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Adsorption Applications for Environmental Sustainability

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Chapter 13

The use of the response surface methodology for the adsorption of heavy metals and dyes by biosorbents

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Globally, there is an increasing search for alternative options to reduce the challenges of the discharge of untreated wastewater from various industrial activities such as tanneries. Large amounts of wastewater are continuously produced through various human activities, from which water can still be recovered and reused. This chapter examines the different pollutants in tannery wastewater and the possible ways of treating these contaminants and reviews the application of the response surface methodology approach for experiments in wastewater treatment. It also presents different techniques and raw materials used in producing porous ceramics, which are viable and cost-effective materials for wastewater treatment.

13.1 Introduction

Wastewater (WW) is often defined as used water that has been affected by commercial, domestic, and industrial activities. WW includes tannery, textile, and refinery effluents, storm runoff, and toxic road runoff. Recent developments in the tannery industry are one reason why the industry is a major source of industrial pollution. For instance, based on statistics, over 300 million cowhide pieces enter the global leather market yearly, which often results in the generation of about 300 million tons of WW [1]. In Kano, Nigeria, 39 tanneries have released their liquid and solid wastes into the environment [2]. Therefore, the discharge of tannery WW into water bodies during leather production has become a pressing issue that restricts the growth of the tannery industry. However, in some developed countries, strict guidelines have been imposed on the release of tannery effluents. For example, the USA and several countries in Europe have created standard procedures for

tannery WW treatment. These countries defined the required standards in terms of the chemical oxygen demand (COD), pH value, biochemical oxygen demand (BOD), sulfides, oil, and chromium (Cr) in the WW bore released into the water body. Further, few countries have stated nitrogen limits for ammonia, which is also a toxic product [3].

Tannery WW is made by the tanning processes used in the production of leather. In some industries, tannery WW is collected separately and then mixed with WW from other sources. The total collected WW is subjected to treatment. The concentrations of BOD, COD, sulfides, suspended solids, and ammonia in tannery WW are generally very high [4]. The tanning process is complex and uses multiple substances and many chemicals. Tannery WW is highly alkaline and saline and contains suspended solids and organic matter. It has high oxygen consumption and a deep color because of the organic matter present.

Based on the treatment degree, tannery WW treatments can be classified as primary, secondary, or tertiary WW treatments. Primary treatment involves general chemical reactions and physical interaction that is completed in the pretreatment stage. The process involves the effective removal of suspended solids in tannery WW through the reduction of the organic load in the treatment plant. The treatment process includes screening and grille processes. In addition, these processes also remove thick materials such as scurf and undesirable substances such as floating organics, sediment, and coagulation products [1]. Secondary treatment for tannery WW is a biological process that involves aerobic and anaerobic secondary treatments. The aerobic treatment includes biofilm, natural biological, and activated sludge methods. Tertiary treatment is a deep and advanced treatment process. A single secondary treatment often fails to remove phosphorus and nitrogen completely. Hence, a combined treatment process is required. The focus of tertiary treatment is to confiscate pollutants that secondary treatment cannot remove completely.

In environmental engineering, optimizing the performance of WW treatment systems is crucial. However, the traditional method of optimization through multiple variables can be inflexible, unreliable, and time-consuming. This is the reason that an alternative, more effective, and adaptable method is preferred. Response surface methodology (RSM) is one such technique that is widely used for system performance optimization. This mathematical and statistical tool can help analyze the effects of various independent factors on a treatment process in order to obtain maximum output. RSM has been efficaciously applied to optimize WW treatment procedures for various industries, including the textile, tannery, paint, olive oil, and palm oil industries. It has also been used for landfill leachate treatment. This chapter aims to provide an assessment of the usability, effectiveness, and limitations of RSM for modeling and optimizing process parameters in WW treatment. By gathering information about the interactions among parameters that can optimize the treatment of WW, RSM can optimize parameters during the process of treating WW.

The process of filtration or separation involves passing a liquid or a gas (i.e. a fluid) through a porous substance to collect particulate matter from suspended solids

as well as suspended substances, such as fine particles, microbes, polymer molecules, mist, and aerosols. Such porous substances are known as ‘filters,’ and ceramic materials have been extensively used to produce these filters. This chapter highlights a few of the different techniques and raw materials used in producing porous ceramics.

Hence, this chapter presents the different pollutants found in tannery WW and the use of various techniques to enhance the effective removal of tannery WW contaminants and heavy metals (HMs). RSM is discussed as a widely used method for system performance optimization, particularly in WW treatment. This chapter also discusses the use of porous ceramics for water filtration applications. This includes their processing techniques, the materials used to fabricate porous ceramics, and industrial applications of WW treatment.

13.2 Tannery wastewater characteristics

Leather production processes are classified into four parts: beam house, tanning, post-tanning, and the finishing stage. Chemicals (Cr salts, sulfates, biocides, sulfides, etc) are used in large quantities during the tanning processes, hence the large quantity of WW generated is characterized by serious physicochemical conditions, i.e. dark brownish WW with a high concentration of Cr, total dissolved solids (TDS), COD, BOD, total nitrogen (TN), total phosphorus (TP), HMs, strong odor, and high pH [5]. The treatment of tannery WW for domestic consumption imposes a series of restrictions into the treatment train which vary according to the supplier’s requirements, the source’s type, and vulnerability. Coagulation, flocculation, filtration, and oxidation systems are all part of the treatment train, while chlorine is the most common oxidative disinfectant [6]. International recommendations and national standards are used to assess the safety of treated water, and the World Health Organization (WHO) Guidelines for drinking-water quality are the most important of all [7]. The various contaminants in WW are presented in the following subsections. The preceding subsection presented some of the pollutants in tannery WW.

13.2.1 Total nitrogen

The eutrophication of water is caused by excessive nitrogen. During the tanning process, the TN is introduced from two sources. The methods used to treat the TN include chemical nitrogen removal (i.e. ion exchange, catalytic oxidation, electrolysis, and ozone oxidation), biological nitrogen removal (i.e. the anaerobic-anoxic-oxic (A_2/O), anaerobic oxic (A/O), and sequencing batch reactor (SBR) methods), and physicochemical nitrogen removal (i.e. air and steam stripping and chemical precipitation). Flocculent precipitation has also been effectively used in nitrogen removal when biological flocculation was used in the treatment of the TN in tannery WW [8].

13.2.2 Total phosphorus

The total phosphorus level describes the eutrophication of water. Its value is a significant parameter used to define water that is contaminated or polluted. Phosphorus is not present in the raw fur and raw hides during fur processing

and tanning. However, phosphorus-containing compounds such as lecithin fatigue might be used during processing. An appropriate amount of phosphorus is sometimes added to balance the nitrogen in the WW [3]. Generally, there are three kinds of phosphorus found in tannery WW, namely: (i) polyphosphate, (ii) organic phosphorus, and (iii) orthophosphate. Membrane technology (MT) and chemical precipitation are the main techniques used in treating phosphorus-containing WW.

13.2.3 Chloride ions

The newly established and existing standards for chloride ion concentration in tannery effluents are set at around 3000 mg l^{-1} , while 4000 mg l^{-1} is permitted for fur processing. Regardless of improvements in technology, it is still difficult to achieve chloride-free tanneries. From a cleaner production point of view, several technologies are used to reduce chloride, from processing fresh hide directly, using salt-free pickling, or the cyclic utilization of WW. However, these methods might not guarantee the complete removal of chlorides. Hence, conventional technologies such as reverse osmosis (RO), ion exchange, and electroosmosis are commonly used [3].

13.2.4 Chromium salt

About 8% of tannery WW consists of chrome tanning WW. A high concentration of Cr, namely $3000\text{--}6000 \text{ mg l}^{-1}$ [1], occurs when Cr combines with protein during cell metamorphosis. Following treatment, its flocculability is completely destroyed in the sludge, which harms the treatment process. A combination of biochemical processes and physical chemistry (ion exchange, electrolysis, and adsorption) is generally used to treat Cr-containing WW. After the physical process is complete, the treated WW is further treated in a biochemical treatment system [9].

13.2.5 Sulfur-containing compounds

Sulfates and sulfides are the main sulfur-containing compounds in WW produced by the leather industry. The sulfides are in the form of hydrogen sulfides, which often have a bad smell and toxicity when compared with cyanates. A high sulfate concentration might also interfere with anaerobic treatments. Methods such as flotation, flocculation, sedimentation, and adsorption have been used for sulfide treatment [10].

13.2.6 Heavy metals

The effluent from leather production contains HMs (i.e. manganese (Mn), iron (Fe), zinc (Zn), copper (Cu), and cobalt (Co)). Elements with atomic weights ranging between 63.50 and 200.60 and densities of more than 5.0 g m^{-3} are called HMs [11]. HMs play significant roles in biochemical/organic processes in the human body, and excess intake has negative consequences for humans. Other HMs, such as cadmium (Cd), Cr, mercury (Hg), arsenic (As), and lead (Pb), are dangerous even at low

concentrations (parts per billion), since the accumulation of these elements over time harms humans [12]. Although the human body can tolerate certain HM levels without experiencing any serious health issues, excess exposure leads to physiological system failure and eventually death. Table 13.1 presents the sources and effects of HMs on humans as adapted from [7, 13].

Table 13.1. Sources of HMs and their health effects on humans.

HM	Sources of the HM	The effects of the HM on humans	Maximum contaminant level (MCL)
Pb	Storage batteries, piping, tank exterior coatings, plating, gasoline, Pb processing industries, insecticides, and medicinal flavorings	Damages the kidney and liver and reduces hemoglobin function. This leads to infertility and abnormalities in pregnancy and central nervous system disorders which might lead to death.	US EPA: 0.015 mg l ⁻¹ WHO standard: 0.01 mg l ⁻¹
Cd	Electroplating, paint pigments, phosphate fertilizers, plastics, smelting, silver Cd batteries, mining, and alloy industries.	Irritation in the respiratory tract. Prolonged exposure cause anemia and a yellowish strain that appears between the teeth.	US EPA: 0.005 mg l ⁻¹ WHO standard: 0.003 mg l ⁻¹
Cu	An environmental contaminant; its causes are mining, printed circuits, and fiber production. Agricultural sources: fertilizers, animal waste, and fungicidal sprays.	It causes jaundice and enlarges livers. Increases the occurrence of lung cancer	US EPA: 1.3 mg l ⁻¹ WHO standard: 2.0 mg l ⁻¹
Zn	Zn salts are used for wood preservatives, photographic papers, ceramics, textile catalysts, batteries, and steel production.	Excessive exposure to Zn causes gastrointestinal distress and diarrhea.	US EPA: 5 mg l ⁻¹ WHO standard: 5.0 mg l ⁻¹
Nickel (Ni)	Sources are washing electroplating baths used in the storage battery industry.	It causes cancer of the nose, bone, and lungs. Acute Ni (II) poisoning causes dizziness, headache, shortness of breath, and dry cough.	US EPA: 0.1 mg l ⁻¹ WHO standard: 0.05 mg l ⁻¹

(Continued)

Table 13.1. (Continued)

HM	Sources of the HM	The effects of the HM on humans	Maximum contaminant level (MCL)
As	Sources include industrial deposits, leaching from pesticides, natural deposits, coal power plants, wood preservatives, and semiconductor manufacture.	Serious skin, lung, and kidney challenges.	US EPA: 0.010 mg l ⁻¹ (or ppm) WHO standard: 0.010 mg l ⁻¹

WHO: World Health Organization, US EPA: US Environmental Protection Agency

13.3 RSM techniques for wastewater treatment

The effectiveness of a treatment process relies on different processing factors, and optimizing these processes results in reduced costs and reduced consumption of resources such as materials and energy. One-factor-at-a-time is the traditional approach for optimizing processes. This studies the effect of one variable while the other variables are kept constant. However, this technique does not reveal the interactions among the variables, and the number of experimental runs required is too large, making this process costly and time-consuming [14]. To overcome these challenges, the design of experiment (DOE) method is used since it requires fewer experimental runs and the interaction between factors can be represented graphically. The DOE methods used with the RSM includes full factorial design (FFD), Box–Behnken design (BBD), and central composite design (CCD) [15]. The RSM is a collection of mathematical and statistical methods for the DOE framework whose aim is to examine the effects of the different factors using a few experimental runs. The RSM is primarily used to improve the yields obtained by chemical and processing companies [16]. However, the RSM is now used widely in other fields, such as aerospace, agricultural settings, the life sciences, automotive applications, and many others [14]. Recently, the RSM has become an important tool for the analysis and optimization of different WW treatment procedures, such as adsorption, disinfection, coagulation–flocculation, electrochemical processes, and advanced oxidation processes. The utilization of different computer software (i.e. Minitab, Design Expert) makes it simpler to apply the RSM.

13.3.1 Procedures for RSM

The mathematical model used for the RSM is obtained using the data from the DOE, the relationships between the process factors (which are the independent variables), and the response (which is composed of the dependent variables). The model thus obtained is then employed for the examination of the effect of the factors, the interaction between the factors and the variables, and the optimization of the process. The results or findings are presented as three-dimensional (3D) and

two-dimensional (2D) graphs/plots. The RSM necessitates the utilization of optimization methods, statistical/mathematical experimental design, and linear regression modeling. There are several steps in the application of the RSM, and these include the identification of the factors and the selection of their ranges, experimental design selection, experimental procedures used to obtain the response parameters, results analysis, the generation of a regression model for the experimental results, determination of the model's competence, graphical representation of the model, and obtaining the optimum values [14].

13.3.1.1 Independent variable selection

Several factors or independent variables affect the response of a given system. However, it is not possible to include all factors in the design due to the high cost of materials production. Hence, the factors are first screened to determine which factors make a significant contribution, and this is done by carrying out experiments using the 'one-factor-at-a-time technique' or 'two-level factorial design.' Using this approach, the proper factor range can be selected, since this affects the overall precision of the developed model. The prior information obtained by the study also helps in selecting narrower ranges for the independent variables.

13.3.1.2 Experimental design

Numerous designs exist that can be used to conduct any study. These designs differ from one another in the ranges of factors used and the number of experimental runs. The main widely used DOEs include: (i) the CCD, (ii) the FFD, and (iii) the BBD. The development of each design model is done through a mathematical matrix. The CCD consists of a two-level (2^k) factorial point combined with a central point (C_0), ' $2k$ ' axial points, and experimental points at a distance α from the central point. The experimental runs are calculated using equation 13.1, and the quadratic equation is estimated from ' $2k$ ' and ' 2^k ,' and the central point is used to estimate the error.

$$N = 2k + 2^k + C_0 \quad (13.1)$$

The BBD consists of a two-level factorial design together with a design block that is not completely fitted to a second order coded as (+1, 0, and -1). The BBD is an important technique and serves as an effective alternative to the CCD when the factors (k) equal three. The experimental runs of the BBD can be calculated using equation (13.2).

$$N = 2k(k - 1) + C_0 \quad (13.2)$$

In the FFD, three levels represent the minimum (-1), the mean (0), and the maximum (+1). The experimental run is defined by n^k , where n is the number of levels and k is the number of factors. After choosing any of the designs for the experiment, the next step is to carry out the adsorption or filtration test; the final removal efficiency is then recorded and the mathematical model is generated [14].

13.3.1.3 Optimization of the response surface

Response surface analysis is conducted to obtain the optimum conditions and minimum or maximum responses. In response surface techniques, optimization involves coefficient estimation and response prediction using a mathematical model, as shown in equation 13.3

$$Y = f(X_1, X_2, \dots, X_n) \pm e, \quad (13.3)$$

where Y is the response, f is the function of the response, X_i is an independent variable ($i=1, 2, \dots, n$), and e is experimental error.

The function f may take a very complicated form that results in a higher-order polynomial (i.e. a quadratic model, as shown in equation (13.4)), and this depends on the relationship that exists between the independent variables, the response, and the interaction between factors. When the responses are considered, the optimum conditions can be graphically attained by overlaying contour plots of the RS regression models; all the input parameters then simultaneously meet the required conditions.

$$Y_m = b_o + \sum_{(i=1)}^k b_i X_i + \sum_{(i=1)}^k b_{ii} X_i^2 + \sum_{i=1}^{(i>j)} \sum_j b_{ij} X_i X_j \quad (13.4)$$

where Y_m is the response variable, X_i and X_j are independent variables, and b_o , b_i , b_{ii} , and b_{ij} are offset terms.

The contour plot shows the feasible area of the responses in the factor axis (X_1 and X_2) and the regions that best fit the optimization criteria. However, it becomes more difficult to obtain the simultaneous response conditions when more than three factors are considered; in this case, the multicriteria methodology can be used. In the multicriteria methodology, the desirability function is used and each one of the responses is converted into a desirability function within the range from zero to one. When a response is within the acceptable region, one is assigned as the desirability function, while the response outside the region is assigned to zero [69].

13.3.2 Applications of RSM in wastewater treatment

Recently, several research studies have described the utilization of the RSM for optimizing and analyzing different procedures used in WW treatment. Some of these studies are presented in the following subsections.

13.3.2.1 Coagulation–flocculation

Flocculation and coagulation are used to remove contaminants and HMs. Coagulation is a chemical process used in the removal of solid particles from WW. Coagulants such aluminum and ferric chloride are introduced into the WW to destabilize the forces keeping the solid particles, oily materials, or colloids together. In the case of flocculation, the process involved is the agglomeration of destabilized particles into microflows. The removal of coagulants is affected by the pH, the concentration of the co-coagulants, the coagulant dose, and the initial turbidity.

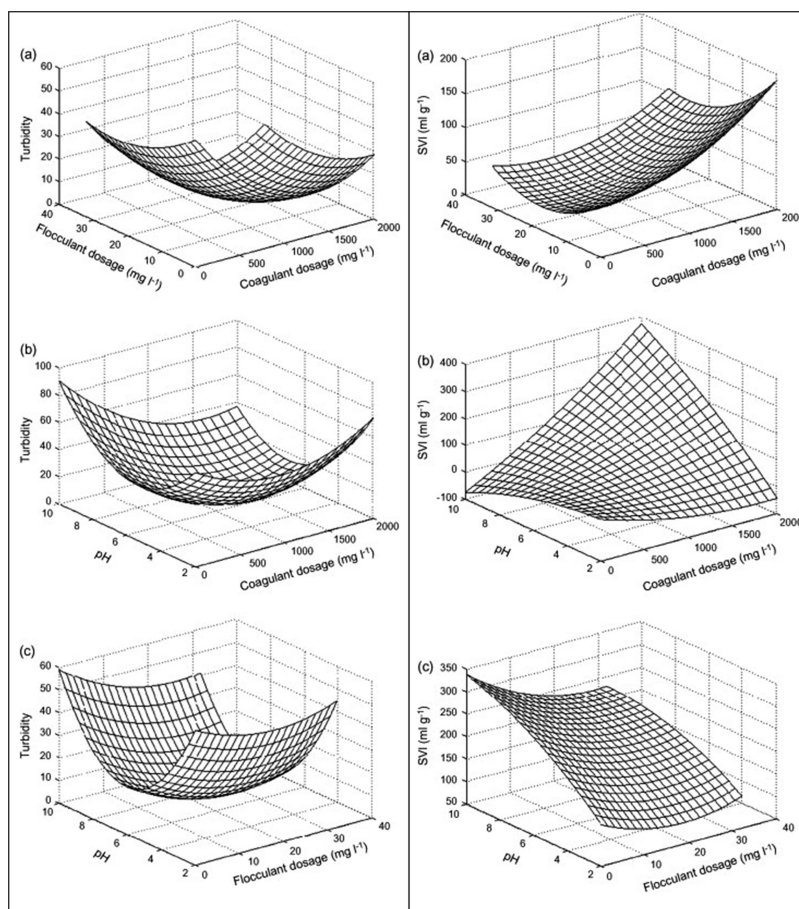


Figure 13.1. Response surface plots of turbidity and sludge volume index against the three input factors.

Using RSM for process optimization is advantageous, since obtaining the optimal conditions is easier, as reported by several studies. Wang *et al* [17] used a coagulation–flocculation process to treat WW, and the processes were optimized using the RSM. The independent variables were the coagulant dosage, the flocculate dosage, and the pH, while the responses were the turbidity (in nephelometric turbidity units, NTU) and the sludge volume index (ml g^{-1}). The resulting contour plot for the responses is shown in figure 13.1 as adapted from [17]. The plot shows the effects of two factors on a response while the third factor is kept constant. Moghaddam *et al* [18] applied the RSM to optimize the initial concentration, coagulant dosage, and initial pH in the removal of dye from an aqueous solution, in which they used the RSM technique to determine which of the factors affected the effectiveness of the removal coagulation/flocculation procedure. The result shows that the three factors significantly affect the efficiency of the process. For instance, an increase in the coagulant dosage increased the removal efficiency, and the

maximum removal rate was attained using the maximum dose of the coagulant. Liu *et al* [19] also optimized the coagulation/flocculation performance using the RSM; the response parameters were traditional indexes such as turbidity removal, color, and the COD. Mensah-Akutteh *et al* [20] used the RSM to optimize coagulation–flocculation; the parameters studied included the alkalinity, pH, and alum dose. The optimal condition for the responses was presented and the mathematical model obtained from the study was suitable for predicting responses that were not included in the experiment. Iber *et al* [21] utilized the Box–Behnken approach in the RSM for the coagulation–flocculation of aquaculture WW treatment to determine the optimal operational values of the pH, chitosan dosage, and settling time before establishing and authenticating quadratic models.

13.3.2.2 Adsorption

Adsorption is a widely known technique for the treatment of HM effluents due to its low cost of production and ease of use. In terms of design and operation, the adsorption process is adaptable, and it is highly effective in the treatment of WW in a variety of situations. Because adsorption is a reversible technique, adsorbents can be reused using a suitable desorption process. Examples of materials used for adsorption include activated carbon (AC), carbon nanotubes (CNTs), low-cost adsorbents, and bioadsorbents. HMs are mainly removed from WW using AC adsorbents due to their huge mesopore and micropore contents and their high adsorbent surface areas. Several researchers have investigated the applicability of AC adsorbents for HM removal [22, 23]. CNTs have great potential for removing HM ions such as Cu [24], and Ni [25] from WW. Although AC is widely used, it is very expensive. Therefore, the search for accessible and low-cost adsorbents has become a major research priority for HM removal. Several studies have been published on the topic of low-cost adsorbents over time, and adsorbents have been made from natural substances, waste products from industrial activities, and agricultural wastes. The use of low-cost biosorbents and their high efficacy in confiscating HM ions are due to the advantages of biosorption. Biosorption systems are particularly well suited to dilute HM effluents. The factors that play a significant role in the adsorption procedure are the adsorbent/adsorbate ratio, the ionic strength, the pH, and the nature of the adsorbent surface [26]. The ‘RSM has been used in the optimization of the process parameters’ according to Yang *et al* [27]. Their research considered the effect of various parameters, such as the coexistence time, the pH, the initial concentrations of fluoride and humic acid, and the adsorption time [27]. The results of the RSM showed which of the parameters had the largest influence on the removal of fluoride [27]. Nguyen *et al* [28] employed the RSM approach to optimize the adsorption capacity of biochar derived from spent coffee grounds; they considered parameters including the ions present, the norfloxacin level, and the pH. Mourabet *et al* [29] examined the confiscation of fluoride from an aqueous solution utilizing the BBD in the RSM. The independent variables considered had three levels, and these included the pH, adsorbent dose, temperature, and initial concentration. The optimal values of an initial concentration of 49.06 mg l⁻¹, a pH of 5.36, and an adsorbent dose of 0.15 g yielded the optimum removal efficiency of the fluoride, which was 90.83%. Iqal *et al* [30] investigated Cd removal from WW and an aqueous solution. The impact of factors such

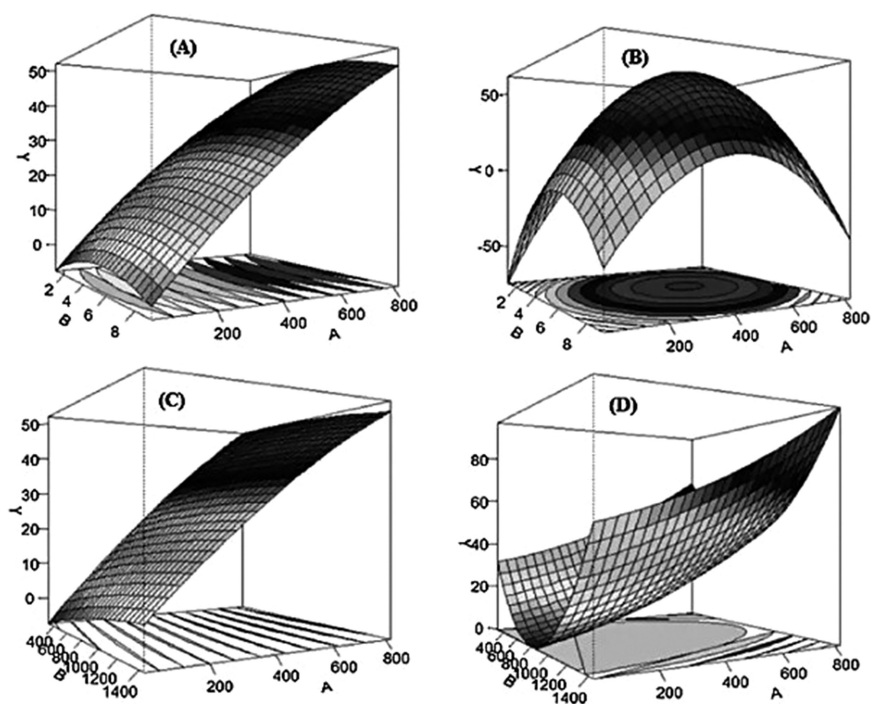


Figure 13.2. (A) The effect of the adsorbent dose and initial ion concentration on the removal of Cd using type I material; (B) the effect of the adsorbent dose and initial ion concentration on the removal of Cd by type II material; (C) the effect of the contact time and pH on the removal of Cd by type I material; (D) the effect of the contact time and pH on the removal of Cd by type II material. (Captions for figures 13.2(A) and (B), A: initial concentration, B: Absorbent dose. Captions for figures 13.2(C) and (D), A: pH, B: contact time. Y is the Cd adsorption rate (mg g^{-1}).)

as the metal ion concentration, adsorbent dosage, pH, and contact time were modeled using the RSM. The effect of each independent variable in terms of its effect on the removal efficiency was studied using contour plots. For example, the effect of 0.1–2.1 (g) of adsorbent dose in combination with the contact time, pH, and initial concentration on the adsorbent is illustrated in figure 13.2 as adapted from [30].

13.3.2.3 Membrane technology

Due to their high effectiveness and ease of use, membrane filtering methods based on various membrane types have the potential to remove HMs. Membrane technologies such as RO, ultrafiltration (UF), electrodialysis, and nanofiltration (NF) are used for HM removal. UF membranes are mainly used to remove colloidal and dissolved particles and operate at low transmembrane pressures. UF membranes have pores with larger diameters, and dissolved HM ions in the form of hydrated ions might easily pass through them. RO is a water treatment (purification) technique that employs a semipermeable membrane to filter out larger particles

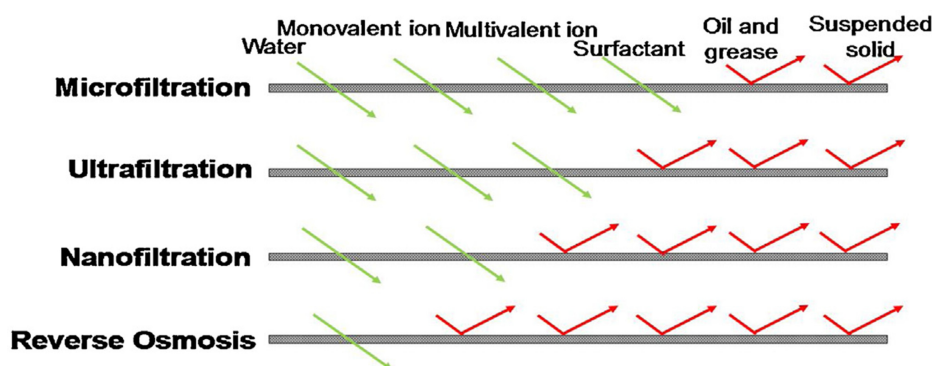


Figure 13.3. The rejection capabilities of membranes.

and pollutants such as salt, soil, and chlorine from drinking (domestic) water. NF is an intermediate between RO and UF. Ni [31], As [32], Cu [33], and Cr [34] are HM ions that can be removed from WW via NF. The NF process has the advantages of reliability, low energy consumption, and ease of operation as well as excellent pollution removal efficiency. Figure 13.3 depicts the rejection capabilities of various membranes as adapted from [35].

Recently, Waqas *et al* [36] optimized biological and filtration efficiency using the RSM; the sludge retention time, disk rotation, and hydraulic retention time were the input parameters considered. The WW filtration was conducted using MT. This research study demonstrated the effectiveness of the RSM in analyzing different filtration parameters, i.e. the COD, turbidity, ammonia removal rate, and MT. Wang *et al* [37] optimized the fabrication of layer-by-layer membranes. In their study, the relationship between the factors was determined by the BBD in the RSM. Maher *et al* [38] studied ‘the elimination of HM from drinking water’ using a NF MT; their procedure was optimized utilizing the RSM. The optimization was performed to determine the HM rejection rate of the membrane. The optimum nickel rejection rate was 93%, and 86% was achieved for Pb ions. Goyal *et al* [39] optimized ‘the process parameters of an emulsion ionic liquid membrane via RSM and experimental work which was designed using BBD.’ The factors considered included the treatment ratio, internal phase concentration, pH, internal-to-organic phase ratio, and the homogenization speed, while the response was the Cr removal rate. The interaction between the homogenization speed and the internal phase concentration is presented in the response surface plot in figure 13.4 as adapted from [39]. The plot shows that an optimum Cr removal rate of 92% can be obtained using homogenization speeds and internal phase concentrations from 0.5 to −0.5.

The future of tannery WW treatment should focus on multifunction treatments, intensification, and recycling. The treatment of tannery WW can be classified into the following stages: pretreatment, major treatment, and advanced treatment. The first stage (pretreatment) is designed to remove sand and large matter from the WW, while the main treatment stage should possess an exceptional capability to detoxify

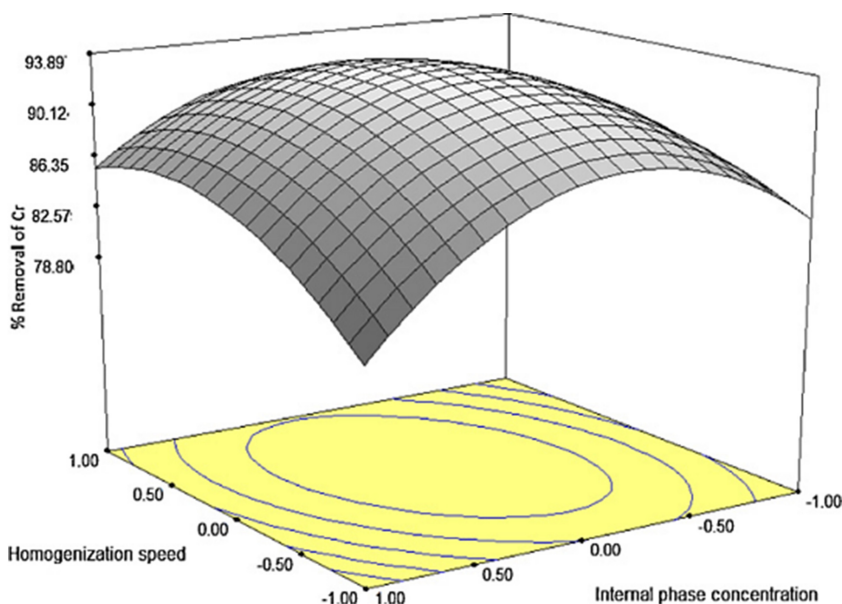


Figure 13.4. A response surface plot showing the dependence of the Cr removal rate on the internal phase concentration and the homogenization speed.

or break down the pollutants. The advanced treatment stage is used for sterilization, disinfection, and deep mineralization. Hence, a single treatment process might not be effective in purifying WW. For instance, electrocoagulation can be used simultaneously with electrooxidation to precipitate inorganic pollutants and degrade organic pollutants [40].

13.4 The application of porous ceramics in tannery WW remediation

Ceramic membranes are utilized in tannery WW treatment owing to their effectiveness, low cost, and good mechanical strength [41]. Ceramic membranes are divided into three types based on pore size (figure 13.5 as adapted from [42]): microporous ($d < 2.0$ nm), macroporous ($d > 50.0$ nm), and mesoporous ($2.0 < \text{nm } d < 50.0$ nm) [42]. Porous ceramics are classified as closed cell or open cell (or reticulated) depending on their basic pore structure, and this property is critical in determining the functions of diverse materials [43]. The pore structure parameters such as pore shape, size, distribution, and connection all play a role in porous ceramic materials' overall functionality. An open-cell shape with interconnected pores is perfect for use in fluid (liquid or gas) transfer applications due to its liquid permeability.

13.4.1 Processing techniques for porous ceramics

13.4.1.1 Partial sintering

Partial sintering is one of the commonest and broadly utilized techniques for fabricating porous ceramics. This technique requires the use of low temperatures

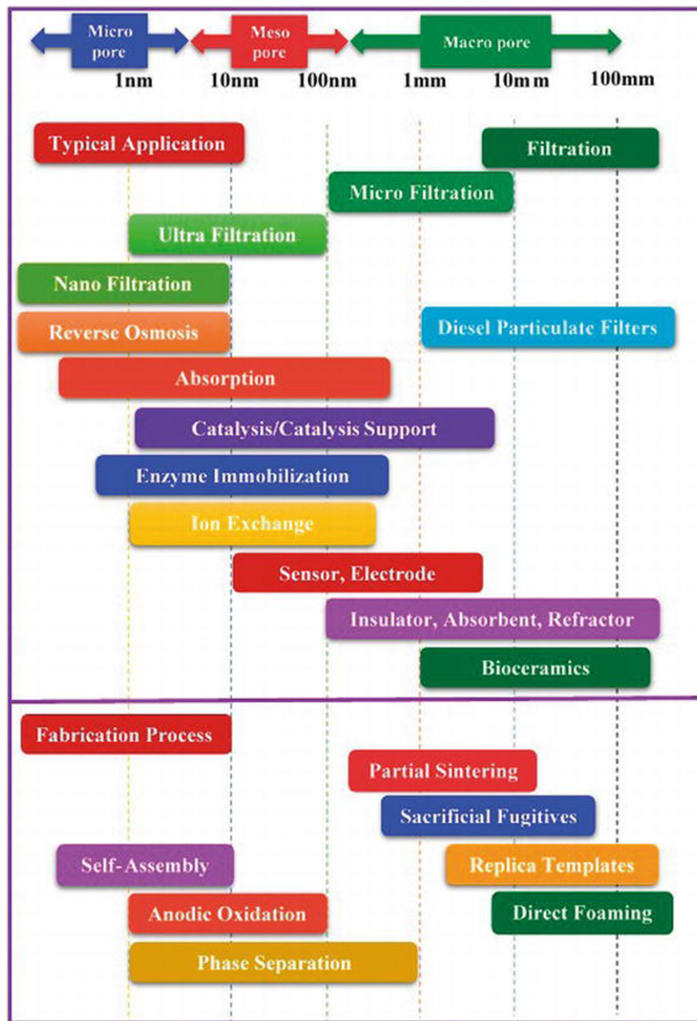


Figure 13.5. Representative fabrication processes of macroporous ceramics.

and reduced processing times on the compacted green body in order to generate its dense counterpart [44–46]. The size and volume of the starting powders as well as the sintering settings determine the microstructure of porous ceramics. The density of the green body and the usage of additives have a big impact on the resulting material's pore size and porosity [42–46]. Meanwhile, the technique's exceptional merit is thought to be due to the interconnected open porosity, extremely narrow size distribution, and ease of dimensional control of the produced structures. Porous ceramics have a low effective thermal conductivity due to these microstructural characteristics when compared to unsintered powder compacts. As a result, their conductivity drops rapidly, although it may still be customized across a wide range. As a result, partial sintering is regarded as a powerful approach for controlling the

final product's thermal properties [47]. Advanced sintering processes, such as spark plasma sintering (SPS) and partial hot pressing, have been developed to improve grain bonding, which in turn improves the mechanical strength, thus satisfying the ever-increasing demands.

Partial sintering occurs when the compacted powder is bonded together by surface diffusion, full densification, and recrystallization; the use of low sintering temperatures results in structures with pores produced by the coarse powder network [48]. Partial sintering techniques result in a porous structure with three interconnected pore stages: (i) pores between agglomerates, whose sizes are less than 10.0 μm ; (ii) pores inside agglomerates, whose sizes lie between 100.0 and 1000.0 nm; and (iii) pores within particles, whose sizes are 100.0 nm [49]. Overall, the porosity, pore size, and shielding effects of aligned fibrous grains all influence porous ceramics' mechanical strength [50].

13.4.1.2 Replica templates

Porous ceramics with interesting properties such as high surface areas and linked pores can be manufactured through the replica method [31]. In this method, a polymeric foam is impregnated into the ceramic slurry to form a template, which is then followed by heat treatment. The organic polymeric constituents disintegrate during the heating cycle, but the ceramic remains [52]. The porous ceramics fabricated using this process have the same structure and shape as the template used in their creation [53]. The replica process allows for precise control of the final morphological and microstructural properties. Solid polymeric sponges (i.e. polyurethane) and natural sponges (i.e. cellulose, marine sponge, and wood) can be utilized as templates to produce porous ceramics with open porosities of more than 70%. Furthermore, the choice of slurry and medium template has a substantial impact on the physical and mechanical characteristics of the finished porous ceramics [54].

13.4.1.3 Sacrificial templates

The sacrificial template approach differs from the replica method in that the latter copies the original template configuration, whilst the former creates a negative reproduction of the original pore features. As a result, the sacrificial template approach can create pores that are either open cell or closed cell. The sacrificial template procedure is used to produce porous ceramics with suitable mechanical strength and porosity by homogeneously inserting a sufficient amount of sacrificial porogen, which is then eliminated via thermal breakdown. The sacrificial porogen burns off, evaporates, or etches due to the thermal treatment. The raw materials used include a powder mixture (combination) of two constituents, a two-phase suspension, a preceramic polymer, or a ceramic slurry [55].

At high temperatures, the parent materials must not react with the sacrificial constituents. The commonly used sacrificial porogens include synthetic organics [56] and natural sources [57]. In comparison to their liquid equivalents, the first three sources are classified as non-liquid templates. The morphology of porous ceramics can be altered by using the right templates. The percentage, kind, and dimensional features of the sacrificial template play a critical role in establishing the shape, size,

and structure of the pores in this process, eventually dictating the qualities of the resultant materials [58, 59]

13.4.1.4 Direct foaming

Direct foaming techniques involve the use of parent foamed materials (i.e. a ceramic suspension containing surfactant) that incorporate air bubbles obtained via chemical blowing or mechanical stirring; the foaming process is then followed by a sintering process and stabilization. This technique produces porous ceramics with closed and open pores and porosities close to 97%, which can be obtained through fast, low-cost, and very simple production stages [60, 61]. Meanwhile, the ability to mass produce these ceramics is an additional benefit. The stabilization of the air bubbles included in the suspension is the most essential issue in direct foaming, especially when the slurry has a large bubble content; under these conditions, the wet foam is prone to cracking and might eventually collapse [62].

13.4.1.5 Additive manufacturing

Porous ceramics have precisely designed structures with important characteristics such as pore size, porosity, and pore interconnectivity to meet the demands of sophisticated applications [63]. However, after decades of work, the strategies outlined above are unlikely to be suitable for the task. Additive manufacturing (AM), which is an evolving technology, enables the production of precisely customized porous scaffolds with complicated structures utilizing a layer-by-layer procedure based on a ‘computer-aided design (CAD)’ without the use of special tooling. The mechanical strength of a scaffold can be attained by designing materials with appropriate porosities and pore sizes [64]. To make porous ceramics perform better, fused deposition has been used. In one case, the initial material filament was created from silicon. A composite with a compressive strength of 689 ± 795 MPa was created using pressureless reactive metal infiltration with aluminum.

13.4.2 Materials used to fabricate porous ceramics

Affordable and traditional materials such as alumina or zirconia have been investigated as suitable materials with which to produce filters for utilization in water filtration. Naturally derived materials such as zeolites, clays, quartz, apatite, and industrial wastes are among the low-cost resources used. Materials made from unprocessed alumina and silica are commonly employed as affordable precursors in the production of inorganic filtration membranes but achieving high performance levels at low cost is still a major issue [65].

13.4.2.1 Kaolin

There are many different types of clay, each with its own mechanical, chemical, and physical features. Kaolinite, illite, and montmorillonite are the most common clay minerals [66]. Clays are abundantly available around the world and require very little processing before they can be used to prepare membranes. As a result, major efforts have been undertaken to prepare less expensive ceramic membranes using

various clay types, due to the mechanical strength and pore architectures that can be attained after heat processing. Kaolin is the most common clay type; its mineral form is kaolinite. As a result, kaolin is an important component of emerging low-cost MT and is particularly ideal for membrane production. Kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) is widely studied as the basic parent material used to produce filters in inorganic membranes, such as those used in microfiltration [67], support [68], and ultrafiltration layers [69]. Kaolin has a particle size that is small enough for membrane manufacture [65].

13.4.2.2 Zeolite minerals

Hydrated aluminosilicates $[(\text{SiO}_2)(\text{AlO}_2)_x]\text{M}_y\text{H}_2\text{O}$ make up the majority of naturally occurring zeolite minerals. The three-dimensional framework structure of these natural materials is characterized by nanoscale porosity [70]. Zeolites are found in a variety of rocks, although they are most prevalent in volcanic elastic sediments, which contain the largest and purest deposits. They are used in a variety of industries, including water treatment, construction, catalysis, agriculture, and medical applications [71]. Grinding, shaping, and sintering are all procedures used in the fabrication of natural zeolite membranes to obtain durable bulk materials with the required aluminosilicate phases. Roque-Malherbe *et al* [72] exploited 'natural zeolite' to make permeable backing layers for membranes.

13.4.2.3 Hydroxyapatite

Hydroxyapatite (HAp) occurs naturally and has applications in the pharmaceutical, chemical, environmental, and biological industries. In the context of water treatment, hydroxyapatite can be used for HM removal from WW using a cation exchange method in which Ca^{2+} replaces the metal ions. HAp is not only efficient in adsorbing metal pollutants and dyes, but it can also adsorb anionic and cationic dyes effectively [73]. In addition, HAp can be produced from waste materials or obtained through naturally deposited low-cost forms [74, 84–99]. To date, studies have demonstrated that naturally obtained minerals are cheaper than synthetic materials in the production of hydroxyapatite-based microfiltration membranes [75, 76].

Apart from dyes and metals, there are emerging pollutants with structures that are highly stable and whose effects are completely unknown. The common emerging pollutants are pharmaceuticals, cosmetics, pesticides, and herbicides. Various secondary and primary treatment processes are less efficient in removing these pollutants. Adsorption using HAp has been shown to have a significant impact in removing pollutants. For instance, HAp sourced from codfish bones and treated with titanium salt has been used to degrade pollutants. The results of a study showed that HAp had a superior adsorption capacity of more than 90% [77].

13.4.2.4 Quartz sand

Quartz sand occurs naturally in sedimentary rock; its constituent is crystalline silica (SiO_2). Quartz is one of the most plentiful and extensively dispersed minerals on the planet [78], since chemical and mechanical weathering has no impact on it. Sands made up almost entirely of quartz grains have occasionally been deposited by

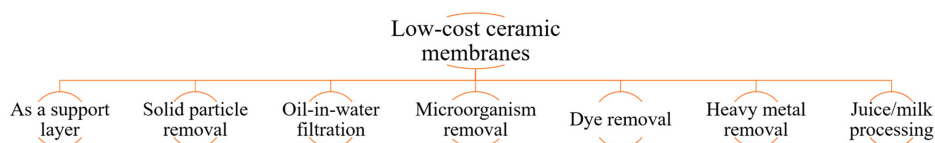


Figure 13.6. Applications of low-cost membranes.

geological processes. These deposits have been discovered to be high-quality silica sand sources. In their natural state, silica sands are known for their chemical uniformity and great purity. Several investigations into the production of filtration membranes produced from quartz sand have been carried out [79].

13.4.2.5 Bauxite

This is a sedimentary rock mostly composed of aluminum minerals, with an estimated global reserve of 55–75 billion tons [80]. The predominant high-temperature residue of bauxite is alumina, along with certain additional Fe and silicon oxides. Bauxite is classified as an alumina precursor that contains some contaminants (in the form of impurities), which are similarly possible contenders for membrane manufacture.

13.5 Industrial applications of membranes for water treatment

MT has numerous applications owing to its cost-effectiveness and simplicity compared to other filtration technologies such as absorption, distillation, and adsorption [81]. The development of innovative technologies to purify water before it is discharged or used is necessitated by water pollution caused by industrial growth, as well as limited access to fresh water. MT is unquestionably one of the most successful methods for treating WW and desalinating saltwater. Low-cost membranes produced from various natural sources and wastes have been widely used for water filtration applications. According to several research studies, low-cost membranes are mainly used for support layers, oil droplet separators, dye removal for the textile industry, microfiltration, and ultrafiltration membranes, as shown in figure 13.6 (adapted from [65]).

Most research into the fabrication of less expensive membranes has focused on the production of a support layer and then covered the support layer with another active layer for additional ultrafiltration, microfiltration, or even desalination applications [82]. Low-cost membranes are used to separate water–oil mixtures, which is one of the most explored water treatment challenges.

13.6 Issues that need to be resolved and possible solutions

The presented treatment techniques have been found to have the potential to improve tannery effluent quality to a great extent. However, there are some challenges caused by the treatment plants, including high salinity and Cr pollution. The real problem arises from the by-products of the treatment, which require advanced segregation techniques. These by-products include adsorbents,

Cr-containing sludge, deposits, etc. which are usually poorly managed, yet they are extremely hazardous. Given the cost of treatment, the Cr content is usually moved to landfill treatment, which causes a significant transfer of pollution.

The reuse or recycling of the by-products is more desirable for various industrial applications than conventional landfill. Strategies such as the use of novel Cr tanning agent carriers, chrome-free organic tanning agents, and Cr exhaustion are examples of ways in which Cr segregation can be eliminated from Cr pollution in the WW treatment processes. High salinity is another serious problem caused by tannery WW treatment, since it undermines the whole treatment process. Several efforts have been made to reduce this effect using biological treatment, membrane filtration, and electrochemical treatment using promising techniques. However, the treated tannery WW still has high salinity and requires post-treatments that include RO, electrodialysis, and electro-deionization [83].

13.7 Conclusions

This chapter evaluated the different pollutants found in tannery WW and the use of different purification techniques in the removal of HMs and industrial effluents. The pollutants in tannery WW include TN, total phosphorus, chloride ions, and sulfur-containing composites; excessive concentrations of these pollutants have significant effects on humans and the environment. This chapter summarized the various methods used for the removal of tannery WW contaminants. Flocculation and coagulation are effective techniques for removing particulates and impurities. Flotation is also used to remove particles. Ion exchange is used in HM removal due to its high treatment capacity, quick kinetics, and high removal efficiency. Adsorption and membrane filtration are the most practical and cost-effective methods for treating HMs in tannery effluent. The merit of these techniques include reliability, low consumption, ease of operation, and excellent pollution removal efficiency. This chapter also presented the application of RSM techniques for WW treatment. The RSM helps in the determination of the optimum conditions needed to maximize the removal efficiency and the interaction between the factors, which can be seen in the graphical illustrations and the models. As seen from the reviewed papers, large amounts of information can be obtained from very few experimental runs, and this results in low production costs and time savings. The response surface techniques aid in optimizing the important variables and in finding the appropriate combination of process factors (e.g. coagulant dose, pH, and initial concentration). This chapter also provided a detailed explanation of various techniques used in the synthesis of porous ceramics, the raw materials used, and the industrial applications of MT. It highlighted the potential for the utilization of porous ceramics in the treatment of tannery WW.

References and further reading

- [1] Zhao C and Chen W 2019 A review for tannery wastewater treatment: some thoughts under stricter discharge requirements *Environ. Sci. Pollut. Res* **26** 26102–111

- [2] Akan J C, Abdulrahman F I, Ayodele J T and Ogugbuaja V O 2009 Impact of tannery and textile effluent on the chemical characteristics of Challawa River, Kano State, Nigeria *Aust. J. Basic Appl. Sci.* **3** 1933–47
- [3] Chen Y, Wang N, Ola O, Xia Y and Zhu Y 2021 Porous ceramics: light in weight but heavy in energy and environment technologies *Mater. Sci. Eng.: R: Rep.* **143** 100589
- [4] Gutierrez M, Benvenuti J and Fontocra J T 2015 Characterisation of raw wastewater from tanneries *J. Soc. Leather Technol. Chem.* **99** 280–7
- [5] Cooman K, Gajardo M, Nieto J, Bornhardt C and Vidal G 2003 Tannery wastewater characterization and toxicity effects on *Daphnia* spp *Environ. Toxicol.: An Inter. J* **18** 45–51
- [6] Fawell J and Nieuwenhuijsen M J 2003 Contaminants in drinking water environmental pollution and health *Br. Med. Bull.* **68** 199–208
- [7] World Health Organization, WHO, and World Health Organisation Staff 2004 *Guidelines for Drinking-Water Quality* (Geneva: World Health Organization)1 <https://www.who.int/publications/i/item/9789241549950>
- [8] Zhang Y, Yang Q, Gao H, Zhao Y, Tang X, Zhao C and Fang C 2021 Application of a modified biological flocculant in total nitrogen treatment of leather wastewater *Water Sci. Technol.* **83** 2901–10
- [9] Li H 2014 Study on treatment of tannery wastewater and chromium sludge for Cr (III) recovery *Doctoral Dissertation* (Harbin: Harbin Institute of Technology)
- [10] Sitko R, Janik P, Zawisza B, Talik E, Margui E and Queralt I 2015 Green approach for ultratrace determination of divalent metal ions and arsenic species using total-reflection X-ray fluorescence spectrometry and mercapto-modified graphene oxide nanosheets as a novel adsorbent *Anal. Chem.* **87** 3535–42
- [11] Srivastava N K and Majumder C B 2008 Novel biofiltration methods for the treatment of heavy metals from industrial wastewater *J. Hazard. Mater.* **151** 1–8
- [12] Žak S 2012 Treatment of the processing wastewaters containing heavy metals with the method based on flotation *Ecol. Chem. Eng. S* **19** 433–8
- [13] Ismail M G, Weng C N, Rahman H A and Zakaria N A 2013 Freundlich isotherm equilibrium equations in determining effectiveness a low cost absorbent to heavy metal removal in wastewater (leachate) at Teluk Kitang Landfill, Pengkalan Chepa, Kelantan, Malaysia *J Geogr Earth Sci.* **1** 1–8
- [14] Nair A T, Makwana A R and Ahammed M M 2014 The use of response surface methodology for modelling and analysis of water and wastewater treatment processes: a review *Water Sci. Technol.* **69** 464–78
- [15] Montgomery D C 2017 *Design and Analysis of Experiments* (New York: Wiley)
- [16] Box G E and Wilson K B 1951 On the experimental designs for exploring response surfaces *Ann. Math. Stat* **13** 1–45
- [17] Wang J P, Chen Y Z, Ge X W and Yu H Q 2007 Optimization of coagulation–flocculation process for a paper-recycling wastewater treatment using response surface methodology *Colloids Surf., A* **302** 204–10
- [18] Moghaddam S S, Moghaddam M A and Arami M 2010 Coagulation/flocculation process for dye removal using sludge from water treatment plant: optimization through response surface methodology *J. Hazard. Mater.* **175** 651–7
- [19] Liu X, Li X M, Yang Q, Yue X, Shen T T, Zheng W, Luo K, Sun Y H and Zeng G M 2012 Landfill leachate pretreatment by coagulation–flocculation process using iron-based coagulants: optimization by response surface methodology *Chem. Eng. J.* **200** 39–51

- [20] Mensah-Akutteh H, Buamah R, Wiafe S and Nyarko K B 2022 Optimizing coagulation–flocculation processes with aluminium coagulation using response surface methods *Appl. Water Sci.* **12** 188
- [21] Iber B T, Torsabo D, Chik C E N C E, Wahab F, Sheikh Abdullah S R, Abu Hassan H and Kasan N A 2023 Response surface methodology (RSM) approach to optimization of coagulation-flocculation of aquaculture wastewater treatment using chitosan from carapace of giant freshwater prawn *Macrobrachium rosenbergii* *Polymers* **15** p 1058
- [22] Kang K C, Kim S S, Choi J W and Kwon S H 2008 Sorption of Cu^{2+} and Cd^{2+} onto acid- and base-pretreated granular activated carbon and activated carbon fiber samples *J. Ind. Eng. Chem.* **14** 131–5
- [23] Jusoh A, Shiung L S, Ali N and Noor M J M M 2007 A simulation study of the removal efficiency of granular activated carbon on cadmium and lead *Desalination* **206** 9–16
- [24] Li Y, Liu F, Xia B, Du Q, Zhang P, Wang D, Wang Z and Xia Y 2010 Removal of copper from aqueous solution by carbon nanotube/calcium alginate composites *J. Hazard. Mater.* **177** 876–80
- [25] Pillay K, Cukrowska E M and Coville N J 2009 Multi-walled carbon nanotubes as adsorbents for the removal of parts per billion levels of hexavalent chromium from aqueous solution *J. Hazard. Mater.* **166** 1067–75
- [26] Metcalf & Eddy Inc. 2003 *Wastewater engineering: treatment and resource recovery* (New Delhi: Tata McGraw-Hill Education) 5th
- [27] Yang Y, Li X, Gu Y, Lin H, Jie B, Zhang Q and Zhang X 2022 Adsorption property of fluoride in water by metal organic framework: optimization of the process by response surface methodology technique *Surf. Interfaces* **28** 101649
- [28] Nguyen V T, Nguyen T B, Dat N D, Huu B T, Nguyen X C, Tran T, Bui M H, Dong C D and Bui X T 2022 Adsorption of norfloxacin from aqueous solution on biochar derived from spent coffee ground: master variables and response surface method optimized adsorption process *Chemosphere* **288** 132577
- [29] Mourabet M, El Rhilassi A, El Boujaady H, Bennani-Ziatni M and Taitai A 2017 Use of response surface methodology for optimization of fluoride adsorption in an aqueous solution by Brushite *Arabian J. Chem.* **10** S3292–302
- [30] Iqbal M, Iqbal N, Bhatti I A, Ahmad N and Zahid M 2016 Response surface methodology application in optimization of cadmium adsorption by shoe waste: a good option of waste mitigation by waste *Ecol. Eng.* **88** 265–75
- [31] Murthy Z V and Chaudhari L B 2009 Separation of binary heavy metals from aqueous solutions by nanofiltration and characterization of the membrane using Spiegler–Kedem model *Chem. Eng. J.* **150** 181–7
- [32] Nguyen C M, Bang S, Cho J and Kim K W 2009 Performance and mechanism of arsenic removal from water by a nanofiltration membrane *Desalination* **245** 82–94
- [33] Ahmad A L and Ooi B S 2010 A study on acid reclamation and copper recovery using low pressure nanofiltration membrane *Chem. Eng. J.* **156** 257–63
- [34] Muthukrishnan M and Guha B K 2008 Effect of pH on rejection of hexavalent chromium by nanofiltration *Desalination* **219** 171–8
- [35] Yang Z, Zhou Y, Feng Z, Rui X, Zhang T and Zhang Z 2019 A review on reverse osmosis and nanofiltration membranes for water purification *Polymers* **11** 1252
- [36] Waqas S, Harun N Y, Bilal M R, Samsuri T, Nordin N A, Shamsuddin N, Nandiyanto A B, Huda N and Roslan J 2022 Response surface methodology for optimization of rotating

- biological contactor combined with external membrane filtration for wastewater treatment *Membranes* **12** 271
- [37] Wang M, Liu C, Fan M, Liu M and Shen S 2022 Optimization of nanofiltration hollow fiber membrane fabrication process based on response surface method *Membranes* **12** 374
- [38] Maher A, Sadeghi M and Moheb A 2014 Heavy metal elimination from drinking water using nanofiltration membrane technology and process optimization using response surface methodology *Desalination* **352** 166–73
- [39] Goyal R K, Jayakumar N S and Hashim M A 2011 A comparative study of experimental optimization and response surface optimization of Cr removal by emulsion ionic liquid membrane *J. Hazard. Mater.* **195** 383–90
- [40] Zhou W, Wu P, Zhang L, Zhu D, Zhao X and Cai Y 2022 Heavy metal ions and particulate pollutants can be effectively removed by a gravity-driven ceramic foam filter optimized by carbon nanotube implantation *J. Hazard. Mater.* **421** 126721
- [41] Saja S, Bouazizi A, Achiou B, Ouammou M, Albizane A, Bennazha J and Younssi S A 2018 Elaboration and characterization of low-cost ceramic membrane made from natural Moroccan perlite for treatment of industrial wastewater *J. Environ. Chem. Eng.* **6** 451–8
- [42] Ohji T and Fukushima M 2012 Macro-porous ceramics: processing and properties *Int. Mater. Rev.* **57** 115–31
- [43] Twigg M V and Richardson J T 2007 Fundamentals and applications of structured ceramic foam catalysts *Ind. Eng. Chem. Res.* **46** 4166–77
- [44] Obada D O *et al* 2021 Fabrication of novel kaolin-reinforced hydroxyapatite scaffolds with robust compressive strengths for bone regeneration *Appl. Clay Sci.* **215** 106298
- [45] Obada D O *et al* 2021 Solution combustion synthesis of strontium-doped hydroxyapatite: effect of sintering and low compaction pressure on the mechanical properties and physiological stability *Mater. Lett.* **304** 130613
- [46] Salami K A, Obada D O, Alabi A A, Csaki S and Oyediji A N 2022 Utilization of sawdust as a pore-former in the fabrication of ceramic adsorbents for water purification *J. Aust. Ceram. Soc.* **58** 1297–309
- [47] Gregorová E, Pabst W, Sofer Z, Jankovský O and Matějček J 2012 Porous alumina and zirconia ceramics with tailored thermal conductivity *J. Phys.: Conf. Ser.* **395** 012022
- [48] Darus F, Isa R M, Mamat N and Jaafar M 2018 Techniques for fabrication and construction of three-dimensional bioceramic scaffolds: effect on pores size, porosity and compressive strength *Ceram. Int.* **44** 18400–7
- [49] Jean G, Sciamanna V, Demuyneck M, Cambier F and Gonon M 2014 Macroporous ceramics: novel route using partial sintering of alumina-powder agglomerates obtained by spray-drying *Ceram. Int.* **40** 10197–203
- [50] Guo Q, Xiang H, Sun X, Wang X and Zhou Y 2015 Preparation of porous YB4 ceramics using a combination of *in situ* borothermal reaction and high temperature partial sintering *J. Eur. Ceram. Soc.* **35** 3411–8
- [51] Kim M, Franco R A and Lee B T 2011 Synthesis of functional gradient BCP/ZrO₂ bone substitutes using ZrO₂ and BCP nanopowders *J. Eur. Ceram. Soc.* **31** 1541–8
- [52] Gómez S Y, Alvarez O A, Escobar J A, Rodrigues Neto J B, Rambo C R and Hotza D 2012 Relationship between Rheological Behaviour and Final Structure of Al₂O₃ and YSZ Foams Produced by Replica *Adv. Mater. Sci. Eng.* **2012** 549508

- [53] Bucharsky E C, Schell K G, Oberacker R and Hoffmann M J 2010 Preparation of transparent glass sponges via replica method using high-purity silica *J. Am. Ceram. Soc.* **93** 111–4
- [54] Sarhadi F, Shafiee Afarani M, Mohebbi-Kalhor D and Shayesteh M 2016 Fabrication of alumina porous scaffolds with aligned oriented pores for bone tissue engineering applications *Appl. Phys. A* **122** 1–8
- [55] Studart A R, Gonzenbach U T, Tervoort E and Gauckler L J 2006 Processing routes to macroporous ceramics: a review *J. Am. Ceram. Soc.* **89** 1771–89
- [56] Petit C, Meille S, Maire E, Tadier S and Adrien J 2016 Mechanical behaviour of a β -TCP ceramic with a random porosity: study of the fracture path with x-ray tomography *J. Eur. Ceram. Soc.* **36** 3225–33
- [57] McNamara S L, Rnjak-Kovacina J, Schmidt D F, Lo T J and Kaplan D L 2014 Silk as a biocohesive sacrificial binder in the fabrication of hydroxyapatite load bearing scaffolds *Biomaterials* **35** 6941–53
- [58] Zhang L, Mao Z, Thomason J D, Wang S and Huang K 2012 Synthesis of a homogeneously porous solid oxide matrix with tunable porosity and pore size *J. Am. Ceram. Soc.* **95** 1832–7
- [59] Konegger T, Williams L F and Bordia R K 2015 Planar, polysilazane-derived porous ceramic supports for membrane and catalysis applications *J. Am. Ceram. Soc.* **98** 3047–53
- [60] Pokhrel A, Seo D N, Lee S T and Kim I J 2013 Processing of porous ceramics by direct foaming: a review *J. Korean Ceram. Soc.* **50** 93–102
- [61] Barg S, Soltmann C, Andrade M, Koch D and Grathwohl G 2008 Cellular ceramics by direct foaming of emulsified ceramic powder suspensions *J. Am. Ceram. Soc.* **91** 2823–9
- [62] Zhang L Y, Zhou D L, Chen Y, Liang B and Zhou J B 2014 Preparation of high open porosity ceramic foams via direct foaming molded and dried at room temperature *J. Eur. Ceram. Soc.* **34** 2443–52
- [63] Butscher A, Böhner M, Hofmann S, Gauckler L and Müller R 2011 Structural and material approaches to bone tissue engineering in powder-based three-dimensional printing *Acta Biomater.* **7** 907–20
- [64] Bose S and Das C 2013 Preparation and characterization of low cost tubular ceramic support membranes using sawdust as a pore-former *Mater. Lett.* **110** 152–5
- [65] Abdullayev A, Bekheet M F, Hanaor D A and Gurlo A 2019 Materials and applications for low-cost ceramic membranes *Membranes* **9** 105
- [66] Rhodes D 2015 *Clay and Glazes for the Potter*. (Ravenio Books)
- [67] Jana S, Purkait M K and Mohanty K 2010 Preparation and characterization of low-cost ceramic microfiltration membranes for the removal of chromate from aqueous solutions *Appl. Clay Sci.* **47** 317–24
- [68] Zhou J, Zhang X, Wang Y, Larbot A and Hu X 2010 Elaboration and characterization of tubular macroporous ceramic support for membranes from kaolin and dolomite *J. Porous Mater.* **17** 1–9
- [69] Ali M B, Hamdi N, Rodriguez M A, Mahmoudi K and Srasra E 2018 Preparation and characterization of new ceramic membranes for ultrafiltration *Ceram. Int.* **44** 2328–35
- [70] Kalló D 2001 Applications of natural zeolites in water and wastewater treatment *Rev. Mineral. Geochem.* **45** 519–0
- [71] Hay R L 1986 Geologic occurrence of zeolites and some associated minerals *Studies in Surface Science and Catalysis* (Amsterdam: Elsevier) 28 35–40

- [72] Roque-Malherbe R, Del Valle W, Marquez F, Duconge J and Goosen M F 2006 Synthesis and characterization of zeolite based porous ceramic membranes *Sep. Sci. Technol.* **41** 73–96
- [73] Bensalah H, Bekheet M F, Younssi S A, Ouammou M and Gurlo A 2017 Removal of cationic and anionic textile dyes with Moroccan natural phosphate *J. Environ. Chem. Eng.* **5** 2189–99
- [74] Bensalah H, Bekheet M F, Younssi S A, Ouammou M and Gurlo A 2018 Hydrothermal synthesis of nanocrystalline hydroxyapatite from phosphogypsum waste *J. Environ. Chem. Eng.* **6** 1347–52
- [75] Masmoudi S, Larbot A, El Feki H and Amar R B 2006 Elaboration and properties of new ceramic microfiltration membranes from natural and synthesised apatite *Desalination* **190** 89–103
- [76] Masmoudi S, Larbot A, El Feki H and Amar R B 2007 Elaboration and characterisation of apatite based mineral supports for microfiltration and ultrafiltration membranes *Ceram. Int.* **33** 337–44
- [77] Brazón E M *et al* 2016 Photodegradation of pharmaceutical persistent pollutants using hydroxyapatite-based materials *J. Environ. Manage.* **182** 486–95
- [78] Bates R L and Jackson J A 1987 *Glossary of Geology* (Alexandria, VA: American Geological Institute) 788–865
- [79] Foughali L, Barama S, Harabi A, Bouzerara F, Guechi A and Boudaira B 2016 Effect of sodium phosphate addition on mechanical properties of porous Sigue quartz sand *Desalin. Water Treat.* **57** 5286–91
- [80] Yao Z T, Ji X S, Sarker P K, Tang J H, Ge L Q, Xia M S and Xi Y Q 2015 A comprehensive review on the applications of coal fly ash *Earth Sci. Rev.* **141** 105–21
- [81] Marchetti P, Jimenez Solomon M F, Szekely G and Livingston A G 2014 Molecular separation with organic solvent nanofiltration: a critical review *Chem. Rev.* **114** 10735–806
- [82] Dong Y, Ma L, Tang C Y, Yang F, Quan X, Jassby D, Zaworotko M J and Guiver M D 2018 Stable superhydrophobic ceramic-based carbon nanotube composite desalination membranes *Nano Lett.* **18** 5514–21
- [83] Zhao J, Wu Q, Tang Y, Zhou J and Guo H 2022 Tannery wastewater treatment: conventional and promising processes, an updated 20-year review *J. Leather Sci. Eng.* **4** 10
- [84] Akpan E S, Dauda M, Kuburi M, Obada L S and D O 2021 Box–Behnken experimental design for the process optimization of catfish bones derived hydroxyapatite: a pedagogical approach *Mater. Chem. Phys.* **272** 124916
- [85] Akpan E S, Dauda M, Kuburi L S, Obada D O and Dodoo-Arhin D 2020 A comparative study of the mechanical integrity of natural hydroxyapatite scaffolds prepared from two biogenic sources using a low compaction pressure method *Results Phys.* **17** 103051
- [86] Akpan E S, Dauda M, Kuburi L S and Obada D O 2020 A facile synthesis method and fracture toughness evaluation of catfish bones-derived hydroxyapatite *MRS Adv.* **5** 1357–66
- [87] Akpan E S, Dauda M, Kuburi L S, Obada D O, Bansod N D and Dodoo-Arhin D 2021 Hydroxyapatite ceramics prepared from two natural sources by direct thermal conversion: from material processing to mechanical measurements *Mater. Today Proc.* **38** 2291–4
- [88] Obada D O *et al* 2023 Hydroxyapatite materials-synthesis routes, mechanical behavior, theoretical insights, and artificial intelligence models: a review *J. Aust. Ceram. Soc.* **59** 565–96
- [89] Obada D O, Dauda E T, Abifarin J K, Dodoo-Arhin D and Bansod N D 2020 Mechanical properties of natural hydroxyapatite using low cold compaction pressure: effect of sintering temperature *Mater. Chem. Phys.* **239** 122099

- [90] Osuchukwu O A, Salihi A, Abdullahi I and Obada D O 2022 Taguchi grey relational optimization of sol–gel derived hydroxyapatite from a novel mix of two natural biowastes for biomedical applications *Sci. Rep.* **12** p 17968
- [91] Osuchukwu O A, Salihi A, Abdullahi I, Etinosa P O and Obada D O 2023 Weibull modulus of a novel mixture of natural hydroxyapatite materials produced from biowastes *Res. Mater.* **18** p 100394
- [92] Osuchukwu O A, Salihi A, Abdullahi I, Etinosa P O and Obada D O 2023 A comparative study of the mechanical properties of sol–gel derived hydroxyapatite produced from a novel mixture of two natural biowastes for biomedical applications *Mater. Chem. Phys.* **297** p 127434
- [93] Osuchukwu O A, Salihi A, Abdullahi I and Obada D O 2022 Experimental data on the characterization of hydroxyapatite produced from a novel mixture of biowastes *Data in Brief* **42** p 108305
- [94] Osuchukwu O A, Salihi A, Abdullahi I and Obada D O 2022 Synthesis and characterization of sol–gel derived hydroxyapatite from a novel mix of two natural biowastes and their potentials for biomedical applications *Mater. Today Proc.* **62** pp 4182–7
- [95] Obada D O *et al* 2022 Trends in the development of hydroxyapatite from natural sources for biomedical applications *WIT Trans. Ecol. Environ.* **257** 199–210
- [96] Akpan E S, Dauda M, Kuburi L S and Obada D O 2023 Bio-inspired synthesis of hydroxyapatite materials from two natural sources: a crack behavior and biological insight *J. Aust. Ceram. Soc.* **59** 511–9
- [97] Osuchukwu O A, Salihi A, Abdullahi I, Abdulkareem B and Nwannenna C S 2021 Synthesis techniques, characterization and mechanical properties of natural derived hydroxyapatite scaffolds for bone implants: a review *SN Appl. Sci.* **3** pp 1–23
- [98] Abifarin J K, Obada D O, Dauda E T and Dodoo-Arhin D 2019 Experimental data on the characterization of hydroxyapatite synthesized from biowastes *Data Brief* **26** p 104485
- [99] Obada D O, Dauda E T, Abifarin J K, Bansod N D and Dodoo-Arhin D 2021 Mechanical measurements of pure and kaolin reinforced hydroxyapatite-derived scaffolds: a comparative study *Mater. Today Proc.* **38** pp 2295–300