Application of zeolites for efficient tannery wastewater remediation

Original
Application of zeolites for efficient tannery wastewater remediation / Bresolin, Bianca Maria; Liguori, Barbara; Gargiulo, Nicola; Campanile, Assunta; Piumetti, Marco; Grifasi, Nadia; Tammaro, Olimpia; Esposito, Serena; Caputo, Domenico; Florio, Claudia. - In: ENVIRONMENTAL SCIENCE AND POLLUTION RESEARCH INTERNATIONAL. - ISSN 1614-7499. - 32:3(2025), pp. 1073-1094. [10.1007/s11356-024-35821-2]

Availability:
This version is available at: 11583/2999281 since: 2025-04-24T07:20:18Z

Publisher:
Springer

Published
DOI:10.1007/s11356-024-35821-2

Environmental Science and Pollution Research

Application of zeolites for efficient tannery wastewater remediation

--Manuscript Draft--

Manuscript Number:	ESPR-D-24-12938R1
Full Title:	Application of zeolites for efficient tannery wastewater remediation
Article Type:	Review Article
Corresponding Author:	Bianca Maria Bresolin Brescia University ITALY
Corresponding Author Secondary Information:	
Corresponding Author's Institution:	Brescia University
Corresponding Author's Secondary Institution:	
First Author:	Bianca Maria Bresolin
First Author Secondary Information:	
Order of Authors:	Bianca Maria Bresolin
	Barbara Liguori
	Nicola Gargiulo
	Assunta Campanile
	Marco Piumetti
	Nadia Grifasi
	Olimpia Tammaro
	Serena Esposito
	Domenico Caputo
	Claudia Florio
Order of Authors Secondary Information:	
Funding Information:	
Abstract:	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.

Application of zeolites for efficient tannery wastewater remediation.

Bianca Maria Bresolin[a,d]**, *Barbara Liguori*[b], *Nicola Gargiulo*[b], *Assunta Campanile*[b], *Marco Piumetti*[c], *Nadia Grifasi*[c], *Olimpia Tammaro*[c], *Serena Esposito*[c], *Domenico Caputo*[b], *Claudia Florio*[d]

[a] Dipartimento di Ingegneria Meccanica e Industriale, Università degli studi di Brescia, Brescia, Italy;

[b] Dipartimento di Ingegneria Chimica, dei materiali e della produzione industriale, Università degli Studi di Napoli Federico II, 80125 Napoli, Italy;

[c] Dipartimento di Scienza Applicata e Tecnologia (DISAT), Politecnico di Torino, 10129 Torino, Italy

[d] Stazione Sperimentale per l'industria delle pelli e delle materie concianti S.r.l., 80143 Napoli, Italy.

*bianca.bresolin@unibs.it

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.

1. Introduction

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

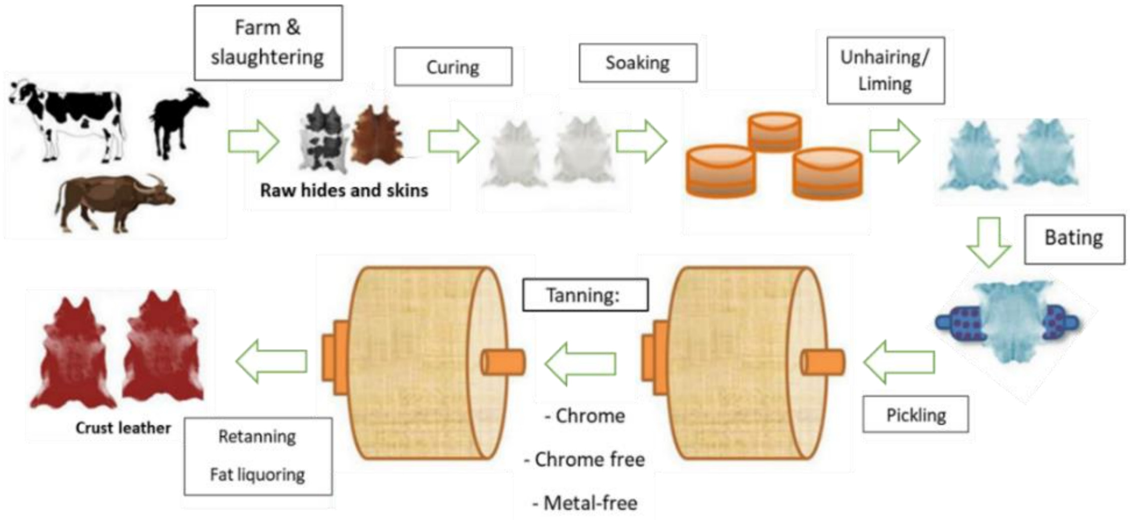

Fig.1: The tanning process

Most of the tanning phases are performed in wet batches leading to a large consumption of water and thus a large production of wastewater where the impurities include suspended, dissolved, or colloidal inorganic and organic substances coming directly from the leather and as residues of chemical products. The tannery wastewater represents a refractory pollution for the environment. It contains not only chromium, metal ions, sulphides, and chlorides, but also oils, proteins, dyes, surfactants, recalcitrant, and persistent organic pollutants. The removal of these contaminants requires cost-effective technologies and a variety of techniques. Nowadays, adsorption is worldwide recognized to be a simple and effective technique for water treatment. The efficiency of this wastewater treatment technology largely depends on the type of adsorbents in terms of chemical and physical properties. Natural, synthetic and modified zeolites are endowed with porous structures showing valuable physicochemical properties such as cation exchange, adsorption and catalytic ones. Cation exchange is an intrinsic property of zeolites that indirectly leads to applications such as catalytic processes or adsorption. Indeed, ion exchange procedures can alter the surface pH of zeolites, control their pore size and create specific surface active sites for targeted adsorption. The use of zeolites in wastewater treatments as adsorbents and ion exchangers is gaining a lot of interest mainly due to their properties and significant worldwide occurrence.

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

2. The tanning process

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

The second macro-phase is the *tanning*. The purpose of the tanning phase is basically to give the leather greater resistance to wear, maximum impermeability to water, and the right permeability to air and water vapour through porosity. Traditionally, the process is performed with trivalent chromium, the tanned leather gains a light blue colour, and this is why it is properly called wet-blue. Vegetable tanning is recognized as one of the oldest types of tanning in the world, most likely it is carried out with nature-based tannins, extractable from trees. There are other types of tanning, such as the chrome-free based agents, which are performed with other minerals including iron, zirconium, aluminium, or more recently titanium, and other metal-free approaches such as oil tanning, and aldehyde tanning. However, the alternative methods are either not as effective as chromium-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 last macro-phase is the *post-tanning*. At the end of the last phase, the amount of water present inside the leather must be reduced by applying strong pressure. Retanning is the process that finalizes the stabilization of the leather and gives character and confers specific properties to the leather, such as mechanical resistance, uniform thickness of the leather, fullness, softness, elasticity, pliability, lightness etc. The dying phase can be accomplished during re-tanning to make the dye penetrate not only superficially but also along its entire thickness. The last wet process is fattening, which aims to introduce soluble oils and fats into the fibres which act as lubricants and enhance the physical-mechanical properties of the leather including softness, elasticity, resistance, and hydrophobicity. From now on, the processes are usually defined as dry phases. The leather is then pressed, stretched, widened, and finally dried to lose useless substances previously absorbed. The last *finishing* treatment aims to enhance the quality of the leather. It consists of processes that can be mechanical or chemical. In general, finishing represents a fundamental macro-objective of the production process, for the final preparation of the material for marketing, which underlies the manufacturer's ability to enhance the valuable aspects of the raw material, expertly camouflage production errors and defects, improve the technical performance and resistance to environmental and anthropic factors, promote an overall improvement in product and sensorial characteristics, confer added value, etc. Physical finishing treatments include rotary perching and milling with control temperature and humidity values to enhance softness; sanding for the creation of leather with a writing effect (e.g., nubuck), repairing defects on the grain, and eliminating any subcutaneous residues.

From a chemical point of view, in the finishing phase, various substances can be applied to the surface of the leather which, after drying, produces a consistent, elastic, and transparent film. The finishing is generally made with overlapping layers of these materials. Traditional finishings are achieved through the use of substances, mainly of a polymeric nature, with particular reference to the use of some synthetic polymers; specifically, except finishings carried out exclusively through the use of waxes or natural protein-based polymers (casein, albumin), synthetic polymers are typically widely used (polyurethanes, polyamides, polysiloxanes, acrylic resins and copolymers, butadiene resins and copolymers, polyvinyl resins, epoxy resins), as well as some modified natural polymers, with particular reference to cellulose derivatives (nitrocellulose, ethyl cellulose, cellulose acetate, cellulose acetobutyrate).

The leather finishing tamper with a huge variety of characteristics of the leather from the desired colour to the desired fashion effect, the physical and mechanical performance, or the touch. There are many finishing machines: spray finishing, veil finishing, pad finishing or roller finishing also known as the coating.

The very final operations are the trimming to have regular edges of the final leather and the measurement for both thickness in millimetres and surface in square feet.

It is now well established that an adequate final quality leather product comes from a complex process that requires a skilled workforce and specialized tools and processes. Unfortunately, the leather industry is also known for its negative environmental impacts: leather creates a range of pollutants that can be harmful to the environment, becoming a growing concern for many countries.

3. Characteristics of tannery wastewater

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

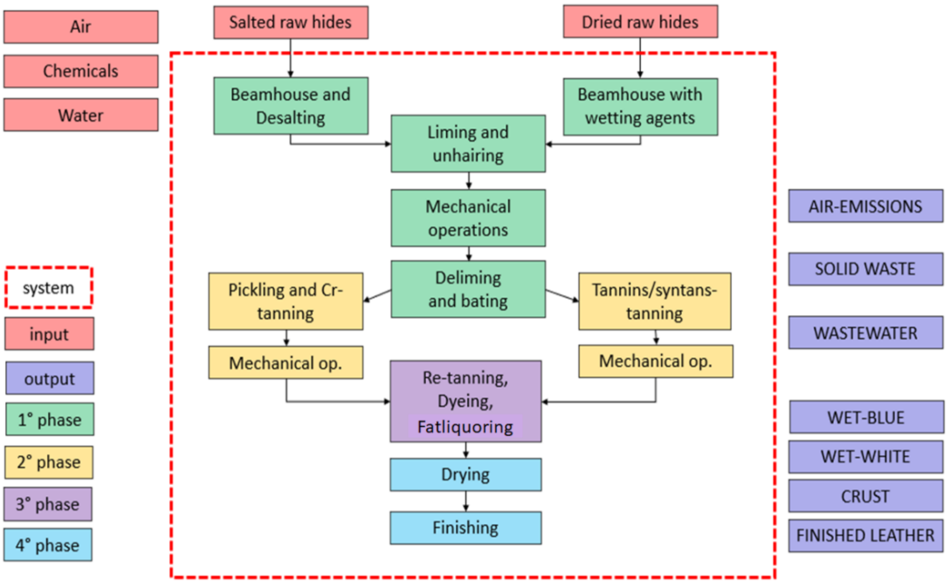

Fig. 2: Tannery input-output system

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**
BOD_5	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**
Cr^{3+}	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

The first phase of tannery treatment includes: degreasing, liming, unhairing, deliming, 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 Mahbubul 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 dying 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).

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

4. Tannery wastewater treatment plant (TWWTP)

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

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

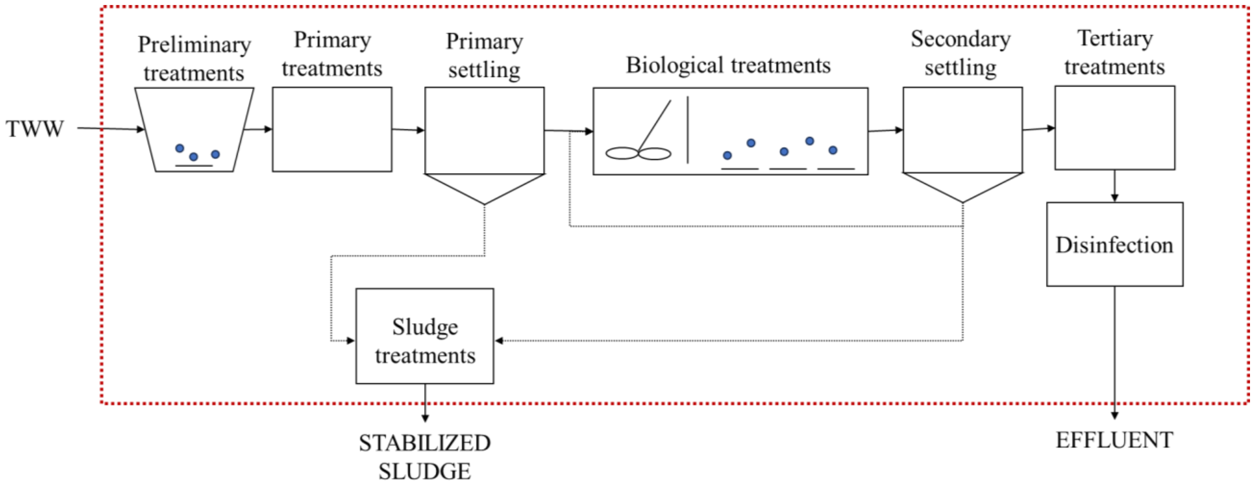

Fig. 3: Scheme of a treatment plant for TWW

Preliminary treatments include (a) coarse screens, sand traps and oil separators for TSS (debris, solid waste, oils, sand), they can be done directly in the tannery, reducing the polluting load and solving the problems of sedimentation of wastewater in the collection pipes at the central plant; (b) equalisation aims to buffer and homogenise the flow; (c) elimination of sulphides gasses with pure oxygen or scrubbers(Lofrano et al. 2008). Primary treatments, also known as physical-chemical treatment approaches include: (a) coagulation and flocculation, to destabilize colloids, form flocs, and aggregate them, followed by a settling tank; (b) adsorption usually applied to decrease metal content, this treatment can be also performed in the tertiary stage of wastewater plant(Ayoub et al. 2011). Biological treatments are also called secondary treatments and include (a) a first anoxic tank for denitrification; (b) an aerated, aerobic tank for nitrification and organic oxidation; and (c) a sedimentation tank to produce biological sludge. Tertiary treatments aim to adjust the purification of the effluent by reducing the loads of pollutants including nutrients or poorly biodegradable substances such as synthetic and natural tannins. Some examples are flotation, membrane, and advanced oxidation process(Dixit et al. 2015). Finally, disinfection, such as UV or ozonisation, reduces the microbial load of the treated wastewater before returning it to the water cycle, decreasing the hazardous concentration values from a health and environmental point of view.

5. Zeolites

5.1 Physical and chemical properties of zeolites

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

$$Me_{x/z}\left[Al_xSi_{(1-x)}O_2\right]\cdot wH_2O$$

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 zeolite, the Si/Al ratio, the cation composition, the temperature, and the partial pressure of environmental water vapour(Breck and Wiley 1975).

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

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

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

Tab. 2: Examples of synthetic zeolites

Zeolites	Typical chemical formula

Zeolite A	$2Na_2O·2Al_2O_3·4SiO_2·9H_2O$
Zeolite L	$2K_2O·Na_2O·3Al_2O_3·18SiO_2·14H_2O$
Zeolite X	$11Na_2O·11Al_2O_3·26SiO_2·60H_2O$
Zeolite Y	$7Na_2O·7Al_2O_3·34SiO_2·60H_2O$
Zeolite P	$Na_2O·Al_2O_3·2SiO_2·4H_2O$
Zeolite ZSM-5	$7Na_2O·7Al_2O_3·82SiO_2·16H_2O$

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):

$$Mg^{++} < Ca^{++} < Na^{+} < K^{+}$$

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

As already mentioned, zeolites are well known for their great selectivity in cation exchange processes while showing remarkable resistance to high temperatures and ionizing radiations and excellent environmental compatibility. *Cation exchange processes* for water purification are usually carried out in two different ways:

- *Fixed Bed Process*, where contaminated water is purified through elution in fixed beds containing granular zeolitic material. The efficiency of these systems depends on the size and density of the packed grains. Small grains and high densities produce significant pressure drops in the column. Exhausted beds must be regenerated: generally, this process is carried out by elution with very concentrated sodium solutions. In an industrial plant, to optimize the process, several columns are used in parallel, which alternate operating and regeneration phases.
- *Direct Addition Processes*, where powdered zeolites are directly added to wastewater. The suspension is mixed in batch reactors and kept in constant agitation for a sufficient time to complete the exchange. Subsequently, the resulting zeolitic sludge is disposed of in landfills or reused. Due to the reversibility of the cation exchange process, zeolitic sludge needs to be safely inserted by ceramization or in a cement matrix. The main applications of zeolites as cation exchangers in the field of water purification concern the removal of NH^{4+} from urban and industrial wastewater, heavy metals from industrial wastewater and radionuclides from nuclear wastewater (Zhao et al. 2004; Wang and Peng 2010; De Magalhães et al. 2022). Natural zeolites are endowed with porous structures showing valuable physicochemical properties such as cation exchange. . Indeed, ion exchange procedures can represent a direct wastewater remediation method but they can also be indirectly used to alter the surface pH of zeolites, control their pore size and create specific surface active sites for targeted adsorption. These approaches and other valuable methods to enhance or adjust the remediation capacity of zeolites are reviewed in the next chapters.

5.2.2 Modification of zeolite surfaces

The modification or additional functionalization of natural and synthetic zeolites involves the modification of their physical and chemical properties, representing a step forward in the common cation exchange process to remove pollutants from liquid phases. The modification approaches aimed at an enhancement of water treatment capabilities can be generally divided into three categories: physical methods, chemical methods and a combination of both. *Physical modification* includes two main approaches: thermal modification and ultrasonic treatment. Physical modifications can improve the cation exchange and adsorption abilities of zeolites, for example when the pores of natural zeolites are blocked by impurities(Kragović et al. 2012). *Thermal modification* aims to reduce the surface resistance of zeolites, improving their cation exchange and adsorption capacities. Muffle furnace heating is a traditional and simple way to treat samples, while microwave heating can save time and perform good penetration with high energy efficiency(Shi et al. 2017). *Ultrasonic modification* is a useful method to eliminate impurities inside the structural pores by high frequencies, inducing higher cation exchange and adsorption efficiencies(Zieliński et al. 2016). *Chemical modification* includes many different methods such as co-precipitation, solvothermal and sol-gel treatments, etc. Cation exchange itself can be considered a performable procedure for the chemical modification of zeolites, e.g., when exchange with H^+ cations is used for increasing surface acidity(An et al. 2013; Matijasevic et al. 2016). Zeolite functionalization can be used to modify the chemical properties of the zeolite structure to make it better akin to the target adsorption system with special requirements. The *functionalization* of zeolites can be achieved either during the zeolite synthesis process or by a post-synthesis modification. The latter method doubtless allows for tighter control and easier manipulation of materials, including the possibility of using natural zeolites(Lee et al. 2021). Moreover, it is possible to adjust the hydrophilic character of traditional zeolites without changing their inherent framework, which means a negligible effect on the crystalline structure. An alternative approach to increase the efficiency of zeolites as sorbent material for water treatment is represented by the *dealumination process*. This method enables zeolites with a very high Si/Al ratio to be obtained, which is reflected in a material with higher hydrophobicity and increased thermal stability of the crystalline and porous structure (ultra-stable zeolite). Navalon et al. used dealuminated large pores of Y zeolite for the selective removal of fatty acid and hydrocarbon from water(Navalon et al. 2009). The extent of a dealumination process drastically influences the ion exchange capacity of the selected zeolite: such procedural aspect is crucial considering that the degree of ion exchange can influence the surface area and pore volume, causing steric hindrance effects and potentially reducing other capabilities such as the adsorption capacity(Serra et al. 2011). Another well-known modification strategy is the *immobilization of surfactant species* on the external surface of zeolite particles as a way of modifying the surface charge and hydrophilicity(Hailu et al. 2017). A cationic surfactant-based modification can enhance the anion removal rate by electrostatic forces or the hydrophobic interaction according to the critical micelle concentration. Another class of molecules frequently used in post-synthesis modification processes is formed by organo-silanes, where *silicon atoms* are bonded to the functional group and *alkoxide-OR groups*(Esposito 2023). By the addition of water, Si-OR can be hydrolyzed to form Si-OH which is prone to form covalent bonds with the hydroxyl groups decorating the surface of zeolites. This approach generates stable Si-O bonds and a solid anchoring of the selected functionality. Alkyl-silanes are generally proposed as hydrophobizing agents(Zapata et al. 2013). On the other hand, *amino-silane* can be introduced for the removal of anionic species, that are not compatible with the cation exchange feature of zeolite(Meftah and Zerafat 2016). Although this method achieves a high degree of functionalization and good stability of the anchored molecule, it requires a multi-step procedure that also includes activation of the zeolite surface. Conversely, the impregnation method is characterized by the simplicity of the experimental setup and involves loading the zeolite with a solution containing the molecule with the specific functionality. The trade-off between the lower level of functionalization achieved and the simplicity of method implementation allows the impregnation to be more versatile and suitable for scale-up of the final material, winking at industrial applications. As an effective example of amino-silane-based modification, a zeolite *functionalized with APTS* (3-amino propyltriethoxysilane) was reported by Meftah and Zerafat for the removal of nitrate from water, with a removal percentage of about 80 wt.%(Meftah and Zerafat 2016). Moreover, Wang et al. demonstrated the effectiveness of an amino functionalization of natural clinoptilolite for the removal of chromate and naphthalene from water. In particular, their results showed a remarkable removal rate, of about 90% and 95%, for both the anionic species and the hydrophobic molecule, respectively(Wang et al. 2018). In a recent work by Omorogie and Helmerich, zeolite amino functionalization was exploited for the removal of microplastic from water(Omorogie and Helmreich 2023). Moreover, a *sulfur-functionalized natural zeolite* was proposed by Ugrina et al. for the enhanced removal of mercury (II) ions from an aqueous solution, achieving a removal efficiency of about 90% (Ugrina et al. 2021).

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

A novel approach to implementing the use of zeolites in water treatment has been proposed by Pansini et al.(Pansini et al. 2018; Marocco et al. 2020; Pirozzi et al. 2023), in their research zeolites were employed as precursors of novel magnetic metal-ceramic composites(Pansini et al. 2017; Manzoli et al. 2021; Tammaro et al. 2023a). Natural and synthetic zeolites were first subjected to a cation exchange procedure and after that treated at high temperatures under a reducing atmosphere. This results in the reduction of the cation in its metallic form and its entrapment in the structure of the collapsed zeolite, which resembles a glassy matrix. Following this procedure, the obtained material showed a magnetic behaviour which turns out to be a crucial aspect when investigating water treatment. The simple separation by an external magnet allowed an easy recovery of the sorbent material. These magnetic metal-ceramic composites obtained starting from clinoptilolite and zeolite A were successfully tested in the removal of sulfanilamide (a sulfonamide antibiotic) from water. It is worth mentioning their multicycle stability and regenerability(Sannino et al. 2022). Eventually, it is worth mentioning the high number of zeolite-based adsorption studies based on *polymer modification*. The use of composites based on zeolites and polymers gained considerable attention due to the effective improvement of the adsorption properties and the ease of reusability and recyclability. The structure of the composites includes different forms such as beads, hydrogels, thin films, nanoparticles, and nanofibers. Natural polymer-modified zeolites include cellulose, chitosan, and alginate. Synthetic polymer modification includes the use of polyvinyl chloride, polycaprolactone, polyacrylamide, polyvinyl alcohol, polypropylene (PP), polypyrrole, polyvinylpyrrolidone, polyamide, polyacrylonitrile, and polysulfone(Roshanfekr Rad and Anbia 2021).

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

As already mentioned, water is among the most important inputs in the tanning process, and leads to the production of large wastewater volumes containing various pollutants coming directly from the raw hides and the chemical products used during the process. The contaminants include heavy metals (chromium, iron, copper, lead), chloride, surfactants, salt ions, fats, oils, and other organic pollutants that can be persistent (POPs) or recalcitrant (ROPs) with toxic effects on human health and ecosystems(Shegani 2014; Hutton and Shafahi 2019). Around the World, each country adopts its regulatory limits that can vary drastically compared to one another: as an example, different limits exist for the sewage 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 a value ranging from 1 to 20 mg L^{-1} in Australia(Bosnic, M., Buljan, J., Daniels 2000). Depending on the nature of the hazardous species involved and their concentration, tannery wastewater can have a high impact on the environment as in water, soil, and air matrix. Based on these assumptions, it is vital to remove the pollutants from TWW and nowadays different technologies are employed for this aim. The removal of contaminants from TWW consists of a complex series of stages, classified as primary, secondary, and tertiary treatments and disinfection(Srinivasan et al. 2012). The shortcomings of most of these methods are high operational and maintenance costs; moreover, they are often environmentally incompatible due to the high production of toxic residues. Worldwide researchers are constantly working to determine a suitable and efficient method for economic and environmentally friendly treatments due to the complexity of the TWW matrix. The most suitable method for wastewater treatment depends on the nature of the substance to remove but, most of the time, the easiest and most cost-effective method is the *adsorption process***,** which envisages the use of an adsorbent material with precise physicochemical properties, i.e., high specific surface area, active adsorption sites, etc. Adsorption and ion-exchange processes are considered a great alternative in water and wastewater treatment because of convenience, ease of operation and simplicity of design. Moreover, they assure a high efficiency in the removal of different kinds of organic, inorganic and mixtures of contaminants as compared to several other treatment processes. In traditional wastewater treatment plants, adsorption is used as a phase transfer process to eliminate substances from both wastewater and gases. The heart of the adsorption process is usually the porous solid medium used as an adsorbent. Adsorption plays an important role in the treatment of wastewater because of its simplicity and cost-effectiveness(Nur-E-Alam et al. 2020). Zeolites have been considered efficient adsorbents mainly for their unique physical and chemical properties including crystallinity, thermal stability, well-defined cage structure of molecular size and ion exchange capabilities; and for their low cost and significant adsorption results with different pollutants(Wen et al. 2018). Tanneries, like all the other factories, face urgent ecological problems to be solved and the use of zeolites shows excellent advantages from this point of view. The next paragraphs review the current literature about the use of zeolites for the removal of specific categories of contaminants from tannery wastewater.

6.1. Heavy metals and inorganic ions

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

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

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 (K2Cr2O7)	100 ug/g (Cr (VI))			Cr (VI) adsorbed ug/g	80.22	(Rangasamy et al. 2014)
Natural zeolite									Chromium Sulphate (Cr2 (SO4)3)	100 ug/g (Cr (VI))			Cr (VI) adsorbed ug/g	92.18	(Rangasamy et al. 2014)
Natural zeolite									Acqueous solution of CrO3		72	9	fractional removal %	0.03	(Bolortamir and Egashira 2008)
Modified zeolite	43								Acqueous solution of CrO3		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 (K2Cr2O7)	1 mg/L (K2Cr2O7)	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 (K2Cr2O7)	1 mg/L (K2Cr2O7)	3	2	Cr (IV) removal %	32.22	(Álvarez et al. 2021)
Modified zeolite 13X (FAU)	578			0.074		1.5	3.52 (meqCr3+/g)	0.4 g	Cr(VI)	500 mg/L (Cr (VI))	24		Cr (IV) retention capacity (molCr2O7-2 /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 (molCr2O7-2 /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 (meqCr3+/g)	0.4 g	Cr(VI)	500 mg/L (Cr (VI))	24		Cr IV retention capacity (molCr2O7-2 /Kg)	15.5	(Covarrubias et al. 2008)

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

In recent studies, Covarrubias and his group(Covarrubias et al. 2005, 2007) studied the removal of Cr (III) in zeolite-packed columns, analysing the effects of pH and interfering ions, discovering that the particle diameter controls the Cr (III) exchange in the zeolite and that the reduction of the organic matter in terms of COD interfered on the removal. In these studies, the effect of the proposed technology on both a synthetic Cr(III) solution and diluted tannery wastewater was evaluated. Sallam et al.(Sallam et al. 2017) prepared a polymer-clinoptilolite composite N,N-methylene-bis-acrylamide as a matrix for the uptake of Cr(VI) from an aqueous solution. Additionally, they studied the effects of soluble ions in tannery wastewater including Na^+, Cl^- and SO_4^{2-}. The results showed that the adsorption of Cr(VI) onto the polymerized samples exhibited higher values than the pristine samples and the experimental kinetics was coherent with a pseudo-second-order model. Ayele et al.(Ayele et al. 2018) synthesized zeolite A from two sources of raw kaolin from Ethiopia and evaluated its application in tannery wastewater treatment, precisely for the removal of Cr(III) with an 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}, 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 the use of zeolites synthesized through cheap raw materials. In some cases, there is the possibility of an oxidation process of Cr (III) to Cr (VI), which is extremely more toxic and more mutagenic than Cr (III). Thus, its removal is essential since it can be very dangerous even at a 10 ppm concentration(Standeven and Wetterhahn 1989; Shekhawat et al. 2015). Aljerf(Aljerf 2018) evaluated the importance of the uptake properties of a modified zeolite for the removal of total chromium and basic dyes such as bromocresol purple. The modified zeolite was prepared by mixing solid waste and clinoptilolite. He studied the optimal parameters for the total chromium uptake and the experimental data were best fitted by the Freundlich isotherm and the pseudo-second-order kinetic model. Thermodynamic studies revealed that the uptake was spontaneous and endothermic, thus suggesting the prevalence of uni-polivalent ion exchange mechanisms. Setiadji et al. (Setiadj et al. 2019) treated chromium metal ions and organic compounds in the tannery wastewater activating a zeolite with a barium salt and pre-treating the inlet with a precipitation method. They revealed the optimum conditions for the combined methods, resulting in a total removal of Cr ions and organic compounds up to 99%.

Besides chromium ions, copper, iron, lead, cadmium**,** etc. are widely present in TWW, as material components of chemicals used during the overall process, and zeolites can also be employed for their removal. For example, in a study conducted by Finish et al.(Finish et al. 2023), the simultaneous removal of six toxic heavy metal cations (namely, Cd^{2+}, Cr^{3+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}) was investigated employing a natural zeolite (clinoptilolite) and two synthetic ones, specifically 13X and 4A. The authors found that the uptake capacity of the natural zeolite was 0.12 mmol of total ions per g of zeolite, whereas 13X and 4A obtained a maximum of 2.9 and 1.65 mmol of total ions/g zeolite, respectively. They also ascribed the low uptake capacity values of clinoptilolite to its low specific surface area (19.5 m^2 g^{-1}) and relatively high Si/Al ratio (equal to 3.5). Moreover, they observed different selectivities depending on the nature of the heavy metal. For example, the two *synthetic zeolites* showed the strongest selectivity towards Pb^{2+} (1.5 mmol g^{-1} for 13X and 0.8 mmol g^{-1} for 4A) and a considerably weaker one towards Ni^{2+} (0.2 mmol g^{-1} for 13X and 0.1 mmol g^{-1} for 4A), Zn^{2+} and Cd^{2+} (0.1 mmol g^{-1} for both zeolites). Concerning Cu^{2+} and Cr^{3+}, 4A zeolite showed similar selectivity towards both ions, slightly favouring Cu^{2+} (0.4 mmol g^{-1}), whereas 13X showed a much higher selectivity for Cr^{3+} (0.85 mmol g^{-1})(Finish et al. 2023).

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

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

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)	Cr2+, 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	

				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	

6.2. Synthetic organic dyes

Zeolites can also be suitable for the removal of *synthetic organic dyes*(Senthil Kumar et al. 2019). For example, clinoptilolite has been widely investigated for the removal of methylene blue (Dosa et al. 2018, 2022) and other dyes that are more complicated to treat, i.e., AO7, whose abatement needs a specific oxidation process(Dosa et al. 2021). In the latter case, the presence of iron is crucial to carry out the oxidation of AO7 through a photo-Fenton process. From a circular economy point of view, it could be interesting to exploit the capability of zeolites to remove heavy metals, i.e., iron (Kim et al. 2001) from wastewater and, at the same time, re-use such exchanged zeolite for the removal of other species, i.e., ammonia and phosphate(Kim et al. 2013; Eljamal et al. 2022), synthetic organic dyes like AO7(Dosa et al. 2021), Congo Red dye (Bencheqroun et al. 2022) and other pollutants (Zhang et al. 2022). As an example, Dosa et al.(Dosa et al. 2021) studied iron-exchanged zeolites for the removal of AO7. As reported in **Fig. 4**, the results showed that degradation occurred via a Fenton-like mechanism, thanks to the presence of H_2O_2 and ascorbic acid (AA) which contribute to the formation of •OH radicals.

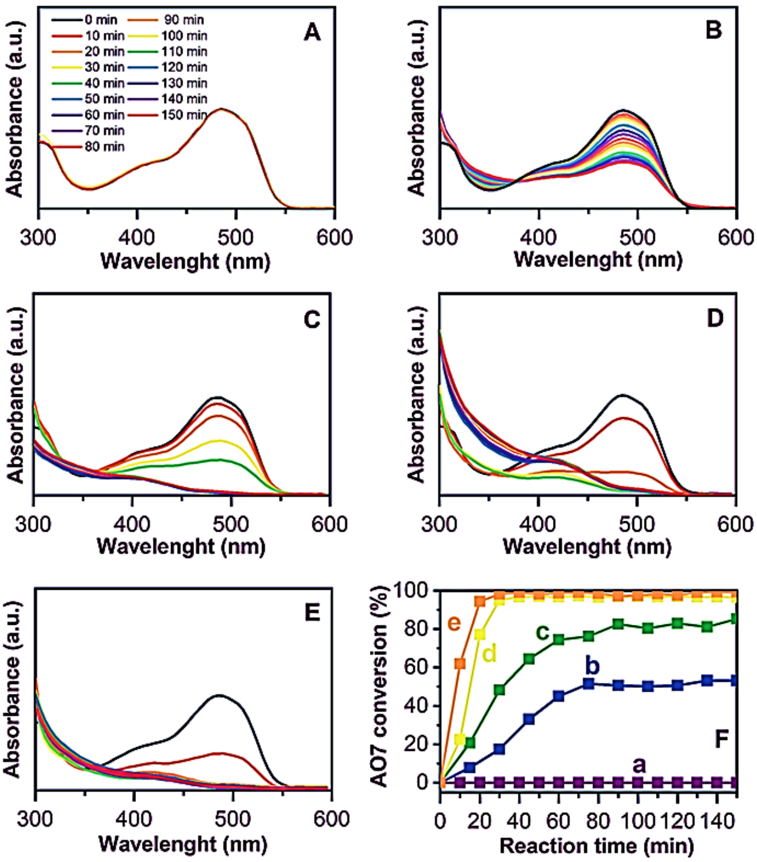

Fig.4: Absorbance peaks over time (from 0 to 150 min) of (a) Fe/Clin, (b) Fe/Clin:H_2O_2:AA (1:1:1), (c) Fe/Clin: H_2O_2:AA (1:10:10), (d) Fe/Clin: H_2O_2:AA (1:20:20) and (e) Fe/Clin: H_2O_2:AA (1:30:30). (f) AO7 conversion (%) over time for a-Fe/Clin, b-Fe/Clin: H_2O_2:AA (1:1:1), c-Fe/Clin: H_2O_2:AA (1:10:10), d-Fe/Clin: H_2O_2:AA (1:20:20) and e-Fe/Clin: H_2O_2:AA (1:30:30). Image adapted from Dosa et al.(Dosa et al. 2021).

6.3. Phenols

It is noteworthy to mention that tannery effluents are challenging to treat due to the presence of *phenols* in tanning amalgamation, which forms polyphenolic structures(Bhardwaj et al. 2023) and their removal has not been extensively studied. Different technologies can be adopted to reduce the concentration of phenols in wastewater, but their application strongly depends on the concentration itself in the stream and the eventual co-presence of other contaminants. However, most of the time, it is possible to use an adsorption process that shows high removal efficiency towards organic and inorganic pollutants. Several studies report phenol adsorption on activated carbon; however, there are some limitations concerning the regeneration and the high cost. Thus, zeolites appear as good alternatives. To be precise, the Si/Al ratio, rather than the pore size of the zeolite, has the predominant effect on the adsorption capacity of phenol. Some studies on Na–Y synthetic zeolites reported that the interaction between zeolite and phenol is based on the hydrogen bonding of phenol to the oxygen atoms of zeolite and also on the interaction of the aromatic ring of phenol with either Na^+ cations or oxygen atoms of the zeolite super cages (**Fig. 5**)(Okolo et al. 2000; Khalil et al. 2020). Damjanović et al.(Damjanović et al. 2010) investigated the use of two synthetic zeolites, mainly BEA (β) and MFI (ZSM-5) for the adsorption of phenol from aqueous solutions. They observed that the former exhibited favourable performance compared to the latter since it showed more hydrophobicity, thus decreasing the competition between water and pollutant molecules. In another work, Yousef et al.(Yousef et al. 2011) reported a maximum adsorption 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 be used as a low-cost alternative adsorbent for the removal of phenols from water.

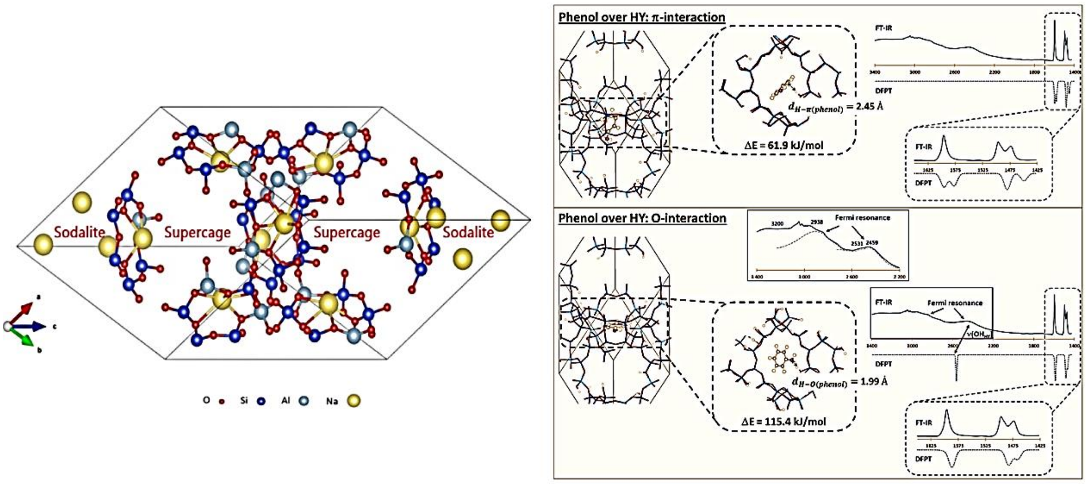

Fig.5: The different adsorption modes of phenol over HY zeolite with their respective interaction energies and predicted vibrational frequencies via DFPT. Image adapted from Khalil et al. (Khalil et al. 2020)

6.4. Surfactants

Other pollutants that are also detected in tannery wastewater are *surfactants*, which are considered emerging contaminants. As well known, they are classified as amphiphilic molecules, which exhibit both hydrophilic and hydrophobic behaviours. Their further chemical peculiarities can be different, i.e., there are anionic, cationic, non-ionic, and amphoteric surfactants: in any case, they provoke adverse effects on humans, aquatic life, and vegetation(Siyal et al. 2020). For the removal of surfactants from wastewater, zeolites represent a good solution. As an example, Shahbazi et al. (Shahbazi et al. 2014) reported how Y and Beta zeolites having SiO_2/Al_2O_3 ratio > 200 showed good adsorption/oxidation of nonionic surfactant TX-100 when compared to a natural zeolite such as clinoptilolite. Moreover, it was demonstrated that the incorporation of Fe into Beta zeolite enhanced the removal of TX-100 as compared to unmodified zeolites thanks to the occurrence of a Fenton-like oxidation process. The authors also demonstrated that the pore size and hydrophobicity (thus high SiO_2/Al_2O_3) of zeolites played important roles in the adsorption/oxidation of surfactants. In another work,(Harutyunyan and Pirumyan 2015) a natural Armenian zeolite was investigated for the removal of cetyltrimethylammonium bromide (CTAB) and sodium dodecyl sulphate (SDS), exhibiting a higher uptake capacity for the former (284 mg g^{-1}) compared to the latter (113 mg g^{-1}). This was ascribed to the higher hydrophobicity of CTAB, which favoured its higher uptake onto the zeolite surface. Interestingly, zeolites containing surfactants can be considered functionalized zeolites and, in turn, reused as substrates for the removal of other compounds. A study conducted by Taffarel and Rubio (Taffarel and Rubio 2010) in 2010 demonstrated the possibility of using a CTAB-modified natural Chilean zeolite to enhance the removal capabilities towards the anionic surfactant sodium dodecyl benzene sulfonate (SDBS), reaching the maximum uptake capacity of 30.7 mg g^{-1}. Such a result is ascribed to the presence of CTAB changing the surface charge of the zeolite from negative to positive, making it suitable for the attraction of anionic surfactants. More recently, De Gennaro et al.(de Gennaro et al. 2020) modified the surface of two natural zeolites (namely, clinoptilolite and phillipsite) with cationic organic surfactants (specifically, CTAB and cetyltrimethylammonium chloride) that can simultaneously act as ion exchangers and organic molecule adsorbents and then reused the zeolite for the removal of As(V) from wastewater. Furthermore, Lin et al.(Lin et al. 2011) studied the efficiency of surfactant-modified zeolites for the removal of another class of pollutants present in tannery wastewater, i.e., tannins. They found that a higher loading amount of surfactant (in this case, cetylpyridinium bromide) exhibited higher tannic acid uptake efficiency. Recently, two Y zeolites were functionalized with different surfactants and subsequently tested for the removal of tannic acid, reaching the maximum uptake capacity of 67.7 mg g^{-1}, which corresponds to *ca.* 85% removal efficiency(Jevremović et al. 2020). Eventually, it appears evident the great potential of zeolites both from an economic and circular economy point of view, since it could be possible to reduce the waste and reuse the zeolite that has already been employed in an exchange process for the removal of other pollutants.

6.5. Other compounds

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

Besides the abatement of the previously mentioned pollutants, the removal of *ammoniacal nitrogen* has received sparse attention(Patil et al. 2021). Although, nitrogen pollution is a serious problem in many industrial wastewaters as a limitation of both biological and conventional physic-chemical methods. Moreover, nitrogenous organic is toxic to humans and upset the equilibrium of water ecology systems. In tannery wastewater ammonia nitrogen (NH_3-N) is mainly produced from deliming and bating wastewaters, and from washing and soaking processes because of the decomposition of proteins, originating from their hydrolysis in a strong alkali environment making the discharge of nitrogen difficult to avoid(Wang et al. 2012). Ding Shao-Ian et al.(Ding et al. 2013) studied also the effects of particle size, dosage, solution temperature, pH, and salt content of tannery wastewater on ammonia treatment by natural and synthetic zeolites. They concluded that synthetic zeolites were more suitable than natural zeolites, but both have an 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.

Funding

"This study was carried out within the MICS (Made in Italy – Circular and Sustainable) Extended Partnership and received funding from the European Union Next-GenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR) – MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.3 – D.D. 1551.11–10–2022, PE00000004). This manuscript reflects only the authors' views and opinions, neither the European Union nor the European Commission can be considered."

Competing Interests

The authors have non-financial interests to disclose.

Data Availability

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

REFERENCES

Ahmed E, Abdulla HM, Mohamed AH, El-Bassuony AD (2016) Remediation and recycling of chromium from tannery wastewater using combined chemical–biological treatment system. Process Safety and Environmental Protection 104:1–10. https://doi.org/10.1016/j.psep.2016.08.004

Alibardi L, Cossu R (2016) Pre-treatment of tannery sludge for sustainable landfilling. Waste Management 52:202–211. https://doi.org/10.1016/j.wasman.2016.04.008

Aljerf L (2018) High-efficiency extraction of bromocresol purple dye and heavy metals as chromium from industrial effluent by adsorption onto a modified surface of zeolite: Kinetics and equilibrium study. J Environ Manage 225:120–132. https://doi.org/10.1016/j.jenvman.2018.07.048

Álvarez AM, Guerrón DB, Calderón CM (2021) Natural zeolite as a chromium VI removal agent in tannery effluents. Heliyon 7:9 e07974. https://doi.org/10.1016/j.heliyon.2021.e07974

An W, Xiao H, Yu M, et al (2013) Adsorptive removal of trace oxytetracycline from water by acid-modified zeolite: Influencing factors. Water Science and Technology 68:2473–2478. https://doi.org/10.2166/wst.2013.505

Ayele L, Pérez E, Mayoral Á, et al (2018) Synthesis of zeolite A using raw kaolin from Ethiopia and its application in removal of Cr (III) from tannery wastewater. Journal of Chemical Technology & Biotechnology 93:146–154. https://doi:10.1002/jctb.5334

Ayoub GM, Hamzeh A, Semerjian L (2011) Post treatment of tannery wastewater using lime/bittern coagulation and activated carbon adsorption. Desalination 273:359–365. https://doi.org/10.1016/j.desal.2011.01.045

Badea E, Carşote C, Hadîmbu E, et al (2019) The effect of halloysite nanotubes dispersions on vegetable-tanned leather thermal stability. Herit Sci 7:. https://doi.org/10.1186/s40494-019-0310-x

Baerlocher Ch., McCusker L.B., Olson D.H. (2007) Atlas of Zeolite Framework Types, 6th revised edition. Amsterdam. ISBN: 978-0-444-53064-6

Barra-Hinojosa J, Marrufo-Saldaña L, Salazar-Leiva V, et al (2024) Optimization of Chromium Removal from Tannery Effluents with the Neonite Natural Zeolite. Ecological Engineering and Environmental Technology 25:41–53. https://doi.org/10.12912/27197050/175201

Basaldella EI, Vázquez PG, Iucolano F, Caputo D (2007) Chromium removal from water using LTA zeolites: Effect of pH. J Colloid Interface Sci 313:574–578. https://doi.org/https://doi.org/10.1016/j.jcis.2007.04.066

Bencheqroun Z, Sahin NE, Soares OSGP, et al (2022) Fe(III)-exchanged zeolites as efficient electrocatalysts for Fenton-like oxidation of dyes in aqueous phase. J Environ Chem Eng 10:107891. https://doi.org/https://doi.org/10.1016/j.jece.2022.107891

Bharagava RN, Saxena G, Mulla SI, Patel DK (2018) Characterization and Identification of Recalcitrant Organic Pollutants (ROPs) in Tannery Wastewater and Its Phytotoxicity Evaluation for Environmental Safety. Arch Environ Contam Toxicol 75:259–272. https://doi.org/10.1007/s00244-017-0490-x

Bhardwaj A, Kumar S, Singh D (2023) Tannery effluent treatment and its environmental impact: a review of current practices and emerging technologies. Water Quality Research Journal 58:128–152. https://doi.org/10.2166/wqrj.2023.002

Bolortamir T, Egashira R (2008) Removal of Hexavalent Chromium from Model Tannery Wastewater by Adsorption Using Mongolian Natural Zeolite. Journal of Chemical Engineering of Japan, 41, 1003-1009. https://doi.org/10.1252/jcej.08we069

Bosnic M, Buljan J, Daniels RP (2000) Pollutants in tannery effluents. United Nations Industrial Development Organization. UNIDO https://www.unido.org/

Breck DW, Wiley J (1975) Zeolite Molecular Sieves: Structure, Chemistry, and Use. John Wiley & Sons, New York..

Buzukashvili S, Sommerville R, Rowson NA, Waters KE (2024) An overview of zeolites synthesised from coal fly ash and their potential for extracting heavy metals from industrial wastewater. Canadian Metallurgical Quarterly 63:130–152. https://doi.org/10.1080/00084433.2022.2160576

Caputo D, Pepe F (2007) Experiments and data processing of ion exchange equilibria involving Italian natural zeolites: a review. Microporous and Mesoporous Materials 105:222–231. https://doi.org/10.1016/j.micromeso.2007.04.024

Cataldo E, Salvi L, Paoli F, et al (2021) Application of zeolites in agriculture and other potential uses: A review. Agronomy 11 (8), 1547; https://doi.org/10.3390/agronomy11081547

Chiampo F, Shanthakumar S, Ricky R, Ganapathy GP (2023) Tannery: Environmental impacts and sustainable technologies. Mater Today Proceeding. https://doi.org/10.1016/j.matpr.2023.02.025

Colella C (1999) Natural zeolites in environmentally friendly processes and applications. Porous materials in environmentally friendly processes : proceedings of the 1st international FEZA conference, Eger, Hungary, September 1-4, 1999. ISSN:01672991

Colella C, Gualtieri AF (2007) Cronstedt's zeolite. Microporous and Mesoporous Materials 105:213–221. https://doi.org/10.1016/j.micromeso.2007.04.056

Covarrubias C, Arriagada R, Yánez J, et al (2007) Natural mordenite derived zeolites: Synthesis, formation, and their evaluation in Cr(III) removal from tannery wastewater. Environ Eng Sci 24:1443–1455. https://doi.org/10.1089/ees.2006.0280

Covarrubias C, Arriagada R, Yáñez J, et al (2005) Removal of chromium(III) from tannery effluents, using a system of packed columns of zeolite and activated carbon. Journal of Chemical Technology and Biotechnology 80:899–908. https://doi.org/10.1002/jctb.1259

Covarrubias C, García R, Yánez J, Arriagada R (2008) Preparation of CPB-modified FAU zeolite for the removal of tannery wastewater contaminants. Journal of Porous Materials 15:491–498. https://doi.org/10.1007/s10934-007-9131-5

Cundy CS, Cox PA (2003) The hydrothermal synthesis of zeolites: History and development from the earliest days to the present time. Chem Rev 103:663–701. https://doi.org/10.1021/cr020060i

Damjanović L, Rakić V, Rac V, et al (2010) The investigation of phenol removal from aqueous solutions by zeolites as solid adsorbents. J Hazard Mater 184:477–484. https://doi /10.1016/j.jhazmat.2010.08.059

De Gennaro B, Aprea P, Liguori B, et al (2020) Zeolite-Rich Composite Materials for Environmental Remediation: Arsenic Removal from Water. Applied Sciences 10:19, 6939. https://doi.org/10.3390/app10196939

De Magalhães LF, Da Silva GR, Peres AEC (2022) Zeolite Application in Wastewater Treatment. Adsorption Science and Technology 2022 4544104. https://doi.org/10.1155/2022/4544104

Ding S-L, Li L, Zhang A-T (2013) Study on the ammonia nitrogen removal fromtannery wastewater by natural and synthetic zeolite. 32nd Congress of the International Union of Leather Technologists and Chemist Societies, IULTCS 2013.

Dixit S, Yadav A, Dwivedi PD, Das M (2015) Toxic hazards of leather industry and technologies to combat threat: A review. J Clean Prod 87:39–49. https://doi.org/10.1016/j.jclepro.2014.10.017

Dosa M, Grifasi N, Galletti C, et al (2022) Natural Zeolite Clinoptilolite Application in Wastewater Treatment: Methylene Blue, Zinc and Cadmium Abatement Tests and Kinetic Studies. Materials 15:22, 8191. https://doi.org/10.3390/ma15228191

Dosa M, Piumetti M, Bensaid S, et al (2018) Properties of the clinoptilolite: characterization and adsorption tests with methylene blue. J of Advanced Catalysis Science and Technology 5:1–10. https://doi.org/10.15379/2408-9834.2018.05.01.01

Dosa M, Piumetti M, Davarpanah E, et al (2021) Natural Zeolites as Sustainable Materials for Environmental Processes. In: Piumetti M, Bensaid S (eds) Nanostructured Catalysts for Environmental Applications. Springer International Publishing, Cham, pp 367–381. ISBN 978-3-030-58933-2

Dyer A (1988) An Introduction to Zeolite Molecular Sieves. OSTI ID: 5362126.

Eisenman G (1962) Cation Selective Glass Electrodes and their Mode of Operation. Biophys J 2:259–323. https://doi.org/10.1016/S0006-3495(62)86959-8

Eljamal O, Eljamal R, Maamoun I, et al (2022) Efficient treatment of ammonia-nitrogen contaminated waters by nano zero-valent iron/zeolite composite. Chemosphere 287:131990. https://doi.org/10.1016/j.chemosphere.2021.131990

Esposito S (2023) Sol-Gel Synthesis Strategies for Tailored Catalytic Materials. Springer International Publishing, Cham, Switzerland 256393032. https://doi.org/10.1007/978-3-031-20723-5

Finish N, Ramos P, Borojovich EJC, et al (2023) Zeolite performance in removal of multicomponent heavy metal contamination from wastewater. J Hazard Mater 457:131784. https://doi.org/10.1016/j.jhazmat.2023.131784

Galletti C, Dosa M, Russo N, Fino D (2021) Zn2+ and Cd2+ removal from wastewater using clinoptilolite as adsorbent. Environmental Science and Pollution Research 28:24355–24361. https://doi.org/10.1007/s11356-020-08483-z

Georgiev D, Bogdanov B, Angelova K, et al (2009) Synthetic zeolites-structure, classification, current trends in zeolite synthesis review. In: International Science Conference, Stara Zagora, pp 1–5.

Gottardi G, Galli E (1986) Natural Zeolites. Minerals and Rocks Series. Geological Magazine, 123:6, pp. 718. https://doi.org/10.1017/S0016756800024456

Guisnet M, Gilson J-P (2002) Zeolites for Cleaner Technologies. Imperial College Press, London ISBN: 1860943292. https://doi.org/10.13140/2.1.3317.8401

Hailu SL, Nair BU, Redi-Abshiro M, et al (2017) Preparation and characterization of cationic surfactant modified zeolite adsorbent material for adsorption of organic and inorganic industrial pollutants. J Environ Chem Eng 5:3319–3329. https://doi.org/10.1016/j.jece.2017.06.039

Hansen É, Monteiro de Aquim P, Hansen AW, et al (2020) Impact of post-tanning chemicals on the pollution load of tannery wastewater. J Environ Manage 269:. https://doi.org/10.1016/j.jenvman.2020.110787

Harutyunyan LR, Pirumyan GP (2015) Purification of waters from anionic and cationic surfactants by natural zeolites. Proceedings of the YSU B: Chemical and Biological Sciences 49:21–28. https://doi.org/10.46991/PYSU:B/2015.49.1.021

Hutton M, Shafahi M (2019) Water pollution caused by leather industry: A review. ASME 2019 13th International Conference on Energy Sustainability, ES 2019, collocated with the ASME 2019 Heat Transfer Summer Conference. https://doi.org/10.1115/ES2019-3949

Igiri BE, Okoduwa SIR, Idoko GO, et al (2018) Toxicity and Bioremediation of Heavy Metals Contaminated Ecosystem from Tannery Wastewater: A Review. J Toxicol 2018. doi: 10.1155/2018/2568038

Islam MR;, Islam JS;, Zatzman GM;, et al (2016) The Greening of Pharmaceutical Engineering: Theories and Solutions, Wiley. USA. ISBN: 978-1-119-15970-4

Jevremović A, Božinović N, Arsenijević D, et al (2020) Modulation of cytotoxicity by consecutive adsorption of tannic acid and pesticides on surfactant functionalized zeolites. Environ Sci Process Impacts 22:2199–2211. https://doi.org/10.1039/D0EM00251H

Kanagaraj J, Senthilvelan T, Panda RC, Kavitha S (2015) Eco-friendly waste management strategies for greener environment towards sustainable development in leather industry: A comprehensive review. J Clean Prod 89:1–17. https://doi.org/10.1016/j.jclepro.2014.11.013

Karahan Ö, Dogruel S, Dulekgurgen E, Orhon D (2008) COD fractionation of tannery wastewaters-Particle size distribution, biodegradability and modeling. Water Res 42:1083–1092. https://doi.org/10.1016/j.watres.2007.10.001

Keane MA (1998) The removal of copper and nickel from aqueous solution using Y zeolite ion exchangers. Colloids Surf A Physicochem Eng Asp 138:11–20. https://doi.org/https://doi.org/10.1016/S0927-7757(97)00078-2

Khalil I, Jabraoui H, Lebègue S, et al (2020) Biofuel purification: Coupling experimental and theoretical investigations for efficient separation of phenol from aromatics by zeolites. Chemical Engineering Journal 402:126264. https://doi.org/https://doi.org/10.1016/j.cej.2020.126264

Kim JS, Zhang L, Keane MA (2001) REMOVAL OF IRON FROM AQUEOUS SOLUTIONS BY ION EXCHANGE WITH NA-Y ZEOLITE. Sep Sci Technol 36:1509–1525. https://doi.org/10.1081/SS-100103885

Kim KS, Park JO, Nam SC (2013) Synthesis of iron-loaded zeolites for removal of ammonium and phosphate from aqueous solutions. Environmental Engineering Research 18:267–276. https://doi.org/10.4491/eer.2013.18.4.267

Kragović M, Daković A, Sekulić Ž, et al (2012) Removal of lead from aqueous solutions by using the natural and Fe(III)-modified zeolite. Appl Surf Sci 258:3667–3673. https://doi.org/10.1016/j.apsusc.2011.12.002

Kumar N, Tiwari KR, Meenu Km, et al (2019) Utilization of Various Analogy of Synthetic Nanoporous Zeolites and Composite of Zeolites for Decontamination/Detoxification of CWA Simulants—An Updated Review. International Journal of Nonferrous Metallurgy 08:35–71. https://doi.org/10.4236/ijnm.2019.84004

Kurniawan TA, Othman MH, Adam MR, et al (2023) Chromium Removal from Aqueous Solution Using Natural Clinoptilolite. Water (Basel) 15:9, 667. https://doi.org/10.3390/w15091667

Lee HS, Kim NS, Kwon D il, et al (2021) Post-Synthesis Functionalization Enables Fine-Tuning the Molecular-Sieving Properties of Zeolites for Light Olefin/Paraffin Separations. Advanced Materials 33:. https://doi.org/10.1002/adma.202105398

Li K, Chen H, Wang Y, et al (2009) A salt-free pickling regime for hides and skins using oxazolidine. J Clean Prod 17:1603–1606. https://doi.org/10.1016/j.jclepro.2009.06.004

Lin J, Zhan Y, Zhu Z, Xing Y (2011) Adsorption of tannic acid from aqueous solution onto surfactant-modified zeolite. J Hazard Mater 193:102–111. https://doi.org/https://doi.org/10.1016/j.jhazmat.2011.07.035

Lofrano G, Aydin E, Russo F, et al (2008) Characterization, fluxes and toxicity of leather tanning bath chemicals in a large tanning district area (IT). Water, Air, and Soil Pollution: Focus 8:529–542. https://doi.org/10.1007/s11267-008-9177-7

Manzoli M, Tammaro O, Marocco A, et al (2021) New Insights in the Production of Simulated Moon Agglutinates: The Use of Natural Zeolite-Bearing Rocks. ACS Earth Space Chem 5:. https://doi.org/10.1021/acsearthspacechem.1c00118

Marocco A, Dell’Agli G, Sannino F, et al (2020) Removal of agrochemicals fromwaters by adsorption: A critical comparison among humic-like substances, zeolites, porous oxides, and magnetic nanocomposites. Processes 8:. https://doi.org/10.3390/pr8020141

Matijasevic S, Zildzovic S, Stojanovic J, et al (2016) Removal of uranium (VI) from aqueous solution by acid modified zeolites. Zastita materijala 57:551–558. https://doi.org/10.5937/zasmat1604551m

Medykowska M, Wiśniewska M, Szewczuk-Karpisz K, et al (2024) Green Synthesis and Efficient Adsorption: Na-X Zeolite vs. C/Mn/SiO2 Composite for Heavy Metals Removal. Materials 17:4, 954. https://doi.org/10.3390/ma17040954

Meftah T, Zerafat MM (2016) Nitrate Removal from Drinking Water using Organo-Silane Modified Natural Nano-Zeolite. Int. J. Nanosci. Nanotechnol.12:4, pp. 223-232. http://www.ijnnonline.net/article_22931.html

Mella B, Glanert AC, Gutterres M (2015) Removal of chromium from tanning wastewater and its reuse. Process Safety and Environmental Protection 95:195–201. https://doi.org/10.1016/j.psep.2015.03.007

Milton RM (1959) United States Patent Office US2,882,243

Mohammad Mahbubul Hassan, Jane Harris, James J. C. Busfield, Emiliano Bilottic (2023) A review of the green chemistry approaches to leather tanning in imparting sustainable leather manufacturing Supplementary Materials Contents. Green Chemistry 25, 7441-7469. https://doi.org/10.1039/D3GC02948D

Morante-Carballo F, Montalván-Burbano N, Carrión-Mero P, Jácome-Francis K (2021) Worldwide research analysis on natural zeolites as environmental remediation materials. Sustainability (Switzerland) 13:. https://doi.org/10.3390/su13116378

Morera JM, Bartolí E, Chico R, et al (2011) Minimization of the environmental impact of chrome tanning: A new process reusing the tanning floats. J Clean Prod 19:2128–2132. https://doi.org/10.1016/j.jclepro.2011.07.018

Mortier W (1982) Compilation Of Extra Framework Sites In Zeolites. Butterworth Scientific Limited, Guildford. ISBN 0861030567

Mpongwana N, Rathilal S, Tetteh EK (2022) Recovery Strategies for Heavy Metal-Inhibited Biological Nitrogen Removal from Wastewater Treatment Plants: A Review. Microorganisms 10:9. https://doi.org/10.3390/microorganisms10091834

Muthu SS (2021) Environmental Footprints and Eco-Design of Products and Processes. Springler. ISSN 2345-7651

Muthukrishnan L (2021) Nanotechnology for cleaner leather production: a review. Environ Chem Lett 19:2527–2549. https://doi.org/10.1007/s10311-020-01172-w

Navalon S, Alvaro M, Garcia H (2009) Highly dealuminated Y zeolite as efficient adsorbent for the hydrophobic fraction from wastewater treatment plants effluents. J Hazard Mater 166:553–560. https://doi.org/10.1016/j.jhazmat.2008.11.057

Nur-E-Alam M, Mia MAS, Ahmad F, Rahman MM (2020) An overview of chromium removal techniques from tannery effluent. Appl Water Sci 10: 205. https://doi.org/10.1007/s13201-020-01286-0

Okolo B, Park C, Keane MA (2000) Interaction of Phenol and Chlorophenols with Activated Carbon and Synthetic Zeolites in Aqueous Media. J Colloid Interface Sci 226:308–317. https://doi.org/10.1006/jcis.2000.6796

Omoloso O, Mortimer K, Wise WR, Jraisat L (2021) Sustainability research in the leather industry: A critical review of progress and opportunities for future research. J Clean Prod 285. https://doi.org/10.1016/j.jclepro.2020.125441

Omorogie MO, Helmreich B (2023) Exploring the Potential of Amino-Functionalized Zeolite Series/H3PO4-Biochar for Environmental Microplastic Removal. Ind Eng Chem Res. https://doi.org/10.1021/acs.iecr.3c03971

Pansini M, Dell’Agli G, Marocco A, et al (2017) Preparation and characterization of magnetic and porous metal-ceramic nanocomposites from a zeolite precursor and their application for DNA separation. J Biomed Nanotechnol 13:337–348. https://doi.org/10.1166/jbn.2017.2345

Pansini M, Sannino F, Marocco A, et al (2018) Novel process to prepare magnetic metal-ceramic nanocomposites from zeolite precursor and their use as adsorbent of agrochemicals from water. J Environ Chem Eng 6:527–538. https://doi.org/10.1016/j.jece.2017.12.030

Park M, Choi L, Lim WT, et al (2000) Molten-salt method for the synthesis of zeolitic materials I. Zeolite formation in alkaline molten-salt system. Microporous and Mesoporous Materials 37:1–2, pp 81-89. https://doi.org/10.1016/S1387-1811(99)00196-1

Patil PB, Bhandari VM, Ranade V V. (2021) Improving efficiency for removal of ammoniacal nitrogen from wastewaters using hydrodynamic cavitation. Ultrason Sonochem 70:. https://doi.org/10.1016/j.ultsonch.2020.105306

Perić J, Trgo M, Vukojević Medvidović N (2004) Removal of zinc, copper and lead by natural zeolite—a comparison of adsorption isotherms. Water Res 38:1893–1899. https://doi.org/https://doi.org/10.1016/j.watres.2003.12.035

Pirozzi D, Pansini M, Marocco A, et al (2023) Adsorption of gallic acid by tailor-made magnetic metal-ceramic nanocomposites. J Mol Liq 371:121083. https://doi.org/10.1016/J.MOLLIQ.2022.121083

Rangasamy S, Alagirisamy B, Santiago M (2014) Effect of natural zeolite material on hexavalent chromium adsorpium. Industrial Pollution Control 30:79–84. ISSN (0970-2083)

Roshanfekr Rad L, Anbia M (2021) Zeolite-based composites for the adsorption of toxic matters from water: A review. J Environ Chem Eng 9:. https://doi.org/10.1016/j.jece.2021.106088

Sallam AEA, Al-Zahrani MS, Al-Wabel MI, et al (2017) Removal of Cr(VI) and toxic ions from aqueous solutions and tannerywastewater using polymer-clay composites. Sustainability (Switzerland) 9:. https://doi.org/10.3390/su9111993

Sannino F, Pansini M, Marocco A, et al (2022) Removal of sulfanilamide by tailor-made magnetic metal-ceramic nanocomposite adsorbents. J Environ Manage 310:. https://doi.org/10.1016/j.jenvman.2022.114701

Sathish M, Madhan B, Sreeram KJ, et al (2016) Alternative carrier medium for sustainable leather manufacturing - A review and perspective. J Clean Prod 112:49–58. https://doi.org /10.1016/j.jclepro.2015.06.118

Saxena G, Chandra R, Bharagava RN (2017a) Environmental pollution, toxicity profile and treatment approaches for tannery wastewater and its chemical pollutants. In: Reviews of Environmental Contamination and Toxicology. Springer New York LLC. https://doi.org 10.1007/398_2015_5009

Schrank SG, José HJ, Moreira RFPM, Schröder HF (2004) Comparison of different advanced oxidation process to reduce toxicity and mineralisation of tannery wastewater. Water Sci Technol . 50:5, 329-34. PMID: 15497865

Senthil Kumar P, Janet Joshiba G, Femina CC, et al (2019) A critical review on recent developments in the low-cost adsorption of dyes from wastewater. Desalination Water Treat 172:395–416. https://doi.org/10.5004/dwt.2019.24613

Serra RM, Miró EE, Sapag MK, Boix A V. (2011) Adsorption and diffusion of toluene on Na and Cs mordenites for hydrocarbon traps. Microporous and Mesoporous Materials 138:102–109. https://doi.org/10.1016/j.micromeso.2010.09.024

Setiadj, Kusman, Mulyasyaroh, et al (2019) Processing of Total Chromium and Organic Compound in Tannery Wastewater Using Eggshell and Zeolite Sand. I CONISTECH 2019, 11-12 July 2019, Bandung, Indonesia. http://dx.doi.org/10.4108/eai.11-7-2019.2298034

Shahbazi A, Gonzalez-Olmos R, Kopinke F-D, et al (2014) Natural and synthetic zeolites in adsorption/oxidation processes to remove surfactant molecules from water. Sep Purif Technol 127:1–9. https://doi.org/https://doi.org/10.1016/j.seppur.2014.02.021

Shankar SN, Prakash U, Kannaian N, et al (2017) Adsorption Isothermal Studies on the Removal of Bod and Cod of a Leather Tannery Effluent using Clinoptilolite. International Journal of ChemTech Research 10:1, pp 496-500. ISSN: 0974-4290

Shegani G (2014) Study on Some Pollutants in the Leather Industry: A Case Study in Albania. International Journal of Sciences: Basic and Applied Research (IJSBAR) 14:115–124. ISSN 2307-4531

Shekhawat K, Chatterjee S, Joshi B (2015) Chromium toxicity and its health hazards. Int J Adv Res 3:167–172. ISSN 2320-5407

Shi J, Yang Z, Dai H, et al (2017) Preparation and application of modified zeolites as adsorbents in wastewater treatment. Water Science and Technology 2017:621–635. https://doi.org/10.2166/wst.2018.249

Singh PK, Kumar V, Pratap SG, et al (2023) Characterization of inorganic and organic pollutants load in tannery wastewater: Biochemical and haematological induced changes in Swiss mice. Journal of Hazardous Materials Advances 12:100387. https://doi.org/10.1016/j.hazadv.2023.100387

Siyal AA, Shamsuddin MR, Low A, Rabat NE (2020) A review on recent developments in the adsorption of surfactants from wastewater. J Environ Manage 254:109797. https://doi.org/https://doi.org/10.1016/j.jenvman.2019.109797

Srinivasan S V., Prea Samita Mary G, Kalyanaraman C, et al (2012) Combined advanced oxidation and biological treatment of tannery effluent. Clean Technol Environ Policy 14:251–256. https://doi.org/10.1007/s10098-011-0393-x

Standeven AM, Wetterhahn KE (1989) Chromium (VI) toxicity: uptake, reduction, and DNA damage. J Am Coll Toxicol 8:1275–1283. ISSN: *0730-0913*

Taffarel SR, Rubio J (2010) Adsorption of sodium dodecyl benzene sulfonate from aqueous solution using a modified natural zeolite with CTAB. Miner Eng 23:771–779. https://doi.org/https://doi.org/10.1016/j.mineng.2010.05.018

Tammaro O, Barrera G, Allia P, et al (2023a) Unravelling the role of the exchanged Ni amount in zeolites A and X for their thermal transformation into magnetic metal-ceramic nanocomposites. Ceram Int 49:30536–30546. https://doi.org/10.1016/J.CERAMINT.2023.07.003

Tammaro O, Morante N, Marocco A, et al (2023b) The beneficial role of nano-sized Fe3O4 entrapped in ultra-stable Y zeolite for the complete mineralization of phenol by heterogeneous photo-Fenton under solar light. Chemosphere 345:. https://doi.org/10.1016/j.chemosphere.2023.140400

Ugrina M, Gaberšek M, Daković A, Nuić I (2021) Preparation and characterization of the sulfur-impregnated natural zeolite clinoptilolite for Hg(II) removal from aqueous solutions. Processes 9:1–25. https://doi.org/10.3390/pr9020217

UNIC Italian Tanneries (2023) Sustainability Report UNIC Italian Tanneries Y2022. https://unic.it/storage/Sustainability%20Report%20UNIC%20Italian%20Tanneries%20Y2022.pdf

UNIDO United Nation Industrial Development Organization (2011) Introduction to treatment of tannery wastewater. https://www.unido.org

Velarde L, Nikjoo D, Escalera E, Akhtar F (2024) Bolivian natural zeolite as a low-cost adsorbent for the adsorption of cadmium: Isotherms and kinetics. Heliyon 10:1, e24006. https://doi.org/10.1016/j.heliyon.2024.e24006

Wang C, Leng S, Xu Y, et al (2018) Preparation of amino functionalized hydrophobic zeolite and its adsorption properties for chromate and naphthalene. Minerals 8:. https://doi.org/10.3390/min8040145

Wang S, Peng Y (2010) Natural zeolites as effective adsorbents in water and wastewater treatment. Chemical Engineering Journal 156:11–24. https://doi.org/10.1016/j.cej.2009.10.029

Wang Y, Zeng Y, Chai X, et al (2012) Ammonia nitrogen in tannery wastewater: distribution, origin and prevention. ournal of the American Leather Chemists Association 107(2):40-50. https://journals.uc.edu/index.php/JALCA/article/view/3381/2632

Wen J, Dong H, Zeng G (2018) Application of zeolite in removing salinity/sodicity from wastewater: A review of mechanisms, challenges and opportunities. J Clean Prod 197:1435–1446. https://doi.org/10.1016/j.jclepro.2018.06.270

Yousef RI, El-Eswed B, Al-Muhtaseb AH (2011) Adsorption characteristics of natural zeolites as solid adsorbents for phenol removal from aqueous solutions: Kinetics, mechanism, and thermodynamics studies. Chemical Engineering Journal 171:1143–1149. https://doi.org/https://doi.org/10.1016/j.cej.2011.05.012

Yu Y, Lin Y, Zeng Y, et al (2021) Life Cycle Assessment for Chrome Tanning, Chrome-Free Metal Tanning, and Metal-Free Tanning Systems. ACS Sustain Chem Eng 9:6720–6731. https://doi.org/10.1021/acssuschemeng.1c00753

Zapata PA, Huang Y, Gonzalez-Borja MA, Resasco DE (2013) Silylated hydrophobic zeolites with enhanced tolerance to hot liquid water. J Catal 308:82–97. https://doi.org/10.1016/j.jcat.2013.05.024

Zhang J, Tang X, Yi H, et al (2022) Synthesis, characterization and application of Fe-zeolite: A review. Appl Catal A Gen 630:118467. https://doi.org/10.1016/j.apcata.2021.118467

Zhang X, Wu W, Wen D, Tang X (2003) Effect and mechanism of removal of nitrogen in the mimic sewage using bio-zeolite system. Huan Jing Ke Xue 24:75–80. PMID: 14719264

Zhang Y, Xu M, Li H, et al (2018) The enhanced photoreduction of Cr(VI) to Cr(III) using carbon dots coupled TiO2 mesocrystals. Appl Catal B 226:213–219. https://doi.org/10.1016/j.apcatb.2017.12.053

Zhao Y, Gao T, Jiang S, Cao D (2004) Ammonium removal by modified zeolite from municipal wastewater. Journal of environmental sciences 16:1001–1004. PMID: 15900738

Zhu R, Yang C, Li K, et al (2020) A smart high chrome exhaustion and chrome-less tanning system based on chromium (III)-loaded nanoparticles for cleaner leather processing. J Clean Prod 277:. https://doi.org/10.1016/j.jclepro.2020.123278

Zieliński M, Zielińska M, Dębowski M (2016) Ammonium removal on zeolite modified by ultrasound. Desalination Water Treat 57:8748–8753. https://doi.org/10.1080/19443994.2015.1024750

Zuriaga-Agustí E, Galiana-Aleixandre M V., Bes-Piá A, et al (2015) Pollution reduction in an eco-friendly chrome-free tanning and evaluation of the biodegradation by composting of the tanned leather wastes. J Clean Prod 87:874–881. https://doi.org/10.1016/j.jclepro.2014.10.066