EEET ECOLOGICAL ENGINEERING & ENVIRONMENTAL TECHNOLOGY

Ecological Engineering & Environmental Technology 2024, 25(2), 41–53
https://doi.org/10.12912/27197050/175201
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Received: 2023.11.03
Accepted: 2023.12.15
Published: 2024.01.01

Optimization of Chromium Removal from Tannery Effluents with the Neonite Natural Zeolite

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ABSTRACT

Chromium is the main constituent of the tanning salts used by tanneries for processing skins into leather, and considered as a pollutant in the effluents that this industry discharge. The present study aimed to evaluate the removal of chromium and other pollutants in effluents from the tanning industry applying the natural zeolite Neonite. Neonite is a commercially available zeolite, which was acquired from NEONITE S.A. Neonite was characterized through FTIR and XRD, identifying clinoptilolite as its main component. Treatment was applied to the samples of real effluents from the tanning stage or chromium bath (CB) and a composite effluent (CE), an experimental design was carried out for each effluent. The designs correspond to 3^2 factorial designs, the variables tested were the Neonite dosage (NE) measured in g/L, stirring time (StT) expressed in minutes and the pH of the sample, and the response variable was the residual chromium content (RCC). Statistical analysis was performed through R-software version 4.2.3 and included Box-Cox transformation and ANOVA to determine the main effects and the behavior of the response variable in relation to the applied model and its optimization by response surface. In CB, a removal above 95% was obtained for RCC, with optimization values at 32 g/L of NE and pH 7. In the CE, a removal of more than 98% was obtained for RCC and values higher than 60% for BOD, COD, TSS and Fats, being the optimal conditions 4.73 g/L of NE and 12.17 minutes of StT. These results demonstrate that the application of Neonite for the removal of chromium and other pollutants from tanning industry effluents has a great potential.

Keywords: Clinoptilolite, Neonite, tannery wastewater, wastewater treatment, zeolite.

INTRODUCTION

The leather and footwear productive chain is a major source of employment in Peru, counting 45557 workers in this industry in 2018, which constituted 4.6% of the economically active population from manufacturing sector. It has been mainly developed in three regions of this country, Lima, Trujillo and Arequipa [Cosavalente, 2019]. One of the main challenges for this industry is the accomplishment of the environmental standards stablished for this sector, where wastewater quality is one the most worrying tasks. Wastewater quality is closely related to the physicochemical characteristics of the chemical products applied at each stage of the tanning process. Agents such as chromium basic sulfate, vegetable tannins, glutaraldehyde, syntans, and other mineral tanning agents like aluminum or titanium salts are widely used during the tanning stage [Chowdhury et al., 2013; Zhang et al., 2016].

One of the advantages that determine the efficacy of a substance as tanning agent, is its capacity to form stable bonds with collagen, the main constituent protein of skin. This bond is the key in transforming the skin into leather, obtaining properties of resistance to bacteria and fungi and thermal resistance [Rahme and Hartman, 2012], which make leather an incredibly versatile material for garment, footwear and other leather goods. Chromium basic sulfate is the main tanning agent due to the good properties and characteristics it grants to the leather when compared to other agents, which make this salt the most used tanning agent in many countries, like Peru [Mann and McMillan, 2017]. This salt is applied on tanning stage, where it adheres to skin through cross-linking process in a percent of 60% to 80%, so the excess salts are discharged with effluents.

However, the chromium, the main constituent of this salt, is a substance that can cause major environmental and health issues. In the tanning salt, chromium is present in the form of Cr(III), but there is evidence that under certain environmental conditions it can oxidize into Cr(VI) [Mohamed et al., 2020; Mou et al., 2021; Xu et al., 2020], this is characterized because of its capacity to cross through cell membrane [Kim et al., 2018; Pavesi and Moreira, 2020]. There is a possibility that Cr(VI) can be found on tannery wastewater from tanning stage, but, previous studies demonstrated that, when the chromium basic sulfate is correctly applied and controlled on tanning process, the content of Cr(VI) is found to be below the detection levels of instrumental characterization (< 0.005 mg/L) [Aguilar-Ascón et al., 2019]. The content of chromium of the tanning stage effluent is usually measured as total chromium; this evaluates the content of chromium in all its chemical forms, but considering the Cr(VI) content is below detection levels, the result is mainly constituted by Cr(III). Because of the toxicity of chromium, its content in effluents discharged is controlled by Peruvian environmental normative, total chromium must not exceed 0.5 mg/L for discharges on freshwater and 10 mg/L for discharges on sewage system [Decreto Supremo Que Aprueba El Reglamento de Valores Máximos Admisibles (VMA) Para Las Descargas de Aguas Residuales No Domésticas En El Sistema de Alcantarillado Sanitario, 2019]. Thus, the importance for tanneries to include wastewater technology to remove chromium (and other parameters, such as BOD, COD, TSS, fats, ammonia), in order to discharge them, simultaneously accomplishing the environmental standards for freshwater and sewage system. In this country, given the difference between tanneries, associated to different production levels, low infrastructure and geographic dispersion, it is necessary for treatment alternatives to be compact and complementary to other technologies, ensuring compliance of environmental standards. Adsorption is a primary treatment technology, characterized by its high efficiency in removal of pollution load [Margeta et al., 2013]. Among the main adsorbents applied in wastewater treatment, zeolites stand out because of their ion-exchange and sorbent properties, which facilitate the removal of metal ions. Zeolites can be chemically modified by inorganic salts or organic surfactants, which enables zeolites to also remove anions. Other properties of zeolites are its selectivity for different cations, cheap cost and easy application.

Zeolites are crystalline aluminosilicates with a three-dimensional anionic structure of tetrahedral TO_4, where "T" can be Si or Al. The zeolite framework structure contains interconnected voids occupied by charge balancing ions and water molecules. These water molecules can be bonded between framework ions and exchangeable ions via aqueous bridges. Additionally, water can serve as a bridge between the exchangeable cations. Because of its unique physicochemical properties of crystallinity, thermal stability, well-defined cage structure of molecular size and ion-exchange, zeolites have been used as heavy metal adsorbents, as chemical sieves and as water softeners [El-Kammar et al., 2015]. Clinoptilolite is one the most common zeolites, suitable as adsorbent due to its natural characteristics. It is characterized because of the presence of primary porosity (micropores), generated by the crystalline structure of mineral grains of zeolite, while secondary porosity is related with the size of zeolite and other mineral grains. Midpores are active surfaces for catalysis, transport channels and for adsorption of relatively large molecules [Mansouri et al., 2013].

The effect of zeolites in chromium removal from tannery wastewater has been evaluated in previous studies, most of them in synthetic samples. As reported in review articles, Toprak and Girgin evaluated the effect of acid activated clinoptilolite on chromium removal from effluents of tanning stage. In the tests, the chromium content was diluted to 100 mg/L. In 2005, Covarrubias et al. conducted a chromium ion-exchange study to evaluate the effect of natural and synthetic zeolites, and other factors as pH and expectant ions, obtaining that synthetic zeolites were more effective. In continuation of their studies, Covarrubias et al. designed a process to synthesize zeolite from mordenite, producing an efficient ion-exchanger for tannery wastewater treatment [Dimos et al., 2012]. Chung et al. evaluated the effect of clinoptilolite on the removal of ammonia and other organic substances, applying regeneration and recirculation of zeolite [Morante-Carballo et al., 2021]. Other studies reported the removal of chromium from synthetic chromium solutions of 100 ppm [Misaelides, 2011]. Córdova-Rodríguez et al. applied natural mordenite from Palmarito de Cauto deposit as an ion exchanger in the removal of Cr^{+3} cations from aqueous alkaline synthetic chromium solutions. In their analysis of previous results, the increase in pH to values close to neutral, also increase chromium removal capacity, associated to adsorption and chromium precipitation. As a result, mordenite removed chromium, independently of the chromium initial concentration and the pH of the solutions [Córdova-Rodríguez et al., 2016]. Sallam et al. synthetized a polymer-zeolite composite applying clinoptilolite. The composite was analyzed through XRD and FTIR and were applied in the removal of chromium from composite effluents, the composite dosage went from 1 to 10 g/L [Sallam et al., 2017]. Díaz and Ayele et al. developed a process for the treatment of tanning stage wastewater, effluent characterized by its high content of chromium, where synthetic zeolites were compared to natural zeolites. As a result, a high removal of chromium was achieved applying synthetic zeolites, with a dosage between 2 to 100 g/L [Ayele et al., 2018; Díaz, 2017]. Aljerf evaluated the mix of clinoptilolite and tannery solid wastes for tannery waste water treatment, emphasizing the removal of chromium and bromocresol purple through an adsorption study, then optimized the results applying a factorial design; hence, determined the optimal liquid-solid ratio [Aljerf, 2018]. Boldrini et al. developed a chemical stabilization process of the tanning stage effluents, applying them as raw material to produce a new kaolinite geopolymer [Boldrini et al., 2021]. Álvarez et al. evaluated the removal of hexavalent chromium in the samples of synthetic and real effluent, applying natural and synthetic zeolites modified with NaOH and HCl. The better results were observed with natural zeolite modified with NaOH, achieving a removal of 45% in real effluent [Álvarez et al., 2021]. Considering the advances and characteristics of this technology, and the fact that a great number of tanneries on this country do not have enough resources to establish the technologies that require large spaces or infrastructure, it is important to determine the efficiency of adsorption with zeolites, as this technology has the potential to facilitate and become a main wastewater treatment that allows the accomplishment of the environmental standards in Peruvian tanneries.

The CITEccal Lima, is an institution responsible for providing technological support to the leather and footwear industry, had the opportunity to contact with Neonite S.A., a company that had successfully developed and applied the Neonite zeolite. Neonite is a commercially available zeolite that yields optimal results in textile effluent treatment. Due to the similar characteristics of these effluents, Neonite has the potential to also yield good results in the treatment of tannery effluents. As part of a collaborative effort, a sample of Neonite was acquired to assess its application in effluents from the tanning industry, with a focus on chromium removal. Chromium is one of the substances present in the tannery effluents that raises significant concerns. The objective was to provide these results to the companies in this sector as an alternative for the treatment of their effluents. Therefore, the present study evaluated the effect of zeolite Neonite in the removal of chromium from a composite effluent (mixture of effluents from soaking, unhairing, deliming and tanning stages) and effluent from tanning stage, treatment conditions were tested for each effluent and were optimized through a factorial design. Moreover, the removal efficacy for other parameters, such as BOD, COD, sulfides and ammonia were tested for optimal conditions in composite effluent.

METHODS

Sample

The present study analyzed two effluents from the tanning process of cow hide, the first a composite effluent (CE) from beamhouse operations and tanning stage and the second a sample of effluent from tanning stage, also known as chromium bath (CB). CB is characterized by its high chromium content, mainly constituted by Cr(III), acidic pH between 3 to 4 and intense blue coloration. On the other hand, CE is a mixture formed by proportional samples of effluents generated from soaking stage to tanning stage. Both samples of effluents were collected from the Tanning Pilot

Plant of CITEccal Lima, after a simple screening process to remove coarse solids.

Both samples were characterized, in the case of CB to determine its content of total chromium (EPA 200.8, Rev 5.4: 1994. Determination of trace elements in waters and wastes by inductively coupled plasma – mass spectrometry and CE was characterized for total chromium, biological oxygen demand (SMEWW-APHA-AWWA-WEF Part 5210 B; 23rd Ed: 2017. Biochemical oxygen demand (BOD): 5-day BOD test, chemical oxygen demand (SMEWW-APHA-AWWA-WEF Part 5220 D; 23rd Ed: 2017. Chemical oxygen demand, closed reflux, colorimetric method, total suspended solids (SMEWW-APHA-AWWA-WEF Part 2540-D; 23rd Ed: 2017. Solids: Total suspended solids dried at 103-105 °C), Fats (ASTM D3921 - 96 (Reapproved 2011). Standard test method for oil and grease and petroleum hydrocarbons in water), ammonia (SMEWW-APHA-AWWA-WEF Part 4500-NH3 D; 23rd Ed: 2017. Nitrogen (ammonia). Ammonia-selective electrode method) and sulfides (SMEWW-APHA-AWWA-WEF Part 4500-S2-I; 23rd Ed: 2017. Distillation, methylene blue flow injection analysis method).

Zeolite Neonite

Neonite is a natural zeolite modified with mineral salts and polymers [Terayama, 2013], obtaining as a result a product with a great capacity for the removal of pollutant load in effluents with different characteristics. The Neonite sample applied in this study (Neonite-MO-1) was acquired from NEONITE S.A. Zeolites applied in wastewater treatment, specific in removal of metal ions, work through two main processes, ion-exchange and adsorption.

Neonite was analyzed by Fourier transform infrared spectroscopy (FT-IR) using a spectrophotometer SHIMADZU QATR 10, through attenuated total reflectance (ATR). FT-IR analyses was performed on zeolite before and after effluent treatment, and spectra were measured in the range of 4000–400 cm^{-1}. Additionally, zeolite was also analyzed by X-ray diffraction (XRD) using a D8 Advance Bruker diffractometer at 40 kV and 40 mA.

Preliminary tests

Preliminary tests were carried out to evaluate the behavior of Neonite on CB and CE, aiming to delimit the experimental region and conditions for the wastewater treatment. Consequently, an experimental design was applied to optimize the treatment process.

The response variable was residual chromium content (RCC) measured in mg/L achieved after the treatment with neonite, the studied variables were Neonite dosage (NE) measured in g/L, stirring time (StT) measured in minutes and the sample pH. Each treatment was carried out with effluent samples of 250 mL with 300 RPM of stirring.

Experimental design

Once the optimal experimental region for both effluents was established, a factorial design 3^2 was carried out to optimize the results obtained in preliminary tests. The application of the 3^2 design allows the identification of curvature, since each variable is evaluated in three levels; however, it is not recommendable for designs with multiple variables, as that would increase a lot the total runs.

The models obtained from both effluents were analyzed through ANOVA, model assumptions (normal distribution, homoscedasticity, independence of errors) were accomplished for both models applying Box-Cox transformation of response variable RCC [Gutiérrez and De la Vara, 2012] according to Equation 1.

$$Box - Cox \rightarrow \begin{cases} \frac{x^{\lambda} - 1}{\lambda}, if\ \lambda \neq 0 \\ \log(x), if\ \lambda = 0 \end{cases} \quad (1)$$

In Equation 1, "x" is the response variable RCC, and "λ" is the Lambda parameter for transformation, calculated using the package "MASS" from the R software. Lack of fit and determination coefficient (R^2 and adjusted R^2) were analyzed to determine the fitting quality for both models. Statistical analysis was carried out using the packages "rsm", "lmtest" and "MASS" from the R software version 4.2.3 (R Core Team, 2023).

RESULTS AND DISCUSSION

Characterization of zeolite Neonite

For IR characterization, Neonite was tested in the range of 4000–400 cm^{-1} and the intensity of the bands was expressed in terms of transmittance (%) as shown in Figure 1. The values between 3700 and 1600 cm^{-1} correspond to the presence of water in the zeolite sample [Bordiga et al., 2015;

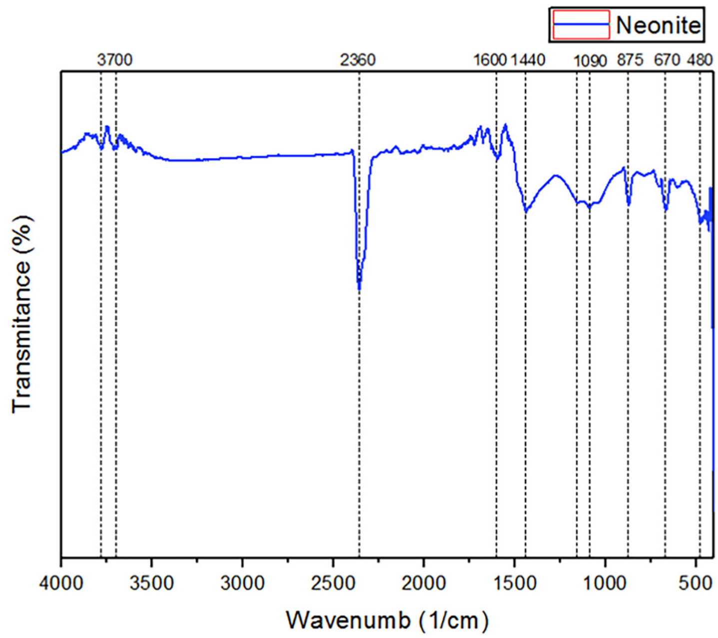

Figure 1. FTIR characterization of Neonite

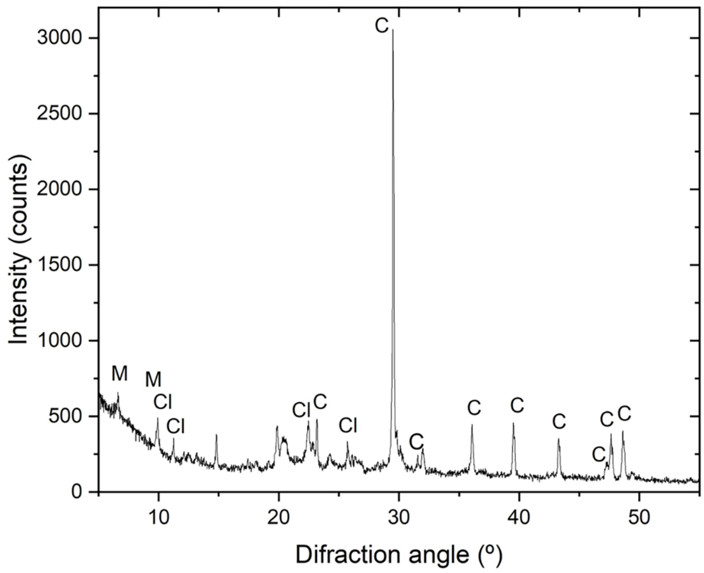

Figure 2. XRD characterization of Neonite

Mansouri et al., 2013]. The bands around 3700 indicate the presence of OH^- groups and the band at 1440, to molecules of water associated to Na and Ca [Mansouri et al., 2013]. The band at 1090 corresponds to the vibration modes of asymmetric stretching of inner bonds T-O in tetrahedral TO. The bands 875 and 480 cm^{-1} characterize the stretching vibration modes of O-T-O groups and the flexion vibrations of T-O bonds respectively [Mansouri et al., 2013]. On the other hand, the bands in 1440, 1600 and 2360 come from calcium carbonate, mostly in form of calcite [El-Kammar et al., 2015]. XRD qualitative analysis presented in Figure 2 identified clinoptilolite as the main zeolite species in Neonite and calcite as an associated mineral.

Results of treatment of CB from tanning stage

The effluents from CB are characterized by its high chromium content and acidic pH, measured between 3 to 4, as this is the pH tanning stage occurs. The characterization of Total Chromium content in CB resulted in 2243.73 mg/L.

The present research aimed to assess the effect of Neonite in chromium removal from CB, consequently the preliminary tests evaluated the treatment of CB with Neonite with and without modification of pH of the sample. For pH adjustment, a solution of NaOH 3M was applied. Neonite dosage was progressively increased, starting at 1 g/L. At doses over 4 g/L, there was a slight removal after an hour of stirring time; however, this removal was not significant. Hence, pH was adjusted to values of 5, 6 and 7. Neonite dosage was increased until 32 g/L, at this dose, at pH 7 and after 14 days of precipitation, what will be called extended precipitation time (EPT), it was observed a significant removal of chromium, as shown in Figure 3. This result took place after leaving the sample in observation, so EPT was not planned; however, this result was considered as a significant finding as chromium removal in CB seemed to be very difficult. For this reason, the treatment with EPT was repeated obtaining the same result. In an attempt to replace EPT, other processes to separate effluent from precipitate were applied, such as vacuum filtration and centrifuge, results of both techniques were not as effective as results from EPT.

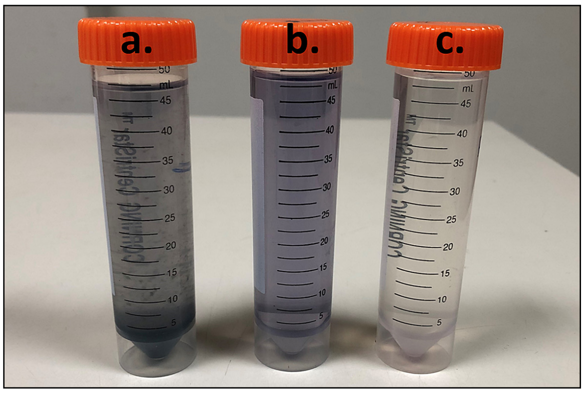

Figure 3. Results of preliminary tests on CB after decantation, (a) results at pH 5, (b) results at pH 6, (c) results at pH 7

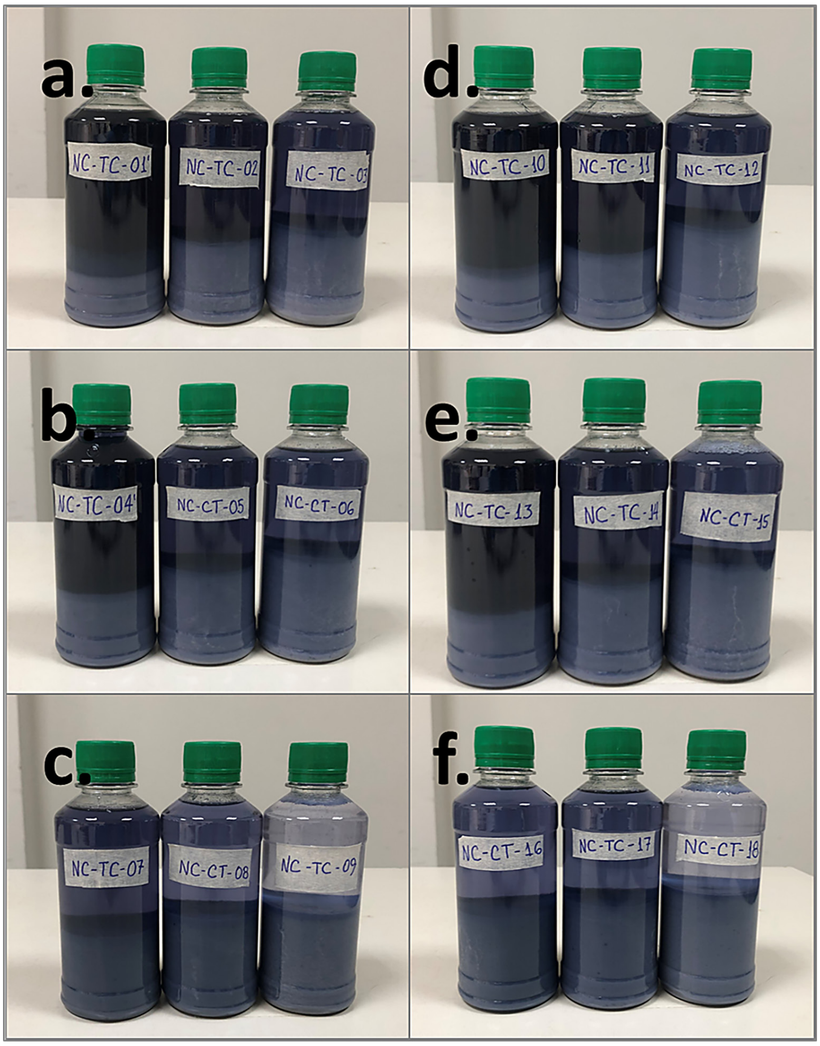

Figure 4. Results of full factorial design, a and d were conducted at pH 5, b and e. were conducted at pH 6, c. and f. were conducted at pH 7

On the basis of preliminary results, a factorial design 3^2 was applied, response variable was Residual Chromium Content (RCC), and independent variables Neonite Dosage (NE) and pH of the treatment (pH), including the application of EPT. For factorial design, Ne was evaluated in doses of 16, 24 and 32 g/L, and pH at 5, 6 and 7, each treatment was performed using samples of 250 mL, for 60 minutes and stirred at 300 RPM. Figure 4 shows the results obtained for each sample after EPT. As well, Table 1 presents the results obtained for RCC for the design.

From results, there is a significant improvement on chromium removal when both pH and NE are increased, as shown in Table 1. It is remarkable that the removal achieved in higher levels of variables, reaching significant lower values of RCC, was equivalent to a chromium removal of 95%. The results from RCC were transformed applying Box-Cox transformation with λ equal to 0.3434, and reported in Table 1. ANOVA of results is presented in Table 2, to evaluate the significant effects in the response surface model at 95% of confidence ($p < 0.05$). Lineal effect from both variables, was significant, as demonstrated by the increase in removal at higher doses of NE and higher pH, also depicted in Figure 4, each panel comprises the results of the treatments at same pH but at different NE doses, where the chromium removed precipitate increases as well. Moreover, in Figure 4, 4.a. - 4.d., 4.b. - 4.e. and 4.c. - 4.f. are the treatments at pH 5, 6 and 7, respectively. As it was shown, the blue tone of the effluent, related to the presence of chromium, becomes more clear at higher pH. The quadratic effect from pH is also significant, with a consistent increase that leads to a negative curvature. Model assumptions were accomplished, the Shapiro-Wilk test showed that the data presents a normal distribution (p-value = 0.3055), the Breusch-Pagan test presents homoscedasticity (p-value = 0.1691) and Breusch-Godfrey test showed there is not autocorrelation between residuals (p-value = 0.1234). The Lack-of-fit test resulted no significant (p-value ≈ 0.11), determination coefficient R^2 for the model is 98.13% and the adjusted coefficient is 97.11%, indicating good fit to experimental data.

From the optimization of the results, the response surface graph is presented in Figure 5, optimal conditions for the treatment are found at pH 7 and 32 g/L of NE. Chromium ion-exchange in zeolites is controlled by pores size, materials exchange capacity and pH [Silva et al., 2016]. Regarding pH, as it increases in solution, greater retention is achieved. The pH effect can be explained by speciation of Cr(III), as it forms hydronium and hydroxyl complexes of different shape and charges in aqueous solution. At pH values lower than 3, chromium mainly exists as Cr(III), competing with hydrogen ions (H^+) for

Table 1. Results of factorial design 3^2 for CB. "Treatment" corresponds to the code assigned to each run. "RCC_Box-Cox" presents the results of RCC transformed applying Box-Cox transformation with λ = 0.3434

Treatment	Block	Ne (g/L)	pH	RCC (mg/L)	RCC_Box-Cox
NC-CT-01	1	16	5	1335.97	-31.5757
NC-CT-02	1	24	5	810.72	-26.1393
NC-CT-03	1	32	5	538.33	-22.3284
NC-CT-04	1	16	6	1079.14	-29.1375
NC-CT-05	1	24	6	526.32	-22.1336
NC-CT-06	1	32	6	351.62	-18.8937
NC-CT-07	1	16	7	410.98	-20.0938
NC-CT-08	1	24	7	214.60	-15.4926
NC-CT-09	2	32	7	66.11	-9.3712
NC-CT-10	2	16	5	1446.97	-32.5342
NC-CT-11	2	24	5	924.92	-27.4843
NC-CT-12	2	32	5	486.18	-21.4604
NC-CT-13	2	16	6	1111.79	-29.4674
NC-CT-14	2	24	6	580.08	-22.9843
NC-CT-15	2	32	6	344.14	-18.7333
NC-CT-16	2	16	7	264.69	-16.8673
NC-CT-17	2	24	7	228.12	-15.8828
NC-CT-18	2	32	7	67.22	-9.4413

Table 2. ANOVA for results of CB

Parameter	Estimate	Std. Error	t value	Pr(>|t|)	
(Intercept)	-9.1148	0.3542	-25.7366	3.52E-11	***
Block	0.0119	0.1893	0.0626	0.951197	
x1: Ne	1.7014	0.1159	14.6764	1.43E-08	***
x2: pH	2.1285	0.1159	18.3613	1.33E-09	***
x1:x2	-0.0933	0.1420	-0.6569	0.524749	
x1^2	0.0094	0.2008	0.0470	0.963361	
x2^2	0.9739	0.2008	4.8503	0.000511	***
Response: Residual Chromium Content					
	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Block	1	0.00	0.00	0.0039	0.9512
FO(x1, x2)	2	89.10	44.55	276.2662	3.96E-10
TWI(x1, x2)	1	0.07	0.07	0.4315	0.5247
PQ(x1, x2)	2	3.79	1.90	11.7636	0.0019
Residuals	11	1.77	0.16		
Lack of fit	3	0.90	0.30	2.7180	0.1148
Pure error	8	0.88	0.11		
Multiple R-squared: 0.9813			Adjusted R-squared: 0.9711		
Model assumptions					
Normal distribution		Shapiro-Wilk normality test		p-value = 0.3055	
Homoscedasticity		studentized Breusch-Pagan test		p-value = 0.1691	
Independence of errors		Breusch-Godfrey test		p-value = 0.1234	

adsorption places, whereas at values between 3 – 4.5, the predominant species is the $Cr(OH)_2$ complex, making it easier to adsorb [Córdova-Rodríguez et al., 2016; Silva et al., 2016]. However, as pH increases, Cr(III) concentration decreases, probably because of the precipitation of hydroxyl species; therefore, the processes taking place in the treatment are simultaneously ion-exchange, precipitation and adsorption of chromium hydrolyzed species [Córdova-Rodríguez et al., 2016]. In conclusion, Cr^{+3}/H^{+} relation appears as a regulating factor of the exchange level reached in the treatment.

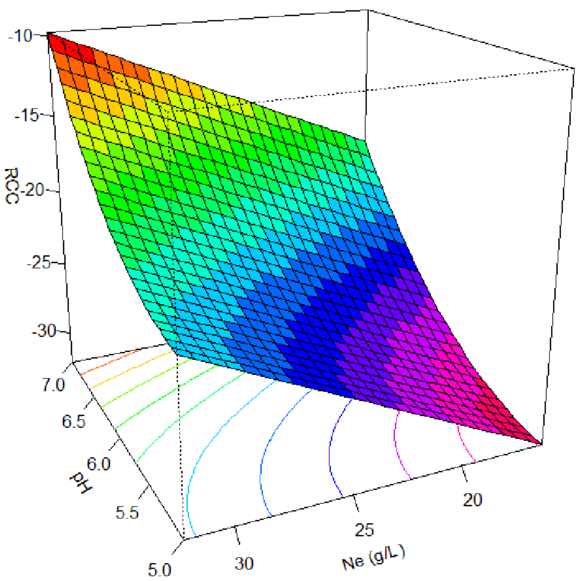

Figure 5. Estimated response surface for chromium removal in CB

Even when pH is such an important variable in chromium removal, NE also contributes and has a great effect, as verified by ANOVA and the results at pH 7, where samples at 32 g/L presented better results compared to lower doses at same pH. This seems to happen due to the chromium adsorption becoming faster and more effective at higher NE doses [Córdova-Rodríguez et al., 2016; Silva et al., 2016]. Thus, zeolite addition would regulate H^{+} concentration, while also improves chromium adsorption in the zeolite. Another important aspect is EPT, as this was a factor in the improvement of chromium precipitation, it can be misunderstood that because of the long time, pH may increase resulting in a chemical precipitation, but pH was measured before treatment and after EPT, without a significant change pH for each sample. For this reason, it can be inferred that this outcome results from the interaction of both NE and pH.

Results of treatment of CE from tanning process

The results from characterization of CE are presented in Table 3. From the results, there is a high content of pollutant load of various parameters and compared to environmental standards for sewage discharges in Peru (VMA), these results exceed the standard by far, especially in DBO and DQO.

In preliminary tests for the treatment of CE, NE was increased progressively, starting at a dosage of 0.1 g/L. This dosage was increased until make evident a qualitative significant effect of Neonite on the treatment, seen by the precipitation and clarification of the sample. Initial pH of CE was 7.8, which was not modified, stirring time was tested between 5 to 30 minutes, using samples of 250 mL, stirring at 300 RPM and 10 minutes of precipitation. The results from preliminary tests are showed in Figure 6, where a photographic register of results at different stirring times and dosage is presented.

From Figure 6, the increase of stirring time generated a higher removal of pollutant load, evidenced by the increase of sediments and clarification, particularly it is clearer in tests over 2 g/L

Table 3. Characterization of CE

Parameter	Units	VMA	NC-TC-01
BOD	mg/L	500.0	1106.30
COD	mg/L	1000.0	2635.40
TSS	mg/L	500.0	900.00
Fats	mg/L	100.0	135.70
Ammonia	mg/L	30.0	67.40
Sulfides	mg/L	5.0	-
Total Chromium	mg/L	10.0	541.36
pH	units	6 - 9	7.80

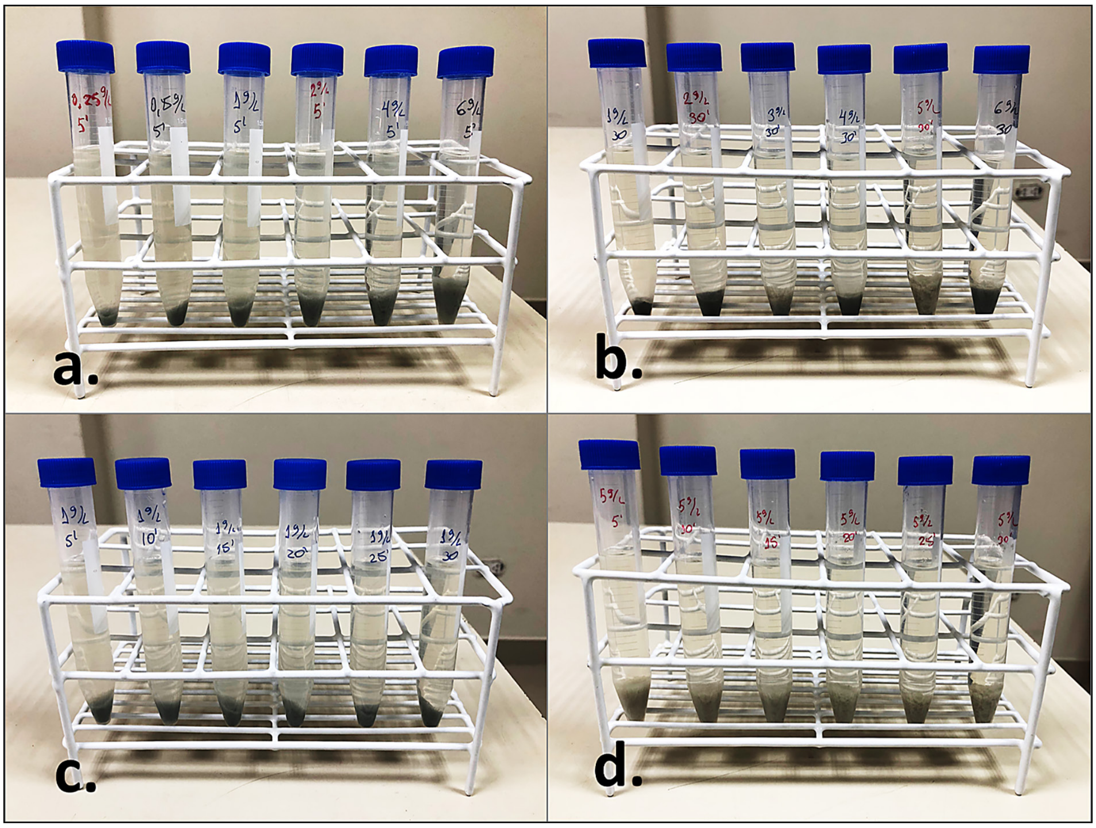

Figure 6. Results of preliminary tests at different Neonite dosages and stirring times, (a) NE from 0.25 to 6 g/L at 5 minutes of StT, (b) NE from 1 to 6 g/L at 30 minutes of StT, (c) Ne at 1 g/L and StT from 5 to 30 minutes, (d) NE at 5 g/L and StT from 5 to 30 minutes

with a notorious clarification and a higher precipitation at 5 g/L compared to lower concentrations. On the basis of results, the experimental region was delimited for the 3^2 factorial design, stablishing as variables the Neonite dosage (NE) and stirring time (StT), and as response variable the Residual Chromium Content (RCC). For factorial design, NE was evaluated in doses of 1, 3 and 5 g/L, and StT at 5, 10 and 15 minutes, each treatment was performed using samples of 250 mL, at sample pH of 7.8 and stirred at 300 RPM.

After running the full 3^2 factorial design, results are presented in Table 4. From results, it is very important to highlight the low RCC values, reaching chromium removal over 98% for the best results, evidencing the great effectivity of Neonite in the removal of this heavy metal.

The results of RCC for CE were transformed applying Box-Cox transformation, with λ equal to -0.2626, the transformed results were reported in Table 4. Results were analyzed by ANOVA and presented in Table 5 to determine the principal effects and behavior of the response variable related to factorial design at 95% of confidence ($p < 0.05$). From ANOVA, it was identified a significant lineal and quadratic behavior effect from both variables. NE showed a higher effect, demonstrating the importance of dosage of zeolite for the treatment. StT and quadratic effects are also significative, this means there was an adequate delimitation of experimental region, as optimal results for the model were found. Model assumptions were met, the Shapiro-Wilk test indicated that the data follows a normal distribution (p-value = 0.9938), the Breusch-Pagan test confirmed homoscedasticity (p-value = 0.2039), and the Breusch-Godfrey test demonstrated no autocorrelation among residuals (p-value = 0.7833). The Lack-of-fit test resulted no significant (p-value ≈ 0.91), determination coefficient R^2 for the model is 85.42% and the adjusted coefficient is 79.35%. On the basis of on these results, it was verified that this model adequately explains the results.

Figure 7 shows the results of the optimization of the treatment of CE applying Neonite zeolite, optimal values of the treatment are 4.73 g/L for NE and 12.17 minutes for StT.

A treatment under optimal conditions was performed, all parameters analyzed for initial CE sample were studied. The results obtained for this test are presented in Table 6, where these are compared with VMA values.

The results show a great removal of BOD, COD, TSS, fats and Total Chromium, accomplishing the VMA values for these parameters. Removal of organic compounds is mostly due to the property of zeolites to adsorb these molecules; nevertheless, these kinds of molecules could full

Table 4. Results of factorial design 3^2 for CE. "Treatment" corresponds to the code assigned to each run. "RCC_Box-Cox" presents the results of RCC transformed applying Box-Cox transformation with λ = -0.2626

Treatment	Block	Ne (g/L)	StT (min)	RCC (mg/L)	RCC_Box-Cox
NC-DT-01	1	1	5	10.2619	-1.7419
NC-DT-02	1	3	5	0.9213	0.0829
NC-DT-03	1	5	5	0.5525	0.6420
NC-DT-04	1	1	10	3.1296	-0.9858
NC-DT-05	1	3	10	0.5952	0.5559
NC-DT-06	1	5	10	0.4913	0.7814
NC-DT-07	1	1	15	2.3701	-0.7721
NC-DT-08	1	3	15	0.7109	0.3570
NC-DT-09	2	5	15	0.4438	0.9055
NC-DT-10	2	1	5	5.3088	-1.3515
NC-DT-11	2	3	5	3.3421	-1.0341
NC-DT-12	2	5	5	1.6478	-0.4681
NC-DT-13	2	1	10	1.8421	-0.5644
NC-DT-14	2	3	10	0.5044	0.7497
NC-DT-15	2	5	10	0.4377	0.9227
NC-DT-16	2	1	15	1.5109	-0.3911
NC-DT-17	2	3	15	0.5843	0.5771
NC-DT-18	2	5	15	0.6796	0.4065

Table 5. ANOVA for results of CE

Parameter	Estimate	Std. Error	t value	Pr(>|t|)	
(Intercept)	1.1825	0.0895	13.2139	1.64E-08	***
Block	-0.0285	0.0478	-0.5966	0.561868	
x1: Ne	0.1969	0.0293	6.7223	2.13E-05	***
x2: StT	0.1084	0.0293	3.7012	3.03E-03	**
x1^2	-0.1137	0.0507	-2.2405	0.044759	*
x2^2	-0.1249	0.0507	-2.4617	0.029944	*
Response: residual chromium content					
	Df	Sum Sq	Mean Sq	F value	Pr(>F)
Block	1	0.00	0.00	0.3559	0.5619
FO(x1, x2)	2	0.61	0.30	29.4439	2.35E-05
PQ(x1, x2)	2	0.11	0.06	5.5399	0.0198
Residuals	12	0.12	0.01		
Lack of fit	4	0.01	0.00	0.2364	0.9101
Pure error	8	0.11	0.01		
Multiple R-squared: 0.8542			Adjusted R-squared: 0.7935		
Model assumptions					
Normal distribution		Shapiro-Wilk normality test		p-value = 0.9938	
Homoscedasticity		Studentized Breusch-Pagan test		p-value = 0.2039	
Independence of errors		Breusch-Godfrey test		p-value = 0.7833	

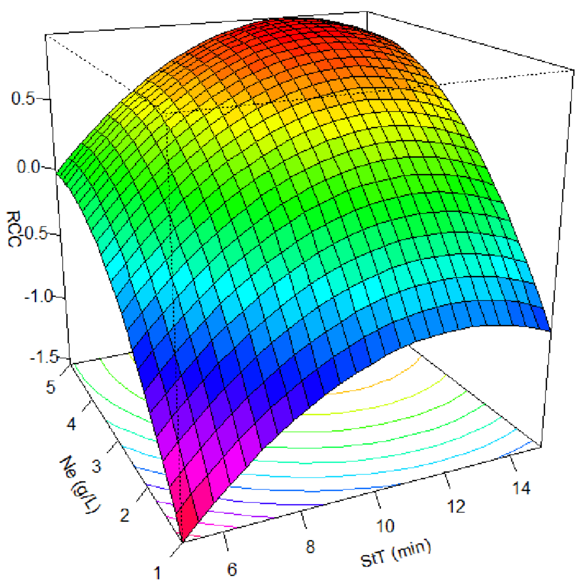

Figure 7. Estimated response surface for chromium removal in CE

its pores and internal channels, reducing then their ion-exchange and adsorption capacity.

When the pH of a chromium containing solution increases over 7, the main chromium species are $Cr(OH)_3$, but there still exists $Cr(OH)_2^+$ [Marinho et al., 2019]. The latter are the soluble species or hydroxyl complexes which are removed by the Neonite through ion-exchange [Córdova-Rodríguez et al., 2016; Silva et al., 2016]. These results are remarkably important, as in one stage treatment process environmental standards are achieved for parameters with high relevance for tanning industry.

On the other hand, Neonite does not evidence significant effect in the removal of ammonia, previous studies showed that zeolites, mainly constituted by clinoptilolite, were not suitable for the removal of ammonia in tanning wastewater, due to the high concentration of

Table 6. Results for optimized conditions

Parameter	Units	VMA	NC-TC-01	NC-TF-01	Removal (%)
BOD	mg/L	500.0	1106.30	76.20	93.11
COD	mg/L	1000.0	2635.40	996.50	62.19
TSS	mg/L	500.0	900.00	22.00	97.56
Fats	mg/L	100.0	135.70	9.80	92.78
Ammonia	mg/L	30.0	67.40	141.00	-
Sulfides	mg/L	5.0	-	-	-
Total Chromium	mg/L	10.0	541.36	0.26	99.95

salts these have; thus, the ion-exchange positions in zeolite are filled with other salts, decreasing the ion-exchange capacity for ammonia [El-Kammar et al., 2015].

CONCLUSIONS

The present study optimized the treatment of effluents from tanning process applying the zeolite Neonite for the removal of chromium and other pollutants. As a result, in composite effluent from the tanning process (CE) at a Neonite dosage of 4.73 g/L and stirring time of 12.17 minutes, achieving a removal of 93.11% for BOD, 62.19% for COD, 97.56% for TSS, 92.78% for fats and 99.95% for total chromium, these results accomplish the Peruvian environmental standards stablished by VMAs. It is remarkable that one stage technology allows the accomplishment of the environmental standards as this is one of the main issues for Peruvian tanneries. Meanwhile, for the effluents from tanning stage (CB), the optimized values were found at Neonite dosage of 32 g/L and pH 7 and applying what was denominated as extended precipitation time (EPT). Under these conditions, a removal of 97% of total chromium was achieved, a considerable result as the initial content of total chromium for this effluent was 2243.73 mg/L. An important interaction effect was identified between variables NE and pH in the treatment of this effluent, as optimal conditions showed a significant higher removal and seems to be affected by EPT, but this higher precipitation is produced by chemical effects, because it does not respond to a physical process. Neonite is a promising technological option for the tannery wastewater treatment, as it allows the treatment of composite effluents in a one stage process and the accomplishment of environmental standards for crucial parameters on tanning industry. Nevertheless, it is necessary to study its application as part of a system, in conjunction with other treatment technologies, to achieve environmental standards for parameters that Neonite was unable to attain in a single stage. Furthermore, when considering the potential scaling-up of the technology, it is important to evaluate the availability of national natural zeolites.

Acknowledgements

Financial support for this study was provided by Productive Innovation and Technological Transfer Center of Leather, Footwear and related Industries (CITEccal Lima).

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