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Abstract:	<p>Leather manufacturing is the process of converting raw animal hides or skins into finished leather. The complex industrial procedures results in a tanning effluent composed of chemical compounds with potential hazardous impacts on humans and ecosystems. Among the traditional and efficient wastewater treatments, adsorption is an effective and well-known approach, able to manage a wide range of contaminants from wastewater. Among the plethora of adsorption substrates used on an industrial scale, zeolites have traditionally shown remarkable performances. Differently from other types of adsorbents, zeolites can also work as cation exchangers, which can remove cationic contaminants without influencing the anionic content of the effluent and (in specific cases) also when the removal process is endothermic. Zeolites are minerals naturally present in the environment, but they can be also easily synthesized and modified to enhance their water remediation features. However, the removal efficiency of zeolites is strictly dependent on the type of target contaminant because its uptake capacity is linked to its chemical and physical characteristics, especially on the surface interlayer. This review intends to present a general description of the tannery process to understand the origin and characterization of tanning wastewater. The core of the study aims to approach the most significant studies about zeolite applications in the removal of tanning contaminants. Drawbacks of the reviewed literature are further discussed, and some potential future research content is eventually revealed by identifying the issues that need further investigation.</p>

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Application of zeolites for efficient tannery wastewater remediation.

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ABSTRACT

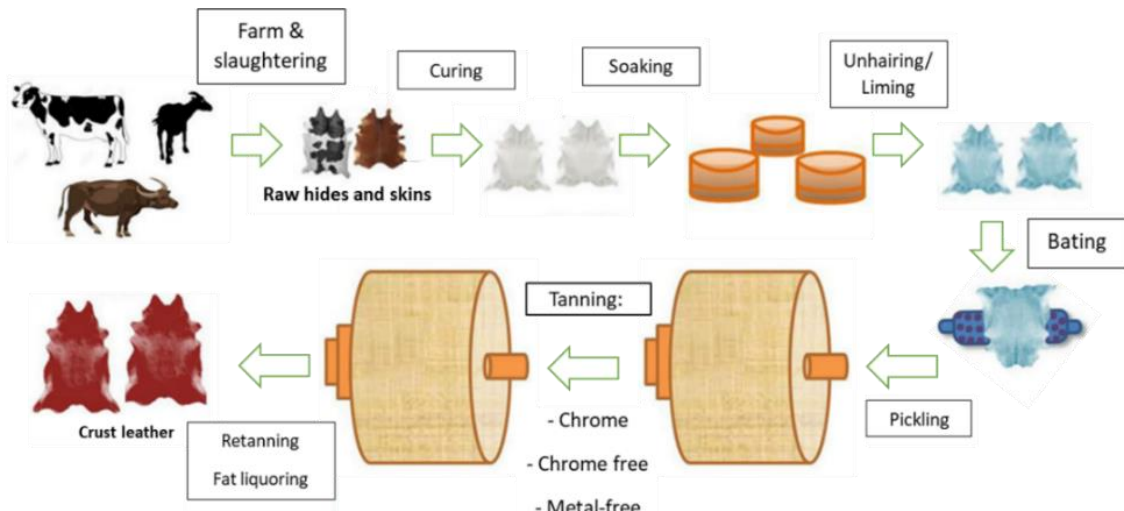
Leather manufacturing is the process of converting raw animal hides or skins into finished leather. The complex industrial procedures result in a tanning effluent composed of chemical compounds with potentially hazardous impacts on humans and ecosystems. Among the traditional and efficient wastewater treatments, adsorption is an effective and well-known approach, able to manage a wide range of contaminants from wastewater. Among the plethora of adsorption substrates used on an industrial scale, zeolites have traditionally shown remarkable performances. Differently from other types of adsorbents, zeolites can also work as cation exchangers, which can remove cationic contaminants without influencing the anionic content of the effluent and (in specific cases) also when the removal process is endothermic. Zeolites are minerals naturally present in the environment, but they can be also easily synthesized and modified to enhance their water remediation features. However, the removal efficiency of zeolites is strictly dependent on the type of target contaminant because its uptake capacity is linked to its chemical and physical characteristics, especially on the surface interlayer. This review intends to present a general description of the tannery process to understand the origin and characterization of tanning wastewater. The core of the study aims to approach the most significant studies about zeolite applications in the removal of tanning contaminants. Drawbacks of the reviewed literature are further discussed, and some potential future research content is eventually revealed by identifying the issues that need further investigation.

KEYWORDS

Leather industry; Tannery wastewater; Zeolites; Environmental remediation; Ion-exchange; Adsorption.

31 **1. Introduction**

32 The leather industry is a worldwide segment of the economy as a dominant player in many countries, contemporarily it
33 contributes to social development through the generation of a significant amount of employment.(Sathish et al. 2016).
34 China is the highest producer, as importer and exporter, joined by the top producing countries: Italy, Korea, India,
35 Russia, and Brazil(Omoloso et al. 2021). Leather manufacturing is one of the earliest man fabrication activities, since
36 animal skins and hides served as major raw materials for essential lifestyle commodities. The tanning industry processes
37 the raw skins and hides converting them into durable, flexible, and non-putrescible materials, known as the finished
38 leathers. Leather is made of polymers of collagen; animal hides and skins are converted into leather using a well-
39 determined series of chemical processes: the tanning phase is the most important because it converts animal skins into
40 leather by stabilising collagen fibre against putrefaction. The foundation for the ‘art of tanning’ is born with greasy
41 substances to last longer the durability of the hide, the smoking phase helped the penetration of these substances
42 through the skin enhancing the preservation and making the skin more flexible. Later, bark and leaf infusions of
43 mimosa, chestnut, and other natural trees were used as readily available natural materials to perform tanning processes,
44 mineral tanning came to be known later. Differently from many other industries, tanning has been practised for a long
45 time and the processes are kept secret from father to son and their succeeding generations(Muthukrishnan 2021). The
46 durability of leather can be accomplished using tanning agents stabilising the collagen matrix, which despite the global
47 industrialization and use of leather, remains a challenging purpose for conservators(Badea et al. 2019). Moreover, there
48 are different methods to stabilize leather depending on many parameters including the final result, properties and
49 performance that should be achieved: for example, if the hair should be kept, if vegetable or chrome-tanned leather is
50 expected, etc. The tanning process can be divided into three fundamental macro-processes, named Beamhouse, Tanning,
51 and Finishing. **Fig.1** shows a scheme of the tanning process.



52 **Fig.1: The tanning process**

53 Most of the tanning phases are performed in wet batches leading to a large consumption of water and thus a large
54 production of wastewater where the impurities include suspended, dissolved, or colloidal inorganic and organic
55 substances coming directly from the leather and as residues of chemical products. The tannery wastewater represents a
56 refractory pollution for the environment. It contains not only chromium, metal ions, sulphides, and chlorides, but also
57 oils, proteins, dyes, surfactants, recalcitrant, and persistent organic pollutants. The removal of these contaminants
58 requires cost-effective technologies and a variety of techniques. Nowadays, adsorption is worldwide recognized to be a
59 simple and effective technique for water treatment. The efficiency of this wastewater treatment technology largely
60 depends on the type of adsorbents in terms of chemical and physical properties. **Natural, synthetic and modified zeolites**

62 are endowed with porous structures showing valuable physicochemical properties such as cation exchange, adsorption
163 and catalytic ones. Cation exchange is an intrinsic property of zeolites that indirectly leads to applications such as
2 64 catalytic processes or adsorption. Indeed, ion exchange procedures can alter the surface pH of zeolites, control their
45 pore size and create specific surface active sites for targeted adsorption. The use of zeolites in wastewater treatments as
5 66 adsorbents and ion exchangers is gaining a lot of interest mainly due to their properties and significant worldwide
767 occurrence.

8 68 In this review, we attempt to describe the recent efforts applied to tannery wastewater treatments using natural,
10 69 modified, or synthetic zeolites, presenting the state-of-the-art, physical and chemical aspects behind the remediation
11 70 process, and future perspectives.

13 71 14 72 2. The tanning process

16 73 The first macro-phase is the *beamhouse*. The raw hides and skins arrive from the slaughterhouse, and their
17 74 decomposition is blocked by conservation processes to prevent damage to the dermis. There are different kinds of
19 75 preserving methods such as dry hides, fresh salted hides, dry salted hides, arsenic hides, patinated hides, and pickled
20 76 hides. The first stage of leather manufacturing is the soaking phase, a process useful for replenishing the water and
22 77 restoring the flexibility and softness in the leather fibres lost during conservation. The liming phase aims to enlarge the
24 78 space between fibres to help the entering of the tanning agents, together with the hair removal, these two processes are
25 79 carried out chemically and can be accomplished simultaneously. The mechanical split process divides the leather into
26 80 two or more layers; the upper layer is called grain and the most valuable, while the lower layers are called crusts.
28 81 Fleshing is a mechanical process to eliminate subcutaneous tissues and excess fat. **The lime is then eliminated during
30 82 the de-liming process with acids strong (hydrochloric and sulfuric acids) or weak (boric, acetic, formic, lactic acid,
31 83 phosphoric or carbonic acids).** The maceration treatment completes the de-liming process by relaxing leather fibres, to
33 84 prepare the leather to receive and fully absorb the tanning agents. **Very oily skins can be processed with a chemical
34 85 degreasing treatment using for example detergents or solvents.** The last phase of beam house is called pickling, it
36 86 definitively blocks the possible maceration of the leather, simultaneously helping the fibres to open.

37 87 The second macro-phase is the *tanning*. The purpose of the tanning phase is basically to give the leather greater
39 88 resistance to wear, maximum impermeability to water, and the right permeability to air and water vapour through
40 89 porosity. Traditionally, the process is performed with trivalent chromium, the tanned leather gains a light blue colour,
42 90 and this is why it is properly called wet-blue. Vegetable tanning is recognized as one of the oldest types of tanning in the
43 91 world, most likely it is carried out with nature-based tannins, extractable from trees. There are other types of tanning,
45 92 such as the chrome-free based agents, which are performed with other minerals including iron, zirconium, aluminium,
46 93 or more recently titanium, and other metal-free approaches such as oil tanning, and aldehyde tanning. However, the
48 94 alternative methods are either not as effective as chromium-tanning, producing leather with lower efficiency in terms of
49 95 dyeability, and functional and organoleptic properties, or being cost-prohibitive treatments, indeed 90% of the
51 96 production remains chrome-based(Zhu et al. 2020).

52 97 The last macro-phase is the *post-tanning*. At the end of the last phase, the amount of water present inside the leather
54 98 must be reduced by applying strong pressure. Retanning is the process that finalizes the stabilization of the leather and
55 99 gives character and confers specific properties to the leather, such as mechanical resistance, uniform thickness of the
57 100 leather, fullness, softness, elasticity, pliability, lightness etc. The dyeing phase can be accomplished during re-tanning to
58 101 make the dye penetrate not only superficially but also along its entire thickness. The last wet process is fattening, which
60 102 aims to introduce soluble oils and fats into the fibres which act as lubricants and enhance the physical-mechanical

103 properties of the leather including softness, elasticity, resistance, and hydrophobicity. From now on, the processes are
104 usually defined as dry phases. The leather is then pressed, stretched, widened, and finally dried to lose useless
105 substances previously absorbed. The last *finishing* treatment aims to enhance the quality of the leather. It consists of
106 processes that can be mechanical or chemical. In general, finishing represents a fundamental macro-objective of the
107 production process, for the final preparation of the material for marketing, which underlies the manufacturer's ability to
108 enhance the valuable aspects of the raw material, expertly camouflage production errors and defects, improve the
109 technical performance and resistance to environmental and anthropic factors, promote an overall improvement in
110 product and sensorial characteristics, confer added value, etc. Physical finishing treatments include rotary perching and
111 milling with control temperature and humidity values to enhance softness; sanding for the creation of leather with a
112 writing effect (e.g., nubuck), repairing defects on the grain, and eliminating any subcutaneous residues.
113 From a chemical point of view, in the finishing phase, various substances can be applied to the surface of the leather
114 which, after drying, produces a consistent, elastic, and transparent film. The finishing is generally made with
115 overlapping layers of these materials. Traditional finishings are achieved through the use of substances, mainly of a
116 polymeric nature, with particular reference to the use of some synthetic polymers; specifically, except finishings carried
117 out exclusively through the use of waxes or natural protein-based polymers (casein, albumin), synthetic polymers are
118 typically widely used (polyurethanes, polyamides, polysiloxanes, acrylic resins and copolymers, butadiene resins and
119 copolymers, polyvinyl resins, epoxy resins), as well as some modified natural polymers, with particular reference to
120 cellulose derivatives (nitrocellulose, ethyl cellulose, cellulose acetate, cellulose acetobutyrate).
121 The leather finishing tamper with a huge variety of characteristics of the leather from the desired colour to the desired
122 fashion effect, the physical and mechanical performance, or the touch. There are many finishing machines: spray
123 finishing, veil finishing, pad finishing or roller finishing also known as the coating.
124 The very final operations are the trimming to have regular edges of the final leather and the measurement for both
125 thickness in millimetres and surface in square feet.
126 It is now well established that an adequate final quality leather product comes from a complex process that requires a
127 skilled workforce and specialized tools and processes. Unfortunately, the leather industry is also known for its negative
128 environmental impacts: leather creates a range of pollutants that can be harmful to the environment, becoming a
129 growing concern for many countries.

3. Characteristics of tannery wastewater

131 The production of finished leather is the result of several well-defined batch processes, as shown in the next chapters
132 this leads to the production of high volumes of wastewater containing a large variety of pollutants. **Fig.2** shows the
133 inputs of the tannery system: the raw hides and skins, as co-products of the agrifood industry; the air; the chemical
134 products; and the water; and its outputs: the semi- or finished products, wet-blue or wet-white, crust or finished leather;
135 air emissions; solid waste with or without tanning agents; and wastewater(Kanagaraj et al. 2015).
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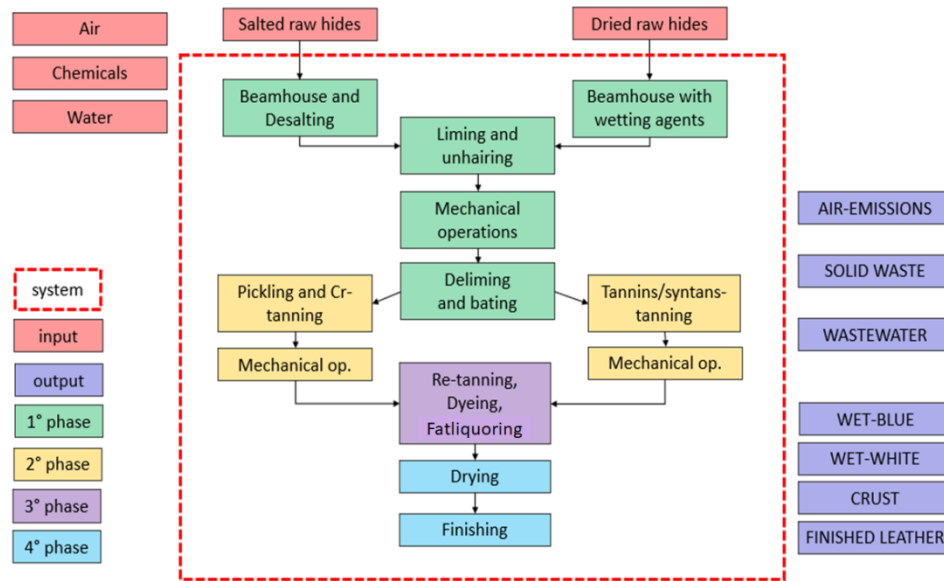


Fig. 2: Tannery input-output system

It is estimated that the tanning process consumes more than one hundred litres of water and about two kilograms of chemicals per square meter of final product (Alibardi and Cossu 2016; UNIC Italian Tanneries 2023). The utilization of a large amount of freshwater and chemicals inevitably leads to the production of high volumes of wastewater containing a large variety of pollutants, some of which can be extremely toxic or hazardous for the environment and human health (Kanagaraj et al. 2015). The tannery wastewater (TWW) is mainly generated during the wet operations of leather processing, it can be summarized in 3 phases: (a) beam house, (b) tanning, (c) re-tanning, dyeing, fat liquoring; finishing is also known as a dry phase with minor wastewater production.

Tannery wastewater differs from civil and other industrial wastewater for three main reasons: the discontinuity, in terms of volumes and concentration of pollutants on the short and long timescale; the presence of inorganics and organics pollutants coming from the chemicals and the raw leather material itself; and the presence of toxic, persistent and recalcitrant pollutants (Bharagava et al. 2018).

Tab. 1 reports some parameters that characterise an example of TWW, the loads in kilograms per kilogram of raw salted hides, the concentration in the tannery wastewater output in mg/L, and in the last column the associated limit concentration according to the Italian legislation (UNIDO, 2021).

Tab. 1 Fundamental characterization of TWW and corresponding Italian limits

Parameter	Load kg/kg (salted raw hides)	Concentration in output wastewater	Italian Limits D.Lgs. 152/2006
BOD₅	90	2 *10 ³ mg/L	<40 mg/L
COD	180	4 000 mg/L	<160 mg/L
TSS	90	2 000 mg/L	<80 mg/L
Cr³⁺	7	150 mg/L	<2 mg/L
Sulphide	7.5	160 mg/L	<1 mg/L
TKN (Kjeldahl)	37.5	160 mg/L	-
Chloride	1125	5 000 mg/L	<1200 mg/L
Sulphates	315	1 400 mg/L	<1000 mg/L
Oil and fats	30	130 mg/L	<20 mg/L

TDS (= $Cl^- + SO_4^{2-}$)	2250	10 000 mg/L	
pH		6 - 9	5.5 - 9.5

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The first phase of tannery treatment includes: degreasing, liming, unhairing, delimiting, and bating. Effluents from the beam-house generally contain sulphides, pH is alkaline, and they are chrome-free (UNIDO, 2021). Effluents emanating from the tanyard contain chrome and are prevalent acidic. Tanning agents, with different molecular structures, give different mechanical and organoleptic properties. The tanning agent used is the most significant substance factor and the main contributor to most of the impact categories in the tanning wastewater composition. Nowadays, chrome tanning is the dominant method for leather processing because it gives an excellent performance to the resultant leather, however, the procedure received much attention in recent years since their Cr (III) may convert into Cr (VI), thereby causing carcinogenic, mutagenic, and teratogenic effects on the biological chain (Kanagaraj et al. 2015; Zhang et al. 2018). Several authors have reported in the literature different methods to minimize the chromium concentration in the effluent with the process for achieving high chrome exhaustion (Li et al. 2009), by optimising the reuse of tanning floats (Morera et al. 2011), and recycling the chromium after its recovery with physical, chemical, and biological methods or combined treatments (Mella et al. 2015; Ahmed et al. 2016). Chrome-free tanning systems, based on alternative metals such as aluminium, zirconium, and titanium complexes, eliminate or reduce chrome pollution and the emission loads as the production of chrome-contaminated shavings, that are not completely biodegradable (Zuriaga-Agustí et al. 2015). Metal-free tanning agents are also considered to have a lower environmental impact with respect chrome-based tanning process. Many sustainable metal-free alternatives based on chemical and enzymatic crosslinking, various bio-derived polymers, and enzymes, have been developed over the years with relevant results as sustainable system (Yu et al. 2021). However, the alternative methods are either not as effective as Cr-tanning, producing leather with lower efficiency in terms of dyeability, and functional and organoleptic properties, or being cost-prohibitive treatments, indeed 90% of the production remains chrome-based (Zhu et al. 2020).

The leather process consumes approximately 130 different types of chemicals, to ensure the desired properties of the leather during the post-tanning phase, some of them include de-acidulants, synthetic and natural retanning agents, synthetic and natural oils, surfactants, dyes, chemical auxiliaries, acids. The retanning phase helps to remove the blemish left and to improve the performance of tanning treatment with syntans or vegetable tannins, they are considered substances harmful to the environment based on melamine resins, acrylic resins, and phenolic syntans. The fat-liquor application aims to fill the voids in between the fibres and helps the improvement of softening, smoothing, and stability. The effluents from this process usually contain natural-based emulsions such as sulphite vegetable oils, fish oils, castor oils, ethoxylated, and propoxylated rapeseed oil fatty acid. Synthetic fat-liquoring agents include block copolymers of ethylene and propylene oxides with rapeseed oil fatty acids, anionic acrylic copolymers, reaction products of tallow with diethanolamine and maleic anhydride and chlorinated aliphatic substances (Mohammad Mahbulul Hassan et al. 2023).

Retanning, fat liquoring, and dyeing wastewater consists of has the highest total dissolved solids load of all post-tanning processes, mainly due to tannins, black, dye, and fixing agents. Due to the use of azodye as dyeing this effluent also accounts for the higher total nitrogen content (Hansen et al. 2020).

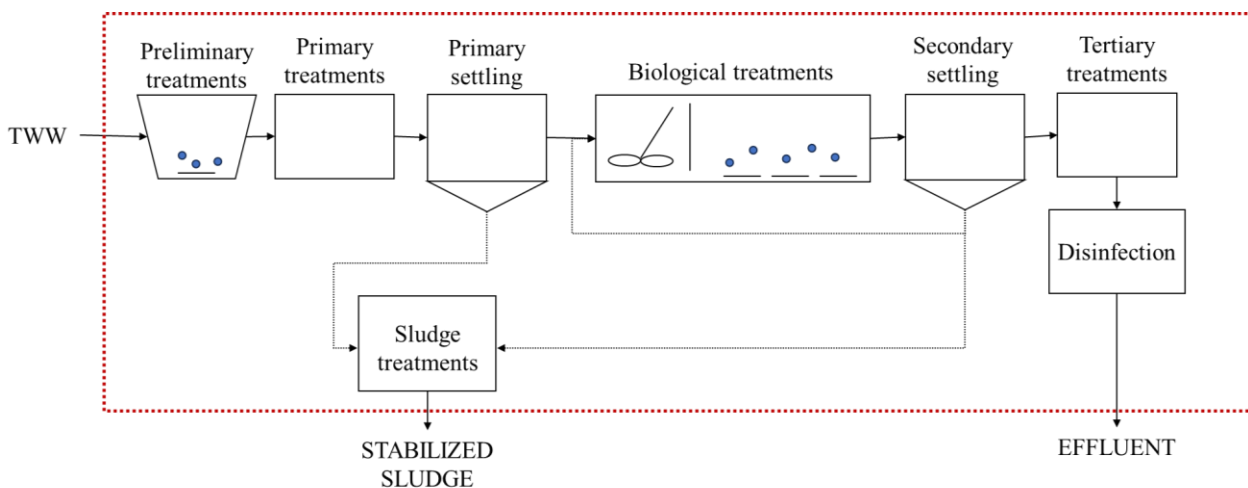
In the end, the finishing process aims to complete the fabric into a more commercial product improving the physical appearance, softening, and waterproofing properties, and disinfecting with biocides to mitigate microbial growth on the leather surface. The main hazardous substances at this phase are formaldehyde-based chemicals, biocides, organometallic compounds etc. (Muthu 2021).

193 Depending on the size of the industry, the chemicals used, the amount of water required, and the result attained, the
194 characteristics of tannery effluents vary significantly from one to the other.

196 4. Tannery wastewater treatment plant (TWWTP)

197 The progress of technical and scientific knowledge and the increase in industrial activities have led to an improvement
198 in the quality of life and to greater production of waste and wastewater with complex characteristics. The environmental
199 issue has thus taken over a fundamental importance, especially in polluting sectors such as tanning. The reasons to push
200 forward the ecological company policy depend on economic reasons such as the recovery or the reuse of compounds,
201 reduction of energy and water consumption; legislative reasons such as waste taxes and discharge limits, ecological
202 labels; and ethical social reasons.

203 TWW is a hazardous source of pollution in soil and water thus it is therefore essential to adequately treat the effluents
204 before their safe disposal into the environment. This can be achieved by using physical, chemical, and biological
205 methods either alone or in combination in collective wastewater treatment plants (Saxena et al. 2017). The construction
206 and management of a wastewater treatment plant is a complex system that must care about different aspects including
207 the volumes and pollution loads of the wastewater to be treated, the legal limits to be respected, the type of the receiving
208 body, the possible reuse of the water or sludge produced. The characteristics of the inlet and outlet wastewater depend
209 on many factors: the type of leather processed, the tanning processes, and the technology used in the process. A typical
210 scheme of a collective treatment plant for TWW is represented in Fig. 3.



211
212 **Fig. 3: Scheme of a treatment plant for TWW**

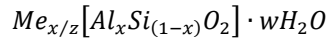
213 Preliminary treatments include (a) coarse screens, sand traps and oil separators for TSS (debris, solid waste, oils, sand),
214 they can be done directly in the tannery, reducing the polluting load and solving the problems of sedimentation of
215 wastewater in the collection pipes at the central plant; (b) equalisation aims to buffer and homogenise the flow; (c)
216 elimination of sulphides gasses with pure oxygen or scrubbers (Lofrano et al. 2008). Primary treatments, also known as
217 physical-chemical treatment approaches include: (a) coagulation and flocculation, to destabilize colloids, form flocs,
218 and aggregate them, followed by a settling tank; (b) adsorption usually applied to decrease metal content, this treatment
219 can be also performed in the tertiary stage of wastewater plant (Ayoub et al. 2011). Biological treatments are also called
220 secondary treatments and include (a) a first anoxic tank for denitrification; (b) an aerated, aerobic tank for nitrification
221 and organic oxidation; and (c) a sedimentation tank to produce biological sludge. Tertiary treatments aim to adjust the
222 purification of the effluent by reducing the loads of pollutants including nutrients or poorly biodegradable substances
223 such as synthetic and natural tannins. Some examples are flotation, membrane, and advanced oxidation process (Dixit et

224 al. 2015). Finally, disinfection, such as UV or ozonisation, reduces the microbial load of the treated wastewater before
 225 returning it to the water cycle, decreasing the hazardous concentration values from a health and environmental point of
 226 view.

228 5. Zeolites

229 5.1 Physical and chemical properties of zeolites

230 Zeolites are crystalline microporous aluminosilicates of both natural and synthetic origin, belonging to the class of
 231 tectosilicates and characterized by the following minimal formula:



233 where Me represents the cation and z its valence; $O/(Si+Al) = 2$ and $x \leq 1/2$; w is variable depending on the type of
 234 zeolite, the Si/Al ratio, the cation composition, the temperature, and the partial pressure of environmental water
 235 vapour (Breck and Wiley 1975).

236 The zeolitic structures can be described as sets of tetrahedra, centred on silicon and aluminium atoms with connecting
 237 oxygen atoms, forming three-dimensional frameworks with cavities and internal channels. Zeolites are distinguished
 238 from other tectosilicates by the presence of intercommunicating channels, large surfaces, and internal
 239 volumes (Baerlocher Ch. et al. 2007). These micropores (less than 20 Å in size) are occupied by water molecules and
 240 metal cations, which can be easily removed and exchanged because they are not part of the three-dimensional
 241 lattice (Breck and Wiley 1975; Mortier 1982). This particular structure justifies the extraordinary properties and
 242 applications of zeolites. The term "zeolite" was introduced in 1756 by the Swedish mineralogist Axel Fredrik Cronstedt
 243 to describe natural minerals that, when heated, release so much water that they appear to be boiling (from the Greek
 244 *zein* = boil and *lithos* = rock) (Colella and Gualtieri 2007).

245 After their discovery, zeolites remained unused for more than 200 years: their industrial-scale application only started in
 246 1905, due to the discovery of an economically available sedimentary deposit, which enabled its introduction into the
 247 detergent industry (Guisnet and Gilson 2002).

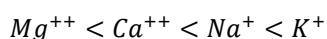
248 *Natural zeolites* are currently used in agriculture, aquaculture, animal nutrition and environmental remediation, where
 249 they can replace substances with low eco-compatibility such as phosphates in detergents or fertilizers in
 250 agriculture (Colella 1999; Cataldo et al. 2021). As cation exchangers, zeolites are excellent candidates for the removal of
 251 polluting metals from industrial or municipal wastewater (Morante-Carballo et al. 2021). Eventually, zeolites can be
 252 used for air purification and as molecular sieves (Breck and Wiley 1975; Dyer 1988). Natural zeolites are cheap
 253 materials (costing around a few tens of euros per kg), but they have a low degree of purity and a limited number of
 254 structural types (Gottardi and Galli 1986). For this reason, since the 1940s particular attention has been paid to the
 255 development of *synthetic zeolites* characterized by different chemical and structural compositions compared to natural
 256 zeolites (Cundy and Cox 2003). The synthesis of zeolites is based on the hydrothermal evolution of an amorphous
 257 aluminium-silicate gel in an alkaline environment. The first lab-produced zeolite that aroused commercial interest was
 258 zeolite A, (Milton 1959) which is still the most widely used due to the ease of production process and its low cost. To
 259 date, more than 200 unique zeolitic frameworks have been identified along with 40 naturally occurring ones (Kumar et
 260 al. 2019). The advantage of synthetic over natural zeolites is the higher thermal stability and purity, together with the
 261 wider range of chemical properties and pore sizes (Georgiev et al. 2009). **Tab. 2** shows some examples of synthetic
 262 zeolites of common use in different real-world applications.

263 **Tab. 2: Examples of synthetic zeolites**

Zeolites	Typical chemical formula
----------	--------------------------

Zeolite A	$2\text{Na}_2\text{O}\cdot 2\text{Al}_2\text{O}_3\cdot 4\text{SiO}_2\cdot 9\text{H}_2\text{O}$
Zeolite L	$2\text{K}_2\text{O}\cdot \text{Na}_2\text{O}\cdot 3\text{Al}_2\text{O}_3\cdot 18\text{SiO}_2\cdot 14\text{H}_2\text{O}$
Zeolite X	$11\text{Na}_2\text{O}\cdot 11\text{Al}_2\text{O}_3\cdot 26\text{SiO}_2\cdot 60\text{H}_2\text{O}$
Zeolite Y	$7\text{Na}_2\text{O}\cdot 7\text{Al}_2\text{O}_3\cdot 34\text{SiO}_2\cdot 60\text{H}_2\text{O}$
Zeolite P	$\text{Na}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\cdot 4\text{H}_2\text{O}$
Zeolite ZSM-5	$7\text{Na}_2\text{O}\cdot 7\text{Al}_2\text{O}_3\cdot 82\text{SiO}_2\cdot 16\text{H}_2\text{O}$

The *physical properties* of zeolites mainly depend on their porosity. The most relevant *physical properties* of zeolites are their relatively low density, high thermal stability and specific surface area. The *chemical properties* of zeolites mainly depend on the type of metal cations within their structure (their cation exchange capability is a relevant chemical property itself) and on the water molecules in their pores. According to the chemical composition (namely, the Si/Al ratio) and the atomic scale structure of the framework of natural and synthetic zeolites, different properties of these materials can sensibly change. Some of these properties are the adsorption capability, the way of influencing the pH when put in water, and the cation exchange properties (Park et al. 2000). Zeolites in contact with electrolyte solutions can exchange the ions present in their framework with those present in the solution. The cations allocated in specific extra-framework positions needed to balance the negative charge deriving from the aluminium in tetrahedral coordination, are electrostatically bound to the zeolite framework and such bond is weakened by the dielectric action of water molecules, therefore, they can be easily exchanged. This gives zeolites a high ion exchange capacity. The **cation exchange capacity** (CEC) of a zeolite corresponds to the milliequivalents of cation exchanged per gram of zeolite, therefore, it provides a measure of the maximum achievable substitution. The cation exchange capacity is a function of the silicon-aluminium ratio and is maximum when this ratio is unitary. Most zeolites have a variable stoichiometry, so they have a range of variation in their CEC. Considering a single cationic species, the actual exchange capacity will depend on the solution concentration of the cation and the selectivity of the zeolite towards it. Such selectivity can be measured by comparing the uptake of two different cationic species and measuring the preference that the exchanger exhibits for one species over the other. For example, phillipsite and chabazite show the same sequence of selectivity (Eisenman 1962):



The usual high cation exchange capacity of zeolites makes them particularly useful in different application fields, from agriculture to the detergent industry and the removal of pollutants from wastewater.

5.2 Zeolites in wastewater treatment

Zeolites are used in many organic chemistry reactions such as oxidation and acid or shape-selective catalysis, as well as in many fuel industry processes including petroleum refining and the production of synfuels and petrochemicals (Kumar et al. 2019). The peculiar structure of zeolites makes them significantly useful as adsorbent materials due to their chemical and physical properties and easily tuneable surface characteristics. Both natural and synthetic zeolites are also used for the removal of polluting cationic species from industrial or municipal wastewater. Compared to the organic resins traditionally used for the removal of ionic pollutants from water, zeolites are selective towards specific cations (Caputo and Pepe 2007) and show better thermal stability. Moreover, they are usually cheaper than organic resins but show lower chemical stability and cation exchange capacity.

5.2.1 Cation exchange processes

299 As already mentioned, zeolites are well known for their great selectivity in cation exchange processes while showing
300 remarkable resistance to high temperatures and ionizing radiations and excellent environmental compatibility. *Cation*
301 *exchange processes* for water purification are usually carried out in two different ways:
302 - *Fixed Bed Process*, where contaminated water is purified through elution in fixed beds containing granular zeolitic
303 material. The efficiency of these systems depends on the size and density of the packed grains. Small grains and high
304 densities produce significant pressure drops in the column. Exhausted beds must be regenerated: generally, this process
305 is carried out by elution with very concentrated sodium solutions. In an industrial plant, to optimize the process, several
306 columns are used in parallel, which alternate operating and regeneration phases.
307 - *Direct Addition Processes*, where powdered zeolites are directly added to wastewater. The suspension is mixed in
308 batch reactors and kept in constant agitation for a sufficient time to complete the exchange. Subsequently, the resulting
309 zeolitic sludge is disposed of in landfills or reused. Due to the reversibility of the cation exchange process, zeolitic
310 sludge needs to be safely inserted by ceramization or in a cement matrix. The main applications of zeolites as cation
311 exchangers in the field of water purification concern the removal of NH_4^+ from urban and industrial wastewater, heavy
312 metals from industrial wastewater and radionuclides from nuclear wastewater (Zhao et al. 2004; Wang and Peng 2010;
313 De Magalhães et al. 2022). **Natural zeolites are endowed with porous structures showing valuable physicochemical**
314 **properties such as cation exchange. . Indeed, ion exchange procedures can represent a direct wastewater remediation**
315 **method but they can also be indirectly used to alter the surface pH of zeolites, control their pore size and create specific**
316 **surface active sites for targeted adsorption. These approaches and other valuable methods to enhance or adjust the**
317 **remediation capacity of zeolites are reviewed in the next chapters.**

319 5.2.2 Modification of zeolite surfaces

320 The modification or additional functionalization of natural and synthetic zeolites involves the modification of their
321 physical and chemical properties, representing a step forward in the common cation exchange process to remove
322 pollutants from liquid phases. The modification approaches aimed at an enhancement of water treatment capabilities can
323 be generally divided into three categories: physical methods, chemical methods and a combination of both. *Physical*
324 *modification* includes two main approaches: thermal modification and ultrasonic treatment. Physical modifications can
325 improve the cation exchange and adsorption abilities of zeolites, for example when the pores of natural zeolites are
326 blocked by impurities (Kragović et al. 2012). *Thermal modification* aims to reduce the surface resistance of zeolites,
327 improving their cation exchange and adsorption capacities. Muffle furnace heating is a traditional and simple way to
328 treat samples, while microwave heating can save time and perform good penetration with high energy efficiency (Shi et
329 al. 2017). *Ultrasonic modification* is a useful method to eliminate impurities inside the structural pores by high
330 frequencies, inducing higher cation exchange and adsorption efficiencies (Zieliński et al. 2016). *Chemical modification*
331 includes many different methods such as co-precipitation, solvothermal and sol-gel treatments, etc. Cation exchange
332 itself can be considered a performable procedure for the chemical modification of zeolites, e.g., when exchange with H^+
333 cations is used for increasing surface acidity (An et al. 2013; Matijasevic et al. 2016). Zeolite functionalization can be
334 used to modify the chemical properties of the zeolite structure to make it better akin to the target adsorption system with
335 special requirements. The *functionalization* of zeolites can be achieved either during the zeolite synthesis process or by
336 a post-synthesis modification. The latter method doubtless allows for tighter control and easier manipulation of
337 materials, including the possibility of using natural zeolites (Lee et al. 2021). Moreover, it is possible to adjust the
338 hydrophilic character of traditional zeolites without changing their inherent framework, which means a negligible effect
339 on the crystalline structure. An alternative approach to increase the efficiency of zeolites as sorbent material for water

340 treatment is represented by the *dealumination process*. This method enables zeolites with a very high Si/Al ratio to be
341 obtained, which is reflected in a material with higher hydrophobicity and increased thermal stability of the crystalline
342 and porous structure (ultra-stable zeolite). Navalon et al. used dealuminated large pores of Y zeolite for the selective
343 removal of fatty acid and hydrocarbon from water (Navalon et al. 2009). The extent of a dealumination process
344 drastically influences the ion exchange capacity of the selected zeolite: such procedural aspect is crucial considering
345 that the degree of ion exchange can influence the surface area and pore volume, causing steric hindrance effects and
346 potentially reducing other capabilities such as the adsorption capacity (Serra et al. 2011). Another well-known
347 modification strategy is the *immobilization of surfactant species* on the external surface of zeolite particles as a way of
348 modifying the surface charge and hydrophilicity (Hailu et al. 2017). A cationic surfactant-based modification can
349 enhance the anion removal rate by electrostatic forces or the hydrophobic interaction according to the critical micelle
350 concentration. Another class of molecules frequently used in post-synthesis modification processes is formed by
351 organo-silanes, where *silicon atoms* are bonded to the functional group and *alkoxide-OR groups* (Esposito 2023). By the
352 addition of water, Si-OR can be hydrolyzed to form Si-OH which is prone to form covalent bonds with the hydroxyl
353 groups decorating the surface of zeolites. This approach generates stable Si-O bonds and a solid anchoring of the
354 selected functionality. Alkyl-silanes are generally proposed as hydrophobizing agents (Zapata et al. 2013). On the other
355 hand, *amino-silane* can be introduced for the removal of anionic species, that are not compatible with the cation
356 exchange feature of zeolite (Meftah and Zerafat 2016). Although this method achieves a high degree of functionalization
357 and good stability of the anchored molecule, it requires a multi-step procedure that also includes activation of the zeolite
358 surface. Conversely, the impregnation method is characterized by the simplicity of the experimental setup and involves
359 loading the zeolite with a solution containing the molecule with the specific functionality. The trade-off between the
360 lower level of functionalization achieved and the simplicity of method implementation allows the impregnation to be
361 more versatile and suitable for scale-up of the final material, winking at industrial applications. As an effective example
362 of amino-silane-based modification, a zeolite *functionalized with APTS* (3-amino propyltriethoxysilane) was reported by
363 Meftah and Zerafat for the removal of nitrate from water, with a removal percentage of about 80 wt.% (Meftah and
364 Zerafat 2016). Moreover, Wang et al. demonstrated the effectiveness of an amino functionalization of natural
365 clinoptilolite for the removal of chromate and naphthalene from water. In particular, their results showed a remarkable
366 removal rate, of about 90% and 95%, for both the anionic species and the hydrophobic molecule, respectively (Wang et al.
367 2018). In a recent work by Omorogie and Helmerich, zeolite amino functionalization was exploited for the removal
368 of microplastic from water (Omorogie and Helmreich 2023). Moreover, a *sulfur-functionalized natural zeolite* was
369 proposed by Ugrina et al. for the enhanced removal of mercury (II) ions from an aqueous solution, achieving a removal
370 efficiency of about 90% (Ugrina et al. 2021).

371 Metal oxide nanoparticles, carbonaceous materials, carbon nanotubes, graphene oxide, hydroxyapatite and silicates can
372 also be blended with zeolites to improve their physicochemical properties for the removal of contaminants from
373 water (Roshanfekar Rad and Anbia 2021). As an example, an ultra-stable Y zeolite with embedded *nano-sized magnetite*
374 (Fe_3O_4) particles was tested for the removal of phenol from water through a photo-Fenton mechanism activated with
375 solar light. The authors achieved the complete mineralization of phenol after 120 min of irradiation (Tammamo et al.
376 2023b).

377 A novel approach to implementing the use of zeolites in water treatment has been proposed by Pansini et al. (Pansini et
378 al. 2018; Marocco et al. 2020; Pirozzi et al. 2023), in their research zeolites were employed as precursors of novel
379 magnetic metal-ceramic composites (Pansini et al. 2017; Manzoli et al. 2021; Tammamo et al. 2023a). Natural and
380 synthetic zeolites were first subjected to a cation exchange procedure and after that treated at high temperatures under a

381 reducing atmosphere. This results in the reduction of the cation in its metallic form and its entrapment in the structure of
382 the collapsed zeolite, which resembles a glassy matrix. Following this procedure, the obtained material showed a
383 magnetic behaviour which turns out to be a crucial aspect when investigating water treatment. The simple separation by
384 an external magnet allowed an easy recovery of the sorbent material. These magnetic metal-ceramic composites
385 obtained starting from clinoptilolite and zeolite A were successfully tested in the removal of sulfanilamide (a
386 sulfonamide antibiotic) from water. It is worth mentioning their multicycle stability and regenerability(Sannino et al.
387 2022). Eventually, it is worth mentioning the high number of zeolite-based adsorption studies based on *polymer*
388 *modification*. The use of composites based on zeolites and polymers gained considerable attention due to the effective
389 improvement of the adsorption properties and the ease of reusability and recyclability. The structure of the composites
390 includes different forms such as beads, hydrogels, thin films, nanoparticles, and nanofibers. Natural polymer-modified
391 zeolites include cellulose, chitosan, and alginate. Synthetic polymer modification includes the use of polyvinyl chloride,
392 polycaprolactone, polyacrylamide, polyvinyl alcohol, polypropylene (PP), polypyrrole, polyvinylpyrrolidone,
393 polyamide, polyacrylonitrile, and polysulfone(Roshanfekr Rad and Anbia 2021).

395 6. Application of zeolites in tannery wastewater (TWW) treatment

396 As already mentioned, water is among the most important inputs in the tanning process, and leads to the production of
397 large wastewater volumes containing various pollutants coming directly from the raw hides and the chemical products
398 used during the process. The contaminants include heavy metals (chromium, iron, copper, lead), chloride, surfactants,
399 salt ions, fats, oils, and other organic pollutants that can be persistent (POPs) or recalcitrant (ROPs) with toxic effects on
400 human health and ecosystems(Shegani 2014; Hutton and Shafahi 2019). Around the World, each country adopts its
401 regulatory limits that can vary drastically compared to one another: as an example, different limits exist for the sewage
402 discharge of chromium ions (both III and VI), e.g., 2 mg L⁻¹ in Argentina, 5 mg L⁻¹ in Hungary is, 4 mg L⁻¹ in Italy and
403 a value ranging from 1 to 20 mg L⁻¹ in Australia(Bosnic, M., Buljan, J., Daniels 2000). Depending on the nature of the
404 hazardous species involved and their concentration, tannery wastewater can have a high impact on the environment as
405 in water, soil, and air matrix. Based on these assumptions, it is vital to remove the pollutants from TWW and nowadays
406 different technologies are employed for this aim. The removal of contaminants from TWW consists of a complex series
407 of stages, classified as primary, secondary, and tertiary treatments and disinfection(Srinivasan et al. 2012). The
408 shortcomings of most of these methods are high operational and maintenance costs; moreover, they are often
409 environmentally incompatible due to the high production of toxic residues. Worldwide researchers are constantly
410 working to determine a suitable and efficient method for economic and environmentally friendly treatments due to the
411 complexity of the TWW matrix. The most suitable method for wastewater treatment depends on the nature of the
412 substance to remove but, most of the time, the easiest and most cost-effective method is the *adsorption process*, which
413 envisages the use of an adsorbent material with precise physicochemical properties, i.e., high specific surface area,
414 active adsorption sites, etc. Adsorption and ion-exchange processes are considered a great alternative in water and
415 wastewater treatment because of convenience, ease of operation and simplicity of design. Moreover, they assure a high
416 efficiency in the removal of different kinds of organic, inorganic and mixtures of contaminants as compared to several
417 other treatment processes. In traditional wastewater treatment plants, adsorption is used as a phase transfer process to
418 eliminate substances from both wastewater and gases. The heart of the adsorption process is usually the porous solid
419 medium used as an adsorbent. Adsorption plays an important role in the treatment of wastewater because of its
420 simplicity and cost-effectiveness(Nur-E-Alam et al. 2020). Zeolites have been considered efficient adsorbents mainly
421 for their unique physical and chemical properties including crystallinity, thermal stability, well-defined cage structure of

422 molecular size and ion exchange capabilities; and for their low cost and significant adsorption results with different
423 pollutants(Wen et al. 2018). Tanneries, like all the other factories, face urgent ecological problems to be solved and the
424 use of zeolites shows excellent advantages from this point of view. The next paragraphs review the current literature
425 about the use of zeolites for the removal of specific categories of contaminants from tannery wastewater.
426

427 **6.1. Heavy metals and inorganic ions**

428 Inorganic ions are among the attentional contaminants of tannery wastewater since they are toxic to the environment
429 and ecosystems, with significantly related human health effects(Chiampo et al. 2023). The continuous discharge of
430 heavy metals poses significant concerns and, in recent years, the strong environmental law has compelled industries to
431 apply sustainable technologies to bring down the concentration of hazardous metal ions such as heavy metals (HMs)
432 below the discharge limits(Singh et al. 2023). The data from various studies indicates that Cr, Cd, Pb, Zn, Cu, Fe, and
433 Ni are the most common HMs present in tanning effluents(Islam et al. 2016; Nur-E-Alam et al. 2020). Toxicity of metal
434 ions is of great environmental concern due to their hazardous bioaccumulation and nonbiodegradability in nature(Igiri
435 et al. 2018). Moreover, HMs, as toxic species, are often responsible for the inhibition of the microorganisms adopted in
436 biological treatments due to their poisonous effect in the interaction with the cell membrane and deoxyribonucleic acid
437 (DNA), thus hampering the wastewater biological treatment process(Mpongwana et al. 2022). The monitoring and
438 removal of the HMs pollution in the newly established tannery wastewater treatments is thus a current challenge. The
439 application of zeolites for HMs sequestration in industrial effluent treatments has found the largest applicability with
440 synthetic zeolites, followed by modified zeolites(De Magalhães et al. 2022). Natural terms, although quite attractive and
441 economically advantageous, show the lowest ion exchange capabilities for HMs due to their mineralogical composition,
442 which varies greatly from region to region and within the same mineral deposit, and due to the several concurrent
443 contaminants contained in TWW that lower the metal uptake capacity. Common natural zeolites are analcime,
444 chabazite, clinoptilolite, ferrierite, mordenite and phillipsite. Synthetic zeolites are usually constituted by a single phase,
445 with high uniform structural characteristics including pore size distribution, hydrophobicity /hydrophilicity, and the
446 presence of a single compensation cation. Concerning heavy metals, different studies were carried out for their removal,
447 (Keane 1998; Perić et al. 2004; Galletti et al. 2021; Medykowska et al. 2024; Velarde et al. 2024; Buzukashvili et al.
448 2024) and among them, *chromium* (both trivalent and hexavalent) is one of the most common heavy metals present in
449 tannery wastewater. Different studies focused attention on its removal by using zeolites (Basaldella et al. 2007;
450 Kurniawan et al. 2023; Barra-Hinojosa et al. 2024). Rangasamy et al.(Rangasamy et al. 2014) carried out their research
451 using natural zeolites and achieved Cr (VI) removal of up to 92% from the solution. Bolortamir and
452 Egashira(Bolortamir and Egashira 2008) proposed to utilize Mongolian natural and modified zeolites to treat hexavalent
453 chromium-containing tannery wastewater: barium-modified zeolites could favourably uptake hexavalent chromium,
454 achieving a fractional removal over 0.9, despite the unmodified zeolites, that could not remove chromium at all. In a
455 work conducted by Álvarez et al.(Álvarez et al. 2021), a natural zeolite (ZN) and a synthetic one (ZS) were activated
456 with HCl and NaOH and subsequently tested for the removal of Cr(VI) in a concentration of 0.6 mg L⁻¹. It was found
457 that the activation with NaOH was better than that with HCl since the acid treatment provoked a decrease in the ion
458 exchange capacity. In the first case, they obtained ca. 44 % and 32 % of removal with natural and synthetic zeolites,
459 respectively. It is important to acknowledge that chromium is not the only heavy metal that is used in tannery processes.
460 Covarrubias et al.(Covarrubias et al. 2008) prepared organo-modified zeolites with different framework structures using
461 N-cetylpyridinium bromide (CPB). A surfactant-modified zeolite based on the FAU framework type presented the
462 highest Cr(VI) retention capacity, exhibiting also high thermal stability as a consequence of special interactions between
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463 the CPB molecules and the zeolite surface. The surfactant was found to be also the reason for the higher intrinsic Cr(III)
464 exchange capacity of FAU zeolite. The authors conclude that CPB-modified FAU zeolite appears as a promising
465 material for the simultaneous removal of Cr(III), Cr(VI) and toluene contaminants.

466
467 **Tab. 3** summarized the results previously mentioned. From the comparison it can be seen that modification of natural
468 zeolite not obviously lead to the achievement of enhanced chromium ions results. Moreover, the species of chromium
469 may differ according to the revised research application, this can implies different remediation mechanism. It is also
470 worthy to observe the lack of information occurred for what concerns the physic-chemical characterization of zeolites
471 (surface area, pores size, pores volume, cation exchange capacity, point of zero charge, Si/Al ratio etc.) and some
472 parameters of the remediation processes such as grams of zeolites used per liter of contaminated water, initial and final
473 pH.

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Tab. 3: Remediation of tannery chromium contaminated wastewater by natural and modified zeolites

material	BET m ² /g	bulk density g/cm ³	real density g/cm ³	pore vol. cm ³ /g	pore %	Si/Al	CEC	Zeolite Load	Contaminants	Conc.	time h	pH	results	results	ref.
Natural zeolite							49.9 meq 100g ⁻¹		Potassium dichromate (K ₂ Cr ₂ O ₇)	100 ug/g (Cr (VI))			Cr (VI) adsorbed ug/g	80.22	(Rangasamy et al. 2014)
Natural zeolite									Chromium Sulphate (Cr ₂ (SO ₄) ₃)	100 ug/g (Cr (VI))			Cr (VI) adsorbed ug/g	92.18	(Rangasamy et al. 2014)
Natural zeolite									Acqueous solution of CrO ₃		72	9	fractional removal %	0.03	(Bolortamir and Egashira 2008)
Modified zeolite	43								Acqueous solution of CrO ₃		72	9	fractional removal %	0.9	(Bolortamir and Egashira 2008)
Natural zeolite	43.9	0.84	2.26		62.98	4.64	84.05	100 mL/ g	Potassium dichromate solution (K ₂ Cr ₂ O ₇)	1 mg/L (K ₂ Cr ₂ O ₇)	3	2	Cr (IV) removal %	44.4	(Álvarez et al. 2021)
Synthetic zeolite		0.78	1.88		58.45	1.6	188.72	100 mL/ g	Potassium dichromate solution (K ₂ Cr ₂ O ₇)	1 mg/L (K ₂ Cr ₂ O ₇)	3	2	Cr (IV) removal %	32.22	(Álvarez et al. 2021)
Modified zeolite 13X (FAU)	578			0.074		1.5	3.52 (meqCr ₃ ⁺ /g)	0.4 g	Cr(VI)	500 mg/L (Cr (VI))	24		Cr (IV) retention capacity (molCr ₂ O ₇ -2 /Kg)	9.54	(Covarrubias et al. 2008)
CBP-modified FAU-type zeolite								0.4 g	Cr(VI)	500 mg/L (Cr (VI))	24		Cr (IV) retention capacity (molCr ₂ O ₇ -2 /Kg)	37	(Covarrubias et al. 2008)
CBP-modified FAU-type zeolite								0.4 g	Cr(III)	500 mg/L (Cr (III))	24		Cr (III) mmol/kg	527	(Covarrubias et al. 2008)
Modified mordenite-type zeolite (MOR)	277			0.11		9.4	0.21 (meqCr ₃ ⁺ /g)	0.4 g	Cr(VI)	500 mg/L (Cr (VI))	24		Cr IV retention capacity (molCr ₂ O ₇ -2 /Kg)	15.5	(Covarrubias et al. 2008)

480 However, the previous works are characterized by the experimental use of simulated wastewater, and the procedure was
481 applied in systems containing single contamination agents. This is a limit for real cases, where measurements for *multi-*
482 *class contaminants* are preferred.

483 In recent studies, Covarrubias and his group(Covarrubias et al. 2005, 2007) studied the removal of Cr (III) in zeolite-
484 packed columns, analysing the effects of pH and interfering ions, discovering that the particle diameter controls the Cr
485 (III) exchange in the zeolite and that the reduction of the organic matter in terms of COD interfered on the removal. In
486 these studies, the effect of the proposed technology on both a synthetic Cr(III) solution and diluted tannery wastewater
487 was evaluated. Sallam et al.(Sallam et al. 2017) prepared a polymer-clinoptilolite composite N,N-methylene-bis-
488 acrylamide as a matrix for the uptake of Cr(VI) from an aqueous solution. Additionally, they studied the effects of
489 soluble ions in tannery wastewater including Na⁺, Cl⁻ and SO₄²⁻. The results showed that the adsorption of Cr(VI) onto
490 the polymerized samples exhibited higher values than the pristine samples and the experimental kinetics was coherent
491 with a pseudo-second-order model. Ayele et al.(Ayele et al. 2018) synthesized zeolite A from two sources of raw kaolin
492 from Ethiopia and evaluated its application in tannery wastewater treatment, precisely for the removal of Cr(III) with an
493 initial concentration of 2036 mg L⁻¹. They obtained a maximum removal rate of 99.8% with a zeolite dose of 100 g L⁻¹,
494 and an uptake capacity of 200 mg g⁻¹ with a zeolite dose of 5 mg L⁻¹. These results could represent great potential for
495 the use of zeolites synthesized through cheap raw materials. In some cases, there is the possibility of an oxidation
496 process of Cr (III) to Cr (VI), which is extremely more toxic and more mutagenic than Cr (III). Thus, its removal is
497 essential since it can be very dangerous even at a 10 ppm concentration(Standeven and Wetterhahn 1989; Shekhawat et
498 al. 2015). Aljerf(Aljerf 2018) evaluated the importance of the uptake properties of a modified zeolite for the removal of
499 total chromium and basic dyes such as bromocresol purple. The modified zeolite was prepared by mixing solid waste
500 and clinoptilolite. He studied the optimal parameters for the total chromium uptake and the experimental data were best
501 fitted by the Freundlich isotherm and the pseudo-second-order kinetic model. Thermodynamic studies revealed that the
502 uptake was spontaneous and endothermic, thus suggesting the prevalence of uni-polivalent ion exchange mechanisms.
503 Setiadji et al. (Setiadji et al. 2019) treated chromium metal ions and organic compounds in the tannery wastewater
504 activating a zeolite with a barium salt and pre-treating the inlet with a precipitation method. They revealed the optimum
505 conditions for the combined methods, resulting in a total removal of Cr ions and organic compounds up to 99%.

506 Besides chromium ions, copper, iron, lead, cadmium, etc. are widely present in TWW, as material components of
507 chemicals used during the overall process, and zeolites can also be employed for their removal. For example, in a study
508 conducted by Finish et al.(Finish et al. 2023), the simultaneous removal of six toxic heavy metal cations (namely, Cd²⁺,
509 Cr³⁺, Cu²⁺, Ni²⁺, Pb²⁺, and Zn²⁺) was investigated employing a natural zeolite (clinoptilolite) and two synthetic ones,
510 specifically 13X and 4A. The authors found that the uptake capacity of the natural zeolite was 0.12 mmol of total ions
511 per g of zeolite, whereas 13X and 4A obtained a maximum of 2.9 and 1.65 mmol of total ions/g zeolite, respectively.
512 They also ascribed the low uptake capacity values of clinoptilolite to its low specific surface area (19.5 m² g⁻¹) and
513 relatively high Si/Al ratio (equal to 3.5). Moreover, they observed different selectivities depending on the nature of the
514 heavy metal. For example, the two *synthetic zeolites* showed the strongest selectivity towards Pb²⁺ (1.5 mmol g⁻¹ for
515 13X and 0.8 mmol g⁻¹ for 4A) and a considerably weaker one towards Ni²⁺ (0.2 mmol g⁻¹ for 13X and 0.1 mmol g⁻¹ for
516 4A), Zn²⁺ and Cd²⁺ (0.1 mmol g⁻¹ for both zeolites). Concerning Cu²⁺ and Cr³⁺, 4A zeolite showed similar selectivity
517 towards both ions, slightly favouring Cu²⁺ (0.4 mmol g⁻¹), whereas 13X showed a much higher selectivity for Cr³⁺ (0.85
518 mmol g⁻¹)(Finish et al. 2023).

520 **Tab. 4** summarized the results presented. The results of chromium ions adsorption revealed that functional groups of
521 modified zeolites can significantly facilitate reactivity of zeolite. Possible mechanisms of chromium ions adsorption
522 onto zeolite surface are:

- 523 • electrostatic interactions or complexation of chromium ions, due to the interaction between negative metal ions and
524 modified positively charged surface of zeolites (ex. Protonation with OH atoms under acidic conditions, complexation
525 with metal oxides);
- 526 • pore filling, by trapping smaller metal ions;
- 527 • reduction process, where at lower pH Cr(VI) is reduced to Cr(III) and chelated with oxides on the modified surface of
528 zeolites.

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Tab. 4: Remediation of tannery multi-contaminated wastewater by natural and modified zeolites

material	Si/Al	CEC meq/g	Ads Load	type of wastewater	Contaminants	Cr concentration mg/L	time h	pH	Results	Results	Ref.
Zeolite 13X	1.5	3.52		TWW diluted	Cr ³⁺ , Ca ²⁺ , Mg ²⁺ , K ⁺	29.64	0.6	3.5	Cr removal %	100	Covarrubias et al. 2005
Zeolite 13X	1.5	3.52		TWW diluted	Cr ³⁺	500	40	3.5	Cr removal %	100	
Zeolite 13X	1.5	3.52		TWW diluted	Cr ³⁺ , Cl ⁻	29.64	20	3.5	Cr removal %	100	
Zeolite 13X	1.5	3.52		TWW diluted	Cr ³⁺ , NO ₃ ⁻	29.64	20	3.5	Cr removal %	100	
Zeolite 13X	1.5	3.52		TWW diluted	Cr ³⁺ , SO ₄ ²⁻	29.64	50	3.5	Cr removal %	100	
Clinoptilolite				TWW factories (Riyadh, Saudi Arabia)	Cr ³⁺	400		2	Cr removal %	59.3	Sallam et al. 2017
Polymer-zeolite				TWW factories (Riyadh, Saudi Arabia)	Cr ³⁺	400		2	Cr removal %	69	
Clinoptilolite			10 g/L	TWW factories (Riyadh, Saudi Arabia)	Cr ²⁺ , Na ⁺ , Cl ⁻ , SO ₄ ²⁻ , EC	195–878.4 *10 ⁻³		8.3-9	Cr removal %	83.5	
Polymer-zeolite			10 g/L	TWW factories (Riyadh, Saudi Arabia)	Cr ²⁺ , Na ⁺ , Cl ⁻ , SO ₄ ²⁻ , EC	195–878.4 *10 ⁻⁴		8.3-9	Cr removal %	86.2	
Clinoptilolite			10 g/L	TWW factories (Riyadh, Saudi Arabia)	Cr ²⁺ , Na ⁺ , Cl ⁻ , SO ₄ ²⁻ , EC	195–878.4 *10 ⁻⁵		8.3-9	Na ⁺ removal %	32.7	
Clinoptilolite			10 g/L	TWW factories (Riyadh, Saudi Arabia)	Cr ²⁺ , Na ⁺ , Cl ⁻ , SO ₄ ²⁻ , EC	195–878.4 *10 ⁻⁶		8.3-9	Cl ⁻ removal %	33.7	
Clinoptilolite			10 g/L	TWW factories (Riyadh, Saudi Arabia)	Cr ²⁺ , Na ⁺ , Cl ⁻ , SO ₄ ²⁻ , EC	195–878.4 *10 ⁻⁷		8.3-9	SO ₄ ²⁻ removal %	60.8	
Clinoptilolite			10 g/L	TWW factories (Riyadh, Saudi Arabia)	Cr ²⁺ , Na ⁺ , Cl ⁻ , SO ₄ ²⁻ , EC	195–878.4 *10 ⁻⁸		8.3-9	EC removal %	48.9	
Polymer-zeolite			10 g/L	TWW factories (Riyadh, Saudi Arabia)	Cr ²⁺ , Na ⁺ , Cl ⁻ , SO ₄ ²⁻ , EC	195–878.4 *10 ⁻⁹		8.3-9	Na ⁺ removal %	65.2	
Polymer-zeolite			10 g/L	TWW factories (Riyadh, Saudi Arabia)	Cr ²⁺ , Na ⁺ , Cl ⁻ , SO ₄ ²⁻ , EC	195–878.4 *10 ⁻¹⁰		8.3-9	Cl ⁻ removal %	63.1	
Polymer-zeolite			10 g/L	TWW factories (Riyadh, Saudi Arabia)	Cr ²⁺ , Na ⁺ , Cl ⁻ , SO ₄ ²⁻ , EC	195–878.4 *10 ⁻¹¹		8.3-9	SO ₄ ²⁻ removal %	88.6	
Polymer-zeolite			10 g/L	TWW factories (Riyadh, Saudi Arabia)	Cr ²⁺ , Na ⁺ , Cl ⁻ , SO ₄ ²⁻ , EC	195–878.4 *10 ⁻¹²		8.3-9	EC removal %	55.6	
synthesized zeolite			100 g/L	TWW Leather Industry Development Institute of Ethiopia	Cr wastewater	2036	3 h		Cr removal %	99.8	Ayele et al. 2018
synthesized zeolite	1.5		5 g/L	TWW Leather	Cr wastewater	2036	3 h		Cr adsorption	200	

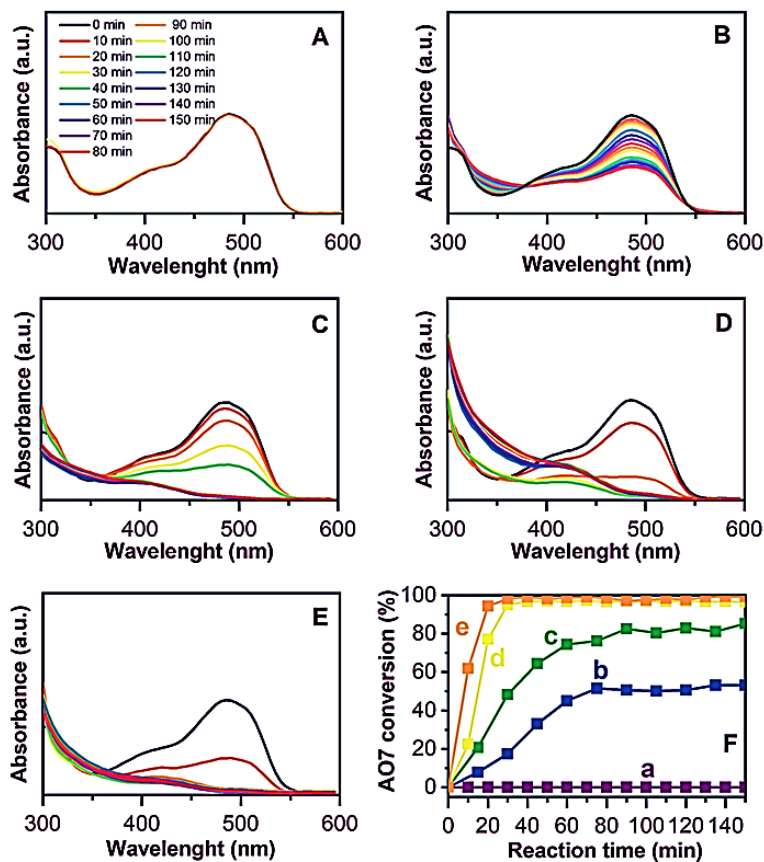
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				Industry Development Institute of Ethiopia					capacity mg/g		
Modified Clinoptilolite:solid waste	8.2	0.20-0.85	60.4 mg	TWW rich in heavy metals and basic dyes as bromocresol purple	Cr	16	1h	6.5	Cr adsorption capacity mg/g	37	Aljerf 2018
Modified Clinoptilolite:solid waste	8.2	0.20-0.85	400 mg	TWW rich in heavy metals and basic dyes as bromocresol purple	BCP	11	1h	8.8	Cr adsorption capacity mg/g	175.5	
Activated Zeolite Sand				TWW	Total Cr, BOD5, COD, TSS, Sulfide (as S)	3920.44		4.6	BOD5 removal %	99.95	Setiadj et al. 2019
Activated Zeolite Sand				TWW	Total Cr, BOD5, COD, TSS, Sulfide (as S)	6771.062		4.6	COD removal %	99.93	
Activated Zeolite Sand				TWW	Total Cr, BOD5, COD, TSS, Sulfide (as S)	624		4.6	TSS removal %	99.51	
Activated Zeolite Sand				TWW	Total Cr, BOD5, COD, TSS, Sulfide (as S)	2646.5		4.6	Cr removal %	99.99	
Activated Zeolite Sand				TWW	Total Cr, BOD5, COD, TSS, Sulfide (as S)	0.205		4.6	Sulfide (as S) removal %	87.8	

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6.2. Synthetic organic dyes

535 Zeolites can also be suitable for the removal of *synthetic organic dyes* (Senthil Kumar et al. 2019). For example,
 536 clinoptilolite has been widely investigated for the removal of methylene blue (Dosa et al. 2018, 2022) and other dyes
 537 that are more complicated to treat, i.e., AO7, whose abatement needs a specific oxidation process (Dosa et al. 2021). In
 538 the latter case, the presence of iron is crucial to carry out the oxidation of AO7 through a photo-Fenton process. From a
 539 circular economy point of view, it could be interesting to exploit the capability of zeolites to remove heavy metals, i.e.,
 540 iron (Kim et al. 2001) from wastewater and, at the same time, re-use such exchanged zeolite for the removal of other
 541 species, i.e., ammonia and phosphate (Kim et al. 2013; Eljamal et al. 2022), synthetic organic dyes like AO7 (Dosa et al.
 542 2021), Congo Red dye (Bencheqroun et al. 2022) and other pollutants (Zhang et al. 2022). As an example, Dosa et
 543 al. (Dosa et al. 2021) studied iron-exchanged zeolites for the removal of AO7. As reported in **Fig. 4**, the results showed
 544 that degradation occurred via a Fenton-like mechanism, thanks to the presence of H₂O₂ and ascorbic acid (AA) which
 545 contribute to the formation of •OH radicals.



546

547 **Fig.4:** Absorbance peaks over time (from 0 to 150 min) of (a) Fe/Clin, (b) Fe/Clin:H₂O₂:AA (1:1:1), (c) Fe/Clin:
 548 H₂O₂:AA (1:10:10), (d) Fe/Clin: H₂O₂:AA (1:20:20) and (e) Fe/Clin: H₂O₂:AA (1:30:30). (f) AO7 conversion (%)
 549 over time for a-Fe/Clin, b-Fe/Clin: H₂O₂:AA (1:1:1), c-Fe/Clin: H₂O₂:AA (1:10:10), d-Fe/Clin: H₂O₂:AA (1:20:20)
 550 and e-Fe/Clin: H₂O₂:AA (1:30:30). Image adapted from Dosa et al. (Dosa et al. 2021).

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6.3. Phenols

553 It is noteworthy to mention that tannery effluents are challenging to treat due to the presence of *phenols* in tanning
 554 amalgamation, which forms polyphenolic structures (Bhardwaj et al. 2023) and their removal has not been extensively
 555 studied. Different technologies can be adopted to reduce the concentration of phenols in wastewater, but their
 556 application strongly depends on the concentration itself in the stream and the eventual co-presence of other

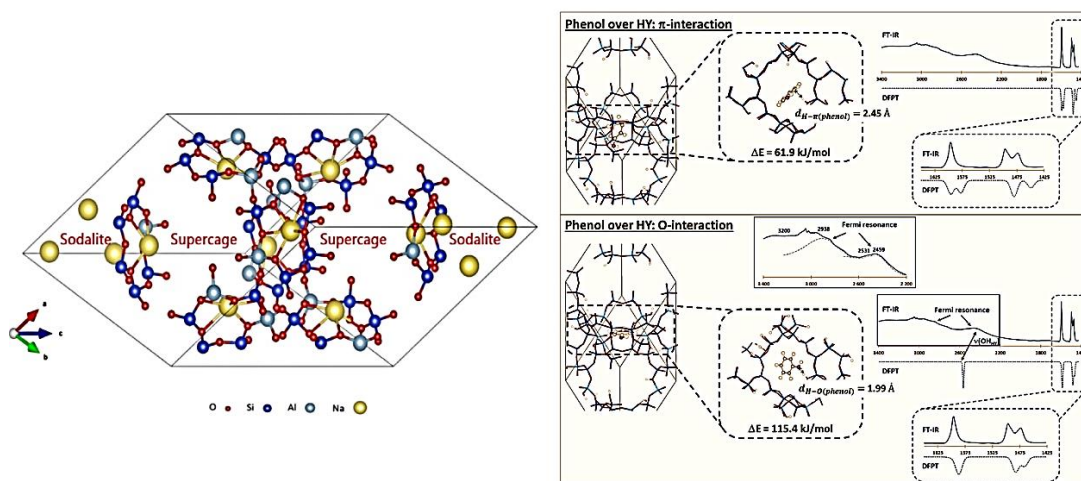
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557 contaminants. However, most of the time, it is possible to use an adsorption process that shows high removal efficiency
 558 towards organic and inorganic pollutants. Several studies report phenol adsorption on activated carbon; however, there
 559 are some limitations concerning the regeneration and the high cost. Thus, zeolites appear as good alternatives. To be
 560 precise, the Si/Al ratio, rather than the pore size of the zeolite, has the predominant effect on the adsorption capacity of
 561 phenol. Some studies on Na–Y synthetic zeolites reported that the interaction between zeolite and phenol is based on
 562 the hydrogen bonding of phenol to the oxygen atoms of zeolite and also on the interaction of the aromatic ring of phenol
 563 with either Na⁺ cations or oxygen atoms of the zeolite super cages (Fig. 5)(Okolo et al. 2000; Khalil et al. 2020).
 564 Damjanović et al.(Damjanović et al. 2010) investigated the use of two synthetic zeolites, mainly BEA (β) and MFI
 565 (ZSM-5) for the adsorption of phenol from aqueous solutions. They observed that the former exhibited favourable
 566 performance compared to the latter since it showed more hydrophobicity, thus decreasing the competition between
 567 water and pollutant molecules. In another work, Yousef et al.(Yousef et al. 2011) reported a maximum adsorption
 568 capacity of 34.5, 24.9, 23.8, and 23.3 mg g⁻¹ at 25, 35, 45, and 55 °C, respectively, on a Jordanian zeolitic tuff that can
 569 be used as a low-cost alternative adsorbent for the removal of phenols from water.



571 **Fig.5: The different adsorption modes of phenol over HY zeolite with their respective interaction energies and**
 572 **predicted vibrational frequencies via DFPT. Image adapted from Khalil et al. (Khalil et al. 2020)**

574 6.4. Surfactants

575 Other pollutants that are also detected in tannery wastewater are *surfactants*, which are considered emerging
 576 contaminants. As well known, they are classified as amphiphilic molecules, which exhibit both hydrophilic and
 577 hydrophobic behaviours. Their further chemical peculiarities can be different, i.e., there are anionic, cationic, non-ionic,
 578 and amphoteric surfactants: in any case, they provoke adverse effects on humans, aquatic life, and vegetation(Siyal et
 579 al. 2020). For the removal of surfactants from wastewater, zeolites represent a good solution. As an example, Shahbazi
 580 et al. (Shahbazi et al. 2014) reported how Y and Beta zeolites having SiO₂/Al₂O₃ ratio > 200 showed good
 581 adsorption/oxidation of nonionic surfactant TX-100 when compared to a natural zeolite such as clinoptilolite. Moreover,
 582 it was demonstrated that the incorporation of Fe into Beta zeolite enhanced the removal of TX-100 as compared to
 583 unmodified zeolites thanks to the occurrence of a Fenton-like oxidation process. The authors also demonstrated that the
 584 pore size and hydrophobicity (thus high SiO₂/Al₂O₃) of zeolites played important roles in the adsorption/oxidation of
 585 surfactants. In another work,(Harutyunyan and Pirumyan 2015) a natural Armenian zeolite was investigated for the
 586 removal of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS), exhibiting a higher uptake
 587 capacity for the former (284 mg g⁻¹) compared to the latter (113 mg g⁻¹). This was ascribed to the higher hydrophobicity

588 of CTAB, which favoured its higher uptake onto the zeolite surface. Interestingly, zeolites containing surfactants can be
589 considered functionalized zeolites and, in turn, reused as substrates for the removal of other compounds. A study
590 conducted by Taffarel and Rubio (Taffarel and Rubio 2010) in 2010 demonstrated the possibility of using a CTAB-
591 modified natural Chilean zeolite to enhance the removal capabilities towards the anionic surfactant sodium dodecyl
592 benzene sulfonate (SDBS), reaching the maximum uptake capacity of 30.7 mg g⁻¹. Such a result is ascribed to the
593 presence of CTAB changing the surface charge of the zeolite from negative to positive, making it suitable for the
594 attraction of anionic surfactants. More recently, De Gennaro et al.(de Gennaro et al. 2020) modified the surface of two
595 natural zeolites (namely, clinoptilolite and phillipsite) with cationic organic surfactants (specifically, CTAB and
596 cetyltrimethylammonium chloride) that can simultaneously act as ion exchangers and organic molecule adsorbents and
597 then reused the zeolite for the removal of As(V) from wastewater. Furthermore, Lin et al.(Lin et al. 2011) studied the
598 efficiency of surfactant-modified zeolites for the removal of another class of pollutants present in tannery wastewater,
599 i.e., tannins. They found that a higher loading amount of surfactant (in this case, cetylpyridinium bromide) exhibited
600 higher tannic acid uptake efficiency. Recently, two Y zeolites were functionalized with different surfactants and
601 subsequently tested for the removal of tannic acid, reaching the maximum uptake capacity of 67.7 mg g⁻¹, which
602 corresponds to *ca.* 85% removal efficiency(Jevremović et al. 2020). Eventually, it appears evident the great potential of
603 zeolites both from an economic and circular economy point of view, since it could be possible to reduce the waste and
604 reuse the zeolite that has already been employed in an exchange process for the removal of other pollutants.

6.5. Other compounds

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607 Tannery effluents, in addition to high amounts of inorganic compounds, are typically characterized also by high values
608 of the *biological and chemical oxygen demand* (BOD, COD) due to the leather itself, and the chemicals added during
609 the manufacturing process. Often these values are above the prescribed limitations(Karahan et al. 2008; Saxena et al.
610 2017). Schrank et al. have suggested that in wastewater treatment plants, many organic pollutants are resistant to
611 conventional chemical and/or biological treatments, thus different degradation techniques have been studied as an
612 alternative (Schrank et al. 2004). Maria Frank Omer et al.(Shankar et al. 2017) used Clinoptilolite–as an adsorbent
613 against BOD and COD, resulting in a removal of 75% and 65% respectively, experimental data fitted Langmuir
614 isotherms. Zang et al. investigated the removal efficiency of ammonium and COD at different influent modes and
615 different hydraulic retention times in a bio-zeolite reactor. The results, in upflowed mode, showed that the removal of
616 ammonium and COD could reach 95% and 85% respectively, and a good effect on the removal of ammonium in real
617 tannery wastewater was also achieved(Zhang et al. 2003).

618 Besides the abatement of the previously mentioned pollutants, the removal of *ammoniacal nitrogen* has received sparse
619 attention(Patil et al. 2021). Although, nitrogen pollution is a serious problem in many industrial wastewaters as a
620 limitation of both biological and conventional physico-chemical methods. Moreover, nitrogenous organic is toxic to
621 humans and upset the equilibrium of water ecology systems. **In tannery wastewater ammonia nitrogen (NH₃-N) is
622 mainly produced from delimiting and bating wastewaters, and from washing and soaking processes because of the
623 decomposition of proteins, originating from their hydrolysis in a strong alkali environment making the discharge of
624 nitrogen difficult to avoid(Wang et al. 2012).** Ding Shao-Ian et al.(Ding et al. 2013) studied also the effects of particle
625 size, dosage, solution temperature, pH, and salt content of tannery wastewater on ammonia treatment by natural and
626 synthetic zeolites. They concluded that synthetic zeolites were more suitable than natural zeolites, but both have an
627 enhancement of efficiency in an alkaline environment.

7. Conclusion

The wastewater produced by the leather-making process is characterized by a combination of organic and inorganic pollutants, with values usually above the regulation limits, and different concentrations and chemicals according to the tanning processes involved. These combinations often result in a difficult efficiency of abatement by traditional treatments, which also imply high costs, a lot of energy, specific technologies, and sometimes failure. Adsorption and ion exchange, as well-consolidated water treatments, can remove a variety of pollutants, including organic and inorganic species, at a relatively low cost, especially when based on natural, easily available, or recycled materials. It is well known that zeolites are very effective adsorbents as well as natural cation exchangers able to remove inorganic and organic hazardous compounds from wastewater. Based on the previously described investigations, several authors affirmed that natural, synthetic, and modified zeolites have great removal capabilities for the various species typically found in tannery wastewater due to their high-order degree of crystalline structure, pore sizes, and cation exchange capacity. Natural zeolites are less efficient but cost-effective; modified and functionalized zeolites are valuable alternatives to enhancing removal efficiency because they have tuneable chemical and physical properties. **Despite the several studies presented in this review, further and deeper knowledge of removal mechanisms, multiple contaminant systems and pilot-scale investigations are needed. In particular, synthetic solutions, as sources of contamination used on a laboratory scale, do not reflect the characteristics of real tannery wastewater and its multivariant composition. Moreover, it could be interesting to evaluate the possible recovery of zeolites directly from the tanning spent liquor, since these materials are often used also as tanning agents. The regeneration and reuse of exhausted zeolites from the tanning process would respect the principles of the circular economy on recycling and waste discharge prevention. From the so-called "zero kilometres" perspective, a more conscious choice would be represented by the use of natural zeolites instead of synthetic ones due to their readily availability in the environment without further waste production and resource depletion including chemical materials, water and energy. Finally, it is certainly very important to consider the emerging classes of recalcitrant and persistent contaminants, as well as the so-called new contaminants. CECs are pollutants with hazardous ecological and human health impacts, typically not regulated under current environmental laws regarding industrial chemicals such as dioxins, Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA), which are commonly found in various water sources.**

Leather manufacturing is a very complex procedure which includes a large number of processes and the use of a large amount of different chemicals. These points lead to a large amount of wastewater production which includes a very complex composition. In real world applications, zeolites are poorly used yet, but they may represent an efficient contribution as part of the entire wastewater remediation process.

Authors' contributions

Bianca Maria Bresolin: first conceptualisation, organisation, writing, reviewing, editing of the paper.

Marco Piumetti, Nadia Grifasi: editing of the paper, critical review, revision.

Barbara Liguori, Nicola Gargiulo, Assunta Campanile, Marco Piumetti, Nadia Grifasi, Olimpia Tammaro, Serena Esposito, Claudia Florio: editing of the paper.

Domenico Caputo: validation, final approval of the version to be published.

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670 manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission
671 can be considered."

672 **Competing Interests**

673 The authors have non-financial interests to disclose.

674 **Data Availability**

675 Data will be available from corresponding authors based on reasonable request.

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