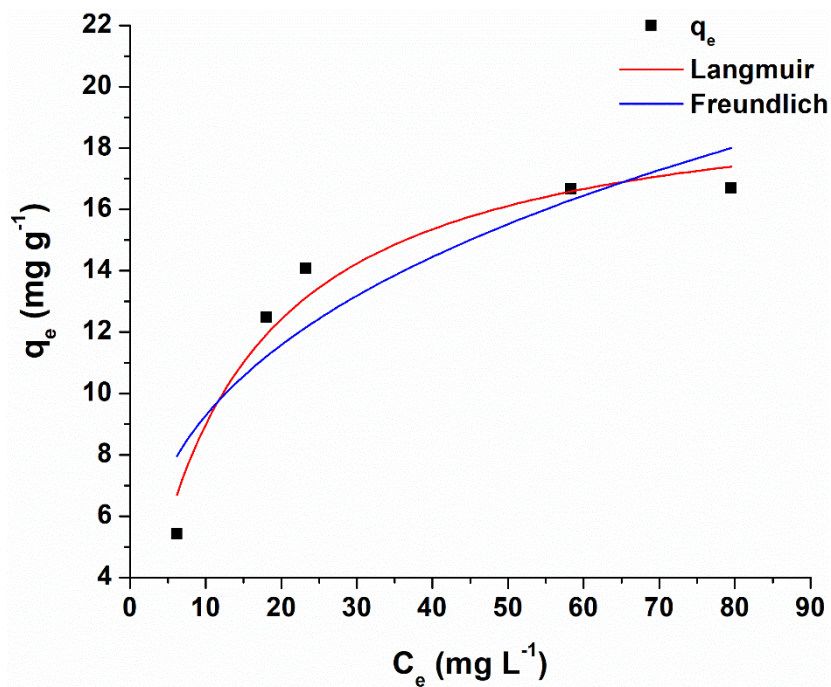
410 where, K<sub>F</sub> is the Freundlich constant (L g<sup>-1</sup>) and n is the heterogeneity factor.



411 The non-linear fitting plots of the two models are represented in Fig. 10 and the  
412 corresponding parameters are summarized in Table 4. The values of the correlation  
413 coefficient show that the Langmuir model ( $r^2 = 0.948$ ) fits better the experimental data,  
414 indicating a monolayer adsorption onto homogenous surface. According to the Langmuir  
415 model, the maximum adsorption capacity of AuNPs is equal to  $20.10 \text{ mg g}^{-1}$ . Table 5 presents  
416 a comparative study between the efficiency of different materials and that of the fibers  
417 prepared in this work towards AuNPs removal. This table shows that several adsorbents  
418 performed better towards the removal of AuNPs than PVA-Lys fibers. However, others  
419 show a lower adsorption capacity, such as cellulosic fibers (Mahanta et al. 2012) and copper  
420 oxide (Mallampati et al. 2013). Studies reporting high adsorption capacity for AuNPs  
421 (Dhandayuthapani et al. 2014, Kumar et al. 2014) have employed glutaraldehyde as a  
422 crosslinker during the fabrication of their materials, however this reagent has shown acute  
423 and chronic toxicity, genotoxicity, developmental toxicity, and carcinogenicity (Oh et al.  
424 2022). In this work, citric acid has been used as an inexpensive and non-toxic crosslinking  
425 agent, to overcome the intrinsic toxicity of the glutaraldehyde (Salihu et al. 2021). It is also  
426 important to mention that the use of synthetic polymers like PVA (Zhang et al. 2019, Zhang  
427 et al. 2021) and PA-12 (poly-amide) (Aldahash et al. 2022) have demonstrated an interesting  
428 perspective and potential in pollutants removal for water.

429 Furthermore, the concentrations of nanoparticles in water are in the range of ppb. The  
430 estimated concentration of AgNPs in U.S. surface water is around  $10 \mu\text{g L}^{-1}$  (Conde-  
431 González et al. 2016). To extract these low amounts of nanoparticles, a green and eco-  
432 friendly material with medium adsorption capacity may be more convenient than an  
433 adsorbent showing a high removal efficiency but prepared with toxic reagents.

434



435

436

**Fig. 10** Isotherms of AuNPs adsorption on PVA-LYS 30%

Tab. 4 Parameters of Langmuir and Freundlich models for AuNPs adsorption on PVA-LYS fibers

	Langmuir model			Freundlich model		
	$q_m$ (mg g <sup>-1</sup> )	$K_L$ (L g <sup>-1</sup> )	$r^2$	$K_F$ (L g <sup>-1</sup> )	$n$	$r^2$
AuNPs	20.105	0.081	0.948	4.449	3.131	0.788

437

438

439

440

441

442

443

444

445

Tab. 5 Maximum AuNPs adsorption capacity ( $\text{mg g}^{-1}$ ) of some adsorbents reported in the literature compared with PVA-LYS fibers

Adsorbent	$Q_{\text{max}}$ ( $\text{mg g}^{-1}$ )	Ref
Cellulosic fibers	13.1	(Mahanta et al. 2012)
Biomimetic metal oxides	3.4	(Mallampati et al. 2013)
PVA/Gluten hybrid fibers	36.5	(Dhandayuthapani et al. 2014)
Dopamine-PEI chitosan-coated micro-sized carbon fiber aerogels	32.1	(Liu et al. 2017)
Amine functionalized block copolymers	50.0	(Qureshi et al. 2014)
Functionalized Carbon Spheres	102	(Kumar et al. 2014)
PVA-LYS fibers	20.10	This work

446 3.3. Proposed adsorption mechanism of AuNPs

447 Both FTIR and elemental analysis proved the presence of significant number of functional  
448 groups on PVA-LYS fibers, such as  $-\text{OH}$ ,  $-\text{COOH}$  and  $-\text{CO}-\text{NH}-$ . These polar functional  
449 groups are responsible of the adsorption process of AuNPs on PVA-LYS fibers. Based on  
450 the literature, adsorption is due to electrostatic interactions between nanoparticles and solid  
451 surfaces (Brenner et al. 2012). The pH of zero charge is a critical parameter to define the  
452 surface charge of the fibers and understand the electrostatic interactions involved in the  
453 adsorption mechanism. PVA-LYS 30% have a pH of zero charge equal to 5.8. Thus, their  
454 surface charge was positive at pH below 5 and the electrostatic attraction between protonated  
455 amino groups of lysine on the fibers and the negatively charged citrate capped AuNPs  
456 explains the increase in nanoparticles removal percentage. Furthermore, the functional  
457 groups present on the surface of the fibers can form hydrogen bonds with the carboxylic acid  
458 groups of citrate capped AuNPs (Dhandayuthapani et al. 2014). The third mechanism that

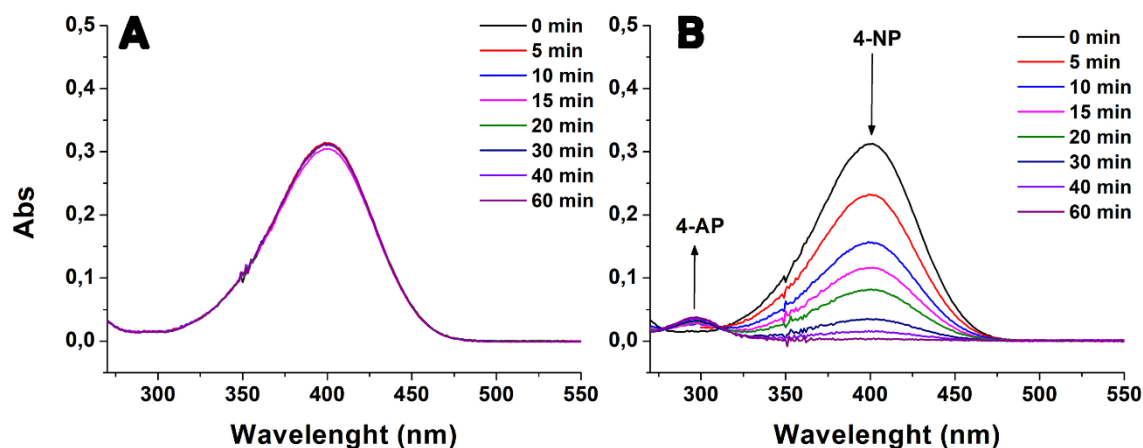
459 can also be involved in the adsorption process is the metal-ligand interactions, as  
460 demonstrated by Li et al. 2014. Amino groups are considered as ligand with nitrogen donor  
461 atom (Nath et al. 2006). These groups have specific affinity towards metallic nanoparticles  
462 and are able to form a coordination bond between gold atoms and functional chemical  
463 groups, including atoms with a lone electron pair (Dzhimak et al. 2019).

#### 464 3.4. Catalytic performance of AuNPs/ PVA-LYS fibers

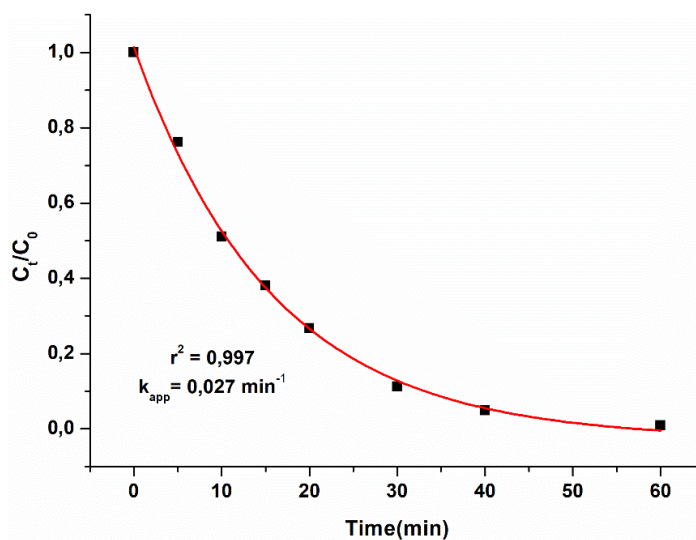
465 To evaluate the catalytic activity of the adsorbed nanoparticles, reduction of 4-nitrophenol  
466 (4-NP) to 4-aminophenol (4-AP) has been widely used in literature as a model reaction (Li  
467 et al. 2019; Kumar et al. 2014; Yin et al. 2020). Nitrophenols are extensively used in  
468 industries of pharmaceuticals, production of paper, petrochemical, fungicides, pesticides,  
469 insecticides, preservatives, explosives, dyes, leather, and wood (Kassem et al. 2021). They  
470 are considered as suspected carcinogens and classified as priority pollutants by the United  
471 States Environmental Protection Agency (Lin and Doong. 2014). Despite the  
472 electrochemical potential values of 4-NP/4-AP (-0.76 V) and  $\text{H}_3\text{BO}_3/\text{BH}_4^-$  (-1.33 V), the  
473 reduction process is unfavorable due to the electrostatic repulsion between nitrophenolate  
474 and borohydride ions (Neal et al. 2019).

475 During the reduction experiment, AuNPs/ PVA-LYS fibers were added to the mixture of 4-  
476 NP (1 mM) with  $\text{NaBH}_4$  (50 mM). The reaction was monitored using UV-Visible  
477 spectrophotometry. In the absence of catalyst, no change was observed in 4-NP peak  
478 intensity after 60 min of reaction (Fig.11 A), indicating that  $\text{NaBH}_4$  was not able to reduce  
479 the 4-NP, as expected. After the addition of AuNPs/PVA-LYS fibers, the absorption peak of  
480 4-NP at 400 nm rapidly decreased and a new peak appeared at 300 nm, corresponding to 4-  
481 AP (Fig. 11 B). The reduction process was completed within 60 min. The reduction  
482 mechanism was elucidated by Neal et al. (2019): the nitrophenolate ion is adsorbed onto the  
483 catalyst surface, where it is reduced to 4-AP by a hydrogen atom derived from  $\text{BH}_4^-$ . The 4-

484 AP, once generated, rapidly desorbs from the surface of the catalyst. The conversion of 4-  
 485 NP to 4-AP follows the pseudo first order kinetic model (Noël et al. 2020). The reaction rate  
 486 was determined using the plot  $C_t/C_0$  versus time, presented in Fig 12. The correlation  
 487 coefficient  $r^2$  and rate constant  $k$  are equal to 0.997 and  $0.027 \text{ min}^{-1}$ , respectively, similar to  
 488 previous data reported in the literature (Neal et al. 2019).



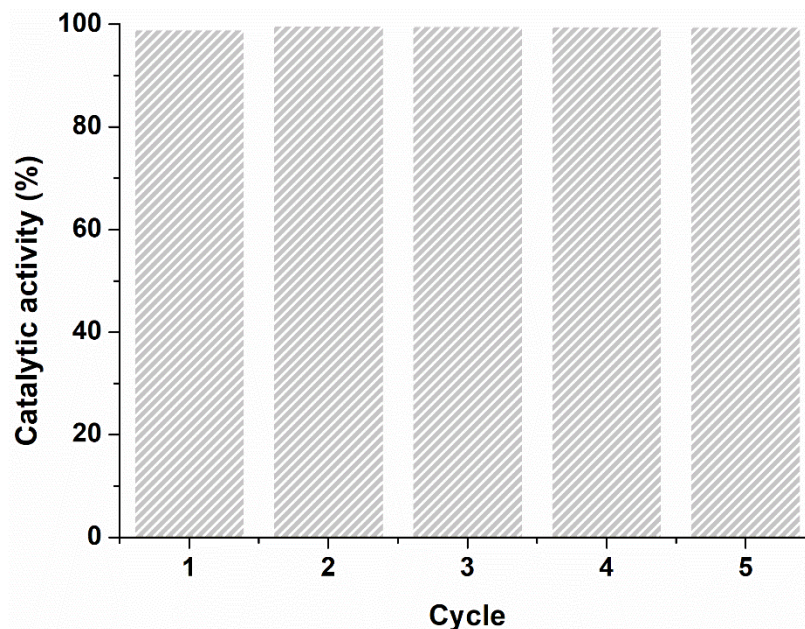
489  
 490 **Fig. 11** Time dependent UV-Visible spectra of 4-NP reduction catalyzed without (A) and  
 491 with AuNPs/PVA-LYS fibers (B)



492  
 493 **Fig. 12** Kinetic of 4-NP reduction

494 The reusability of the adsorbed AuNPs on PVA-LYS fibers was tested and the results are  
 495 presented in Fig. 13. When the reduction was completed, AuNPs/PVA-LYS fibers were  
 496 collected and added again to a 4-NP solution for the next catalysis cycle. The catalytic

497 activity was expressed in terms of removal percentage of 4-NP. The reduction process was  
498 completed with more than 99% of 4-NP removal during the 5 cycles, indicating the good  
499 reusability of this catalyst.



500

501

**Fig. 13** Reusability of AuNPs/PVA-LYS fibers

502

### 3.5. Operational cost of the preparation of PVA-LYS fibers

503

A cost estimate of the production of these fibers has been elaborated based on the raw

504

materials cost and the energy consumption for the treatment of 1 L of water containing 0.1

505

mM ( $19.7 \text{ mg L}^{-1}$ ) AuNPs. The total cost of raw material was estimated to 1.46 €. In addition,

506

the cost of electricity was determined using the fare for electrical supply per kWh in Italy

507

(0.053 €/kWh). Thus, the total cost for treating 1L of water is equal to 3.05 €. It is important

508

to mention that the real concentration of nanoparticles in water is lower than  $1 \text{ mg L}^{-1}$  (Islam

509

et al. 2022). This amount of fibers can treat 20 times more than the considered volume of

510

water. There is still a lack of literature dealing with the economic feasibility of this process.

511

(Beck et al. 2017) has found that the annual electrical cost of production of lignin based

512

carbon fibers is around 53,900 \$. The scale up of this process is related to the high energy

513 consumption, which need to be adjusted and produced by renewable resources to reduce the  
514 cost.

### 515 3.6. Practical applications and perspectives

516 The prepared PVA-LYS fibers have shown interesting physicochemical properties, such as  
517 their smooth morphology without the presence of beads, low diameter size, water stability  
518 and presence of different functional groups (hydroxyl, ester, and amide) on their surface.  
519 These characteristics can make this adsorption support a promising candidate for the removal  
520 of other metallic nanoparticles like AgNPs. Anionic dyes like methylene blue and crystal  
521 violet can show electrostatic interactions with the positively charged surface of PVA-LYS  
522 fibers at pH lower than 5.8 ( $\text{pH}_{zc}$ ).

523 To enhance the adsorption capacity of this material and the amount of lysine grafted onto  
524 the fibers, other green crosslinking methods can be employed as demonstrated by (Ding et  
525 al. 2017).

### 526 Conclusion

527 A green adsorbent was successfully prepared by grafting lysine on biodegradable PVA  
528 fibers. The characterization analysis confirms that the amino acid binds covalently to the  
529 PVA chain, through amide and ester groups formation during crosslinking in the presence  
530 of citric acid. The removal rate reached 65 % at pH equal to 5, by using an adsorbent amount  
531 of 20 mg. AuNPs adsorption by PVA-LYS fibers well fitted a pseudo-first-order kinetic and  
532 the Langmuir isotherm, with a maximum adsorption capacity of  $20.1 \text{ mg g}^{-1}$ . The adsorption  
533 mechanism of AuNPs involved electrostatic interaction between protonated amino group of  
534 lysine and negatively charged AuNPs and metal-ligand interaction between nitrogen atom  
535 and gold. Given the increasing demand for green solutions for water remediation, these  
536 findings contribute to the development of green and sustainable approaches for nanoparticles  
537 removal from aqueous solution, while the reuse of the exhaust material as a catalyst

538 represents an important added value. Although PVA-LYS fibers are promising green and  
539 biodegradable adsorbers, the adsorption capacity of AuNPs nanoparticles should be  
540 improved by increasing the amount of nitrogen incorporated in the fibers and remained after  
541 washing.

## 542 **Statements and Declarations**

## 543 **Acknowledgments**

544 The authors acknowledge support from Project CH4.0 under MUR (Italian Ministry for the  
545 University) program "Dipartimenti di Eccellenza 2023-2027" (CUP: D13C22003520001).

## 546 **Funding**

547 This work was financially supported by Compagnia di San Paolo and University of Turin  
548 (Bando Ex-Post Anno 2018 and Bando Ex-Post Anno 2020). The fundings of Ricerca Locale  
549 2020 and Ricerca Locale 2021, supplied by University of Turin, are greatly appreciated

## 550 **Declaration of Competing Interest**

551 The authors declare that they have no competing financial interests or personal relationships  
552 that could have appeared to influence the work reported in this paper

## 553 **Author contributions**

554 All authors contributed to the study conception and design. Eya Ben  
555 Khalifa: Conceptualization, Investigation, Methodology, Validation, Writing – original  
556 draft, Writing – review and editing. Claudio Cecone: Methodology, Investigation,  
557 Validation, Writing – review and editing. Mery Malandrino: Supervision, Project  
558 administration, Writing – review & editing. Pierangiola Bracco: Supervision, Project  
559 administration, Writing – review & editing. Maria Cristina Paganini: Supervision, Project  
560 administration, Funding acquisition, Writing – review & editing. Giuliana Magnacca:  
561 Supervision, Project administration, Funding acquisition, Writing – review & editing. All  
562 authors read and approved the final manuscript



563 **Data Availability**

564 All data generated or analyzed during this study are included in this article

565 **Ethics declarations**

566 Ethics approval: Not applicable

567 Consent to participate: All authors participate to this work

568 Consent for publication: All authors accept to publish this work

569 **References**

570 Ahmed M, Mashkoo F, Nasar A (2020) Development, characterization, and utilization of  
571 magnetized orange peel waste as a novel adsorbent for the confiscation of crystal violet dye  
572 from aqueous solution. *Groundw Sustain Dev* 10:100322.

573 <https://doi.org/10.1016/j.gsd.2019.100322>

574 Al-Ghouti M A, Da'ana D A (2020) Guidelines for the use and interpretation of adsorption  
575 isotherm models: A review. *J Hazard Mater* 393:122383.

576 <https://doi.org/10.1016/j.jhazmat.2020.122383>

577 Alarifi I, Uddin M, Awan A, et al (2020) Synthesis of PAN-nanofibers for the separation of  
578 aqueous pollutants and performance of the net-zero energy water treatment plant.  
579 *Desalination Water Treat* 200:90–108. <https://doi.org/10.5004/dwt.2020.26064>

580 Aldahash SA, Higgins P, Siddiqui S, Uddin MK (2022) Fabrication of polyamide-12/cement  
581 nanocomposite and its testing for different dyes removal from aqueous solution:  
582 characterization, adsorption, and regeneration studies. *Sci Rep* 12:13144.

583 <https://doi.org/10.1038/s41598-022-16977-8>

584 Alkafeef SF, Al-Marri SS (2016) Kinetics and isotherms of asphaltene adsorption in narrow  
585 pores. *Curr Opin Colloid Interface Sci* 24:44–51.

586 <https://doi.org/10.1016/j.cocis.2016.06.005>

587 Amendola V, Pilot R, Frascioni M, Maragò O M, Iatì M A (2017) Surface plasmon resonance  
588 in gold nanoparticles: a review. *J Phys Condense Matter* 29:202017.  
589 <https://doi.org/10.1088/1361-648X/aa60f3>

590 ANSES (2021) [https://www.anses.fr/fr/content/evaluation-des-risques-sanitaires-liés-à-la-](https://www.anses.fr/fr/content/evaluation-des-risques-sanitaires-liés-à-la-présence-de-formaldéhyde)  
591 [présence-de-formaldéhyde](https://www.anses.fr/fr/content/evaluation-des-risques-sanitaires-liés-à-la-présence-de-formaldéhyde), Accessed 28-12-2021

592 Aparecida Toledo Costa L, Contino Vianna de Aguiar L, de Souza Gomes, José Bento Brum  
593 E F (2022) Characterization of PVA and phenol salt modified tin dioxide cationic  
594 membranes. *Int J Hydrog Energy* 47:7415–7431.  
595 <https://doi.org/10.1016/j.ijhydene.2021.12.074>

596 Beck RJ, Zhao Y, Fong H, Menkhaus TJ (2017) Electrospun lignin carbon nanofiber  
597 membranes with large pores for highly efficient adsorptive water treatment applications. *J*  
598 *Water Process Eng* 16:240–248. <https://doi.org/10.1016/j.jwpe.2017.02.002>

599 BCC research reports (2021) [https://www.bccresearch.com/market-](https://www.bccresearch.com/market-research/nanotechnology/nanotechnology-fuel-cell-research-review.html)  
600 [research/nanotechnology/nanotechnology-fuel-cell-research-review.html](https://www.bccresearch.com/market-research/nanotechnology/nanotechnology-fuel-cell-research-review.html), Accessed 28-12-  
601 2021

602 Brenner T, Paulus M, Schroer MA, et al (2012) Adsorption of nanoparticles at the solid–  
603 liquid interface. *J Colloid Interface Sci* 374:287–290.  
604 <https://doi.org/10.1016/j.jcis.2012.02.010>

605 Ceccone C, Hoti G, Zanetti M, Trotta F, Bracco P (2022) Sustainable production of curable  
606 maltodextrine-based electrospun microfibers. *RSC Adv* 12:762.  
607 <https://doi.org/10.1039/D1RA06785K>

608 Conde-González JE, Peña-Méndez EM, Rybáková S, et al (2016) Adsorption of silver  
609 nanoparticles from aqueous solution on copper-based metal organic frameworks (HKUST-  
610 1). *Chemosphere* 150:659–666. <https://doi.org/10.1016/j.chemosphere.2016.02.005>

611 Dhandayuthapani B, Mallampati R, Sriramulu D, Fredrick Dsouza R, Valiyaveettil S (2014)  
612 PVA/Gluten hybrid nanofibers for removal of nanoparticles from water, ACS Sustain Chem.  
613 Eng 2:1014-1021. <https://doi.org/10.1021/sc500003k>

614 Ding W, Zhou J, Zeng Y, et al (2017) Preparation of oxidized sodium alginate with different  
615 molecular weights and its application for crosslinking collagen fiber. Carbohydr Polym  
616 157:1650–1656. <https://doi.org/10.1016/j.carbpol.2016.11.045>

617 Du X, Zhou W, Zhang W, Sun S, Han Y, Tang Y, Shi W, Liu G (2021) Toxicities of three  
618 metal oxide nanoparticles to a marine microalga: Impacts on the motility and potential  
619 affecting mechanisms. Environ Pollut 290 :118027.  
620 <https://doi.org/10.1016/j.envpol.2021.118027>

621 Dzhimak SS, Malysko VV, Goryachko AI, et al (2019) ADSORPTION OF SILVER  
622 NANOPARTICLES ON MONO- AND POLYFILAMENT FIBERS. Nanotechnologies  
623 Russ 14:48–54. <https://doi.org/10.1134/S199507801901004X>

624 Elkady M, Salama E, Amer WA, et al (2020) Novel eco-friendly electrospun nanomagnetic  
625 zinc oxide hybridized PVA/alginate/chitosan nanofibers for enhanced phenol  
626 decontamination. Environ Sci Pollut Res 27:43077–43092. [https://doi.org/10.1007/s11356-](https://doi.org/10.1007/s11356-020-10247-8)  
627 [020-10247-8](https://doi.org/10.1007/s11356-020-10247-8)

628 El-Sayed S, Mahmoud K H, Fatah A A, Hassen A (2011) DSC, TGA and dielectric  
629 properties of carboxymethyl cellulose/polyvinyl alcohol blends, Physica B Condens Matter  
630 406:4068-4076. <https://doi.org/10.1016/j.physb.2011.07.050>

631 Faria P C C, Órfão J M M, Pereira M F R (2004) Adsorption of anionic and cationic dyes on  
632 activated carbons with different surface chemistries. Water Res 18 :2043-2052.  
633 <https://doi.org/10.1016/j.watres.2004.01.034>

634 Franco R A, Min Y-K, Yang H-M, Lee B-T (2012) On Stabilization of PVPA/PVA  
635 Electrospun Nanofiber Membrane and Its Effect on Material Properties and  
636 Biocompatibility. *J Nanomater* 393042. <https://doi.org/10.1155/2012/393042>.

637 Fu D, Huang Y, Zhang X, et al (2017) Uncovering potentials of integrated TiO<sub>2</sub>(B)  
638 nanosheets and H<sub>2</sub>O<sub>2</sub> for removal of tetracycline from aqueous solution. *J Mol Liq* 248:112–  
639 120. <https://doi.org/10.1016/j.molliq.2017.10.020>

640 Fu D, Kurniawan TA, Avtar R, et al (2021) Recovering heavy metals from electroplating  
641 wastewater and their conversion into Zn<sub>2</sub>Cr-layered double hydroxide (LDH) for  
642 pyrophosphate removal from industrial wastewater. *Chemosphere* 271:129861.  
643 <https://doi.org/10.1016/j.chemosphere.2021.129861>

644 Fu D, Kurniawan TA, Li H, et al (2019) Applicability of HDPC-supported Cu nanoparticles  
645 composite synthesized from anaerobically digested wheat straw for octocrylene degradation  
646 in aqueous solutions. *Chem Eng J* 355:650–660. <https://doi.org/10.1016/j.cej.2018.08.188>

647 Gicheva G, Yordanov G (2013) Removal of citrate-coated silver nanoparticles from aqueous  
648 dispersions by using activated carbon. *Colloids. Surf. A Physicochem Eng Asp* 431:51-59.  
649 <https://doi.org/10.1016/j.colsurfa.2013.04.039>

650 Grieger K, Jones J L, Hansen S F, Hendren C O, Jensen K A, Kuzma A, Baun A (2019) Best  
651 practices from nano-risk analysis relevant for other emerging technologies, *Nat.*  
652 *Nanotechnol.* 14:998-1001. <https://doi.org/10.1038/s41565-019-0572-1>

653 Haase A, Rott S, Manton A, Graf P, Plendl J, Thünemann A F, Meier W P, Taubert A, Luch  
654 A, Reiser G (2012) Effects of silver nanoparticles on primary mixed neural cell cultures:  
655 uptake, oxidative stress and acute calcium responses. *Toxicol Sci* 126:457-  
656 468. <https://doi.org/10.1093/toxsci/kfs003>

657 Hammami I, Alabdallah N M, Aljomaa A, Kamoun M (2021) Gold nanoparticles: Synthesis  
658 properties and applications. J K Saud Univ Sci 33:101560.  
659 <https://doi.org/10.1016/j.jksus.2021.101560>

660 Hamoudi S A, Hamdi B, Brendlé J (2018) Removal of ions  $Pb^{2+}$  and  $Cd^{2+}$  from aqueous  
661 solution by containment geomaterials. in: Dincer I, Ozgur Colpan C, Kizilkan O (ed)  
662 Exergetic, Energetic and Environmental Dimensions, Academic Press, 1029-1043

663 Hashimi A S, Mohd Nohan M A N, Chin S X, Zakaria S, Chia C H (2019) Rapid Catalytic  
664 Reduction of 4-Nitrophenol and Clock Reaction of Methylene Blue using Copper Nanowire.  
665 Nanomaterials 9:936. <https://doi.org/10.3390/nano9070936>

666 Hochella M F et al. (2019) Natural, incidental, and engineered nanomaterials and their  
667 impacts on the Earth system. Science 363:6434. <https://doi.org/10.1126/science.aau8299>

668 Huang X, El-Sayed M A (2010) Gold nanoparticles: Optical properties and implementations  
669 in cancer diagnosis and photothermal therapy. J Adv Res 1:13-28.  
670 <https://doi.org/10.1016/j.jare.2010.02.002>

671 Islam MA, Dada TK, Parvin MI, et al (2022) Silver ions and silver nanoparticles removal by  
672 coffee derived biochar using a continuous fixed-bed adsorption column. J Water Process  
673 Eng 48:102935. <https://doi.org/10.1016/j.jwpe.2022.102935>

674 Karmakar A, Mallick T, Fouzder Ch, Mukhuty A, Kundu R, Ara Begum N (2019)  
675 Antioxidant flavone functionalized fluorescent and biocompatible metal nanoparticles:  
676 Exploring their efficacy as cell imaging agents. Nano-Struct Nano-Objects 18:100278.  
677 <https://doi.org/10.1016/j.nanoso.2019.100278>

678 Kassem A A, Abdelhamid H N, Fouad D M, Ibrahim S A (2021) Catalytic reduction of 4-  
679 nitrophenol using copper terephthalate frameworks and  $CuO@C$  composite. J Environ Chem  
680 Eng 9:104401. <https://doi.org/10.1016/j.jece.2020.104401>

681 Kuchur O A, Tsymbal S A, Shestovskaya M V, Serov N S, Dukhinova, M S, Shtil A A,  
682 (2020) Metal-derived nanoparticles in tumor theranostics: Potential and limitations. *J Inorg*  
683 *Biochem* 209:111117. <https://doi.org/10.1016/j.jinorgbio.2020.111117>

684 Kumar J, Mallampati R, Adin A, Valiyaveetti S (2014) Functionalized carbon spheres for  
685 extraction of nanoparticles and catalyst support in water. *ACS Sustain Chem Eng* 2:2675-  
686 2682. <https://doi.org/10.1021/sc5004242>

687 Lagergren S (1898) About the theory of so-called adsorption of soluble substances. *Handl*  
688 24:1-39

689 Lapenna A, Dell'Aglio M, Palazzo G, Mallardi A (2020) "Naked" gold nanoparticles as  
690 colorimetric reporters for biogenic amine detection. *Colloids Surf A Physicochem Eng Asp*  
691 600:124903. <https://doi.org/10.1016/j.colsurfa.2020.124903>

692 Li C, Li D, Wan G, Xu J, Hou W (2011) Facile synthesis of concentrated gold nanoparticles  
693 with low size-distribution in water: temperature and pH controls. *Nanoscale Res Lett* 6:440.  
694 <https://doi.org/10.1186/1556-276X-6-440>

695 Li Q, Liu J, Sun X, Xu L (2019) Hierarchically porous melamine-formaldehyde resin  
696 microspheres for the removal of nanoparticles and simultaneously as the nanoparticle  
697 immobilized carrier force *ACS Sustain Chem Eng* 7:867-876.  
698 <https://doi.org/10.1021/acssuschemeng.8b04490>

699 Liguori A, Uranga J, Panzavolta S, Guerrero P, de la Caba K, Focarete M L (2019)  
700 Electrospinning of Fish Gelatin Solution Containing Citric Acid: An Environmentally  
701 Friendly Approach to Prepare Crosslinked Gelatin Fibers. *Materials* 12:2808.  
702 <https://doi.org/10.3390/ma12172808>.

703 Lin F, Doong R (2014) Highly efficient reduction of 4-nitrophenol by heterostructured gold-  
704 magnetite nanocatalysts. *App Cat A Gen* 486:32-41.  
705 <https://doi.org/10.1016/j.apcata.2014.08.013>

706 Liu R L, Mao S, Wang Y, Wang L, Ge Y H, Xu X Y, Fu Q (2017) A mussel-inspired hybrid  
707 copolymer adhered to chitosan-coated micro-sized carbon fiber aerogels for highly efficient  
708 nanoparticle scavenging, *Environ Sci Nano*  
709 4:2164- 2174. <https://doi.org/10.1039/C7EN00615B>.

710 Mahanta N, Leong W Y, Valiyaveetil S (2012) Isolation and characterization of cellulose-  
711 based nanofibers for nanoparticle extraction from an aqueous environment. *J Mater Chem*  
712 22:1985-1993. <https://doi.org/10.1039/C1JM15018A>

713 Mallampati R, Valiyaveetil S (2013) Biomimetic metal oxides for the extraction of  
714 nanoparticles from water. *Nanoscale* 5 :3395-3399. <https://doi.org/10.1039/c3nr34221b>

715 Mansur H S, Sadahira C M, Souza A N, Mansur A A P (2008) FTIR spectroscopy  
716 characterization of poly (vinyl alcohol) hydrogel with different hydrolysis degree and  
717 chemically crosslinked with glutaraldehyde. *Mater Sci Eng C* 28:539-548.  
718 <https://doi.org/10.1016/j.msec.2007.10.088>

719 Manuja A, Kumar B, Kumar R, Chhabra D, Ghosh M, Manuja M, Brar B, Pal Y, Tripathi B  
720 N, Prasad M (2021) Metal/metal oxide nanoparticles: Toxicity concerns associated with their  
721 physical state and remediation for biomedical applications, *Toxicol Rep* 8:1970-1978.  
722 <https://doi.org/10.1016/j.toxrep.2021.11.020>

723 Mao B H, Chen Z Y, Wang Y J, Yan S J (2018) Silver nanoparticles have lethal and  
724 sublethal adverse effects on development and longevity by inducing ROS-mediated stress  
725 responses, *Sci Rep* 8:2445. <https://doi.org/10.1038/s41598-018-20728-z>

726 Montes-Garcı V, Squillaci M A, Diez-Castellnou M, Khac Ong Q, Stellacci F, Samori P  
727 (2021) Chemical sensing with Au and Ag nanoparticles. *Chem Soc Rev* 50:1269-1304.  
728 <https://doi.org/10.1039/D0CS01112F>.

729 Mozaffari Majd M, Kordzadeh-Kermani V, Ghalandari V, Askari A, Sillanpää M (2022)  
730 Adsorption isotherm models: A comprehensive and systematic review (2010-2020). *Sci*  
731 *Total Environ* 812:151334. <https://doi.org/10.1016/j.scitotenv.2021.151334>  
732 Nath S, Ghosh SK, Kundu S, et al (2006) Is Gold Really Softer than Silver? HSAB Principle  
733 Revisited. *J Nanoparticle Res* 8:111–116. <https://doi.org/10.1007/s11051-005-8025-1>  
734 Neal R D, Inoue Y, Hughes R A, Neretina S (2019) Catalytic reduction of 4-nitrophenol by  
735 gold catalysts: the influence of borohydride concentration on the induction time. *J Phys*  
736 *Chem C* 123:2894-12901. <https://doi.org/10.1021/acs.jpcc.9b02396>  
737 Nezarati R M, Eifert M B, Cosgriff-Hernandez E (2013) Effects of humidity and solution  
738 viscosity on electrospun fiber morphology. *Tissue Eng Part C Methods* 19:810-819.  
739 <https://doi.org/10.1089/ten.TEC.2012.0671>  
740 Noël S, Bricout H, Addad A, Sonnendecker C, Zimmermann W, Monflier E, Léger B (2020)  
741 Catalytic reduction of 4-nitrophenol with gold nanoparticles stabilized by large-ring  
742 cyclodextrins. *New J Chem* 44:21007-21011. <https://doi.org/10.1039/D0NJ03687K>  
743 Oh H-N, Yoo D, Park S, et al (2022) Developmental neurotoxicity induced by  
744 glutaraldehyde in neuron/astrocyte co-cultured cells and zebrafish. *Ecotoxicol Environ Saf*  
745 242:113891. <https://doi.org/10.1016/j.ecoenv.2022.113891>  
746 Omer S, Forgách L, Zelkó R, Sebe I (2021) Scale-up of Electrospinning: Market Overview  
747 of Products and Devices for Pharmaceutical and Biomedical Purposes. *Pharmaceutics*  
748 13:286. <https://doi.org/doi:10.3390/pharmaceutics13020286>  
749 Park J A, Kang J K, Lee S C, Kim S B (2017) Electrospun poly(acrylic acid)/poly(vinyl  
750 alcohol) nanofibrous adsorbents for Cu(II) removal from industrial plating wastewater. *RSC*  
751 *Adv* 7:18075-18084. <https://doi.org/10.1039/C7RA01362K>



752 Picón D, Torasso N, Baudrit JRV, et al (2022) Bio-inspired membranes for adsorption of  
753 arsenic via immobilized L-Cysteine in highly hydrophilic electrospun nanofibers. *Chem Eng*  
754 *Res Des* 185:108–118. <https://doi.org/10.1016/j.cherd.2022.06.042>

755 Qureshi Z S, Dsoza R, Mallampati R, Valiyaveetil S (2014) Synthesis of amine-  
756 functionalized block copolymers for nanopollutant removal from water. *J Appl Polym*  
757 *Sci* 131:1366-1373. <https://doi.org/10.1002/app.40943>

758 Rosli N, Nisa Yahya W Z, Hakim Wirzal M D (2022) Crosslinked chitosan/poly(vinyl  
759 alcohol) nanofibers functionalized by ionic liquid for heavy metal ions removal. *Int J Biol*  
760 *Macromol* 195:132-141. <https://doi.org/10.1016/j.ijbiomac.2021.12.008>

761 Rudakov G. A, Tsiberkin K B, Ponomarev R S, Henner V K, Ziolkowska D A, Jasinski J  
762 B, Sumanasekera G (2019) Magnetic properties of transition metal nanoparticles enclosed  
763 in carbon nanocages. *J Magn Mater* 472:34-39. <https://doi.org/10.1016/j.jmmm.2018.10.016>

764 Salihu R, Abd Razak SI, Ahmad Zawawi N, et al (2021) Citric acid: A green cross-linker of  
765 biomaterials for biomedical applications. *Eur Polym J* 146:110271.  
766 <https://doi.org/10.1016/j.eurpolymj.2021.110271>

767 Santiago-Castillo K, Del Angel-López D, Torres-Huerta A M, Domínguez-Crespo M A,  
768 Palma-Ramírez D, Willcock H Brachetti-Sibaja S B (2021) Effect on the processability,  
769 structure and mechanical properties of highly dispersed in situ ZnO:CS nanoparticles into  
770 PVA electrospun fibers. *J Mater Res Technol* 11:929-945.  
771 <https://doi.org/10.1016/j.jmrt.2021.01.049>

772 Santos C, Silva C J, Büttel Z, Guimarães R, Pereira S B, Tamagnini P, Zille A (2014)  
773 Preparation and characterization of polysaccharides/PVA blend nanofibrous membranes by  
774 electrospinning method. *Carbohydr Polym* 99:584-592.  
775 <https://doi.org/10.1016/j.carbpol.2013.09.008>

776 Selvakannan P R, Mandal S, Phadtare S, Pasricha R, Sastry M (2003) Capping of gold  
777 nanoparticles by the amino acid lysine renders them water-dispersible. *Langmuir* 19:3545-  
778 3549. <https://doi.org/10.1021/la026906v>

779 Singh S, Ghorai M K, Kar K K (2022) Extraction of unburned carbon from coal fly ash. In  
780 Kar K K (ed), *Handbook of Fly Ash*, Butterworth-Heinemann, 403-449

781 Stagi L, Farris R, Engelbrecht L V, Mocchi F, Maria Carbonaro C, Innocenzi P (2022) At the  
782 root of l-lysine emission in aqueous solutions, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*  
783 283:121717. <https://doi.org/10.1016/j.saa.2022.121717>

784 Teixeira M A, Amorim M, Felgueiras H P (2019) Poly(Vinyl Alcohol)-Based Nanofibrous  
785 Electrospun Scaffolds for Tissue Engineering Applications. *Polymers* 12:7.  
786 <https://doi.org/10.3390/polym12010007>.

787 Thakur M, Sharma A, Chandel M, Pathania D (2022) Modern applications and current status  
788 of green nanotechnology in environmental industry. In: U Shanker, Ch Mustansar Hussain,  
789 M Rani (ed), *In Micro and Nano Technologies, Green Functionalized Nanomaterials for*  
790 *Environmental Applications*, 259-281

791 Thong C C, Teo D C L, Ng C K (2016) Application of polyvinyl alcohol (PVA) in cement-  
792 based composite materials: A review of its engineering properties and microstructure  
793 behavior. *Constr Build Mater* 107:172-180.  
794 <https://doi.org/10.1016/j.conbuildmat.2015.12.188>

795 Uranga J, Leceta I, Etxabide A, Guerrero P, de la Caba K (2016) Cross-linking of fish  
796 gelatins to develop sustainable films with enhanced properties. *Eur Polym J* 78:82-90.  
797 <https://doi.org/10.1016/j.eurpolymj.2016.03.017>.

798 Wang J, Guo X (2020a) Adsorption isotherm models: Classification, physical meaning,  
799 application and solving method. *Chemosphere* 258:127279,  
800 <https://doi.org/10.1016/j.chemosphere.2020.127279>

801 Wang J, Guoa X (2020b) Adsorption kinetic models: Physical meanings, applications, and  
802 solving methods. *J Hazard Mater* 390:122156.  
803 <https://doi.org/10.1016/j.jhazmat.2020.122156>

804 Wang H, Wang Y, Li C, Jia L (2022) Fabrication of eco-friendly calcium crosslinked  
805 alginate electrospun nanofibres for rapid and efficient removal of Cu(II). *Int J Biol*  
806 *Macromol* 219:1–10. <https://doi.org/10.1016/j.ijbiomac.2022.07.221>

807 Wen Y et al. (2021) Electrospinning as a route to advanced carbon fibre materials for  
808 selected low-temperature electrochemical devices: A review. *J Energy Chem.* 59:492-529.  
809 <https://doi.org/10.1016/j.jechem.2020.11.014>

810 Yao G, Huang Q (2022) Theoretical and experimental study of the infrared and Raman  
811 spectra of L-lysine acetylation. *Spectrochim Acta A Mol Biomol Spectrosc* 278:121371.  
812 <https://doi.org/10.1016/j.saa.2022.121371>

813 Yin W, Liu M, Zhao T-L, Qian F-J, Li H, Yao Q-Z, Fu S-Q, Zhou G-T (2020) Removal and  
814 recovery of silver nanoparticles by hierarchical mesoporous calcite: Performance,  
815 mechanism, and sustainable application. *Environ Res* 187:109699.  
816 <https://doi.org/10.1016/j.envres.2020.109699>

817 Zhan F, Yan X, Li J, Sheng F, Li B (2021) Encapsulation of tangeretin in PVA/PAA  
818 crosslinking electrospun fibers by emulsion-electrospinning: Morphology characterization,  
819 slow-release, and antioxidant activity assessment. *Food Chem* 337:127763.  
820 <https://doi.org/10.1016/j.foodchem.2020.127763>

821 Zhang A, Zhang Y, Liu Z, Huang G, Wu L, Fu Y, Wang X, Du Y (2022) Anisotropic gold  
822 nanostructures applied to improve solar energy conversion. *Applied Materials Today*  
823 29101575. <https://doi.org/10.1016/j.apmt.2022.101575>

824 Zhang Q, Uchaker E, Candelaria S L, Cao G (2013) Nanomaterials for energy conversion  
825 and storage. *Chem Soc Rev* 42:3127-3171. <https://doi.org/10.1039/C3CS00009E>

826 Zhang S, Shi Q, Christodoulatos C, Meng X (2019) Lead and cadmium adsorption by  
827 electrospun PVA/PAA nanofibers: Batch, spectroscopic, and modeling study, *Chemosphere*.  
828 233:405-413. <https://doi.org/10.1016/j.chemosphere.2019.05.190>

829 Zhang S, Shi Q, Korfiatis G, Christodoulatos C, Wang H, Meng X (2020) Chromate removal  
830 by electrospun PVA/PEI nanofibers: Adsorption, reduction, and effects of co-existing ions.  
831 *Chem Eng J*. 387:124179. <https://doi.org/10.1016/j.cej.2020.124179>

832 Zhang X, Xie L, Wang X, Shao Z, Kong B (2022) Electrospinning super-assembly of  
833 ultrathin fibers from single- to multi-Taylor cone sites. *Appl Mater Today* 26:1-35.  
834 <https://doi.org/10.1016/j.apmt.2021.101272>

835 Zhang X, Zhang Y, Zhang X, Li S, Huang Y (2017) Nitrogen rich core-shell magnetic  
836 mesoporous silica as an effective adsorbent for removal of silver nanoparticles from water.  
837 *J Hazard Mater* 337:1-9. <https://doi.org/10.1016/j.jhazmat.2017.04.053>

838 Zhang Y, Zhu P C, Edgren D (2010) Crosslinking reaction of poly(vinyl alcohol) with  
839 glyoxal. *J Polym Res* 17:725-730. <https://doi.org/10.1007/s10965-009-9362-z>