CHEMICAL ENGINEERING TRANSACTIONS

VOL. 110, 2024

A publication of AIDIC

The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Marco Bravi, Antonio Marzocchella, Giuseppe Caputo

ISBN 979-12-81206-10-6; **ISSN** 2283-9216

DOI: 10.3303/CET24110030

Optimizing SCFAs Production from Tannery Sludge: Insights from Zeolite-Assisted Fermentation with Mild Thermal Pretreatment

Giulia A. Tuci*, Marco Gottardo, Giorgia Trevisanato, Paolo Pavan, Francesco Valentino

Department of Environmental Sciences, Informatics, and Statistics, Ca' Foscari University of Venice, Via Torino 155, Mestre 30172, Venice, Italy
giuliaadele.tuci@unive.it

This study explores the potential of utilizing tannery sludge for short-chain fatty acids (SCFAs) production through fermentation, incorporating zeolites in the process. The study involved a mild thermal pretreatment of the sludge as well, aimed at enhancing the subsequent fermentation process by increasing the solubilization of the organic matter. Six thermophilic continuously stirred tank reactor runs with varying hydraulic retention times (HRT) and zeolite addition are conducted. Zeolites, known for their low cost and absorption properties, significantly impacted chromium concentrations. SCFA production levels remain relatively consistent across tests. However, the acidification efficiency, as reflected in the SCFAs/sCOD ratios, shows improvement in the presence of Chabazite. Specifically, the acidification efficiency is highest in test RB8 (0.92 COD/COD). This suggests that the addition of Chabazite enhances acidification efficiency in tannery sludge applications. The findings highlight zeolites' potential to absorb heavy metals and improve acidification efficiency, indicating promising practical applications for tannery sludge treatment.

1. Introduction

Tanning is a process that converts raw hides into leather, aiming to produce a durable material resistant to microbial degradation, thermal stress, and humidity (Alibardi and Cossu, 2016). Trivalent chromium sulfate (Cr(III)) is commonly used in this process, but it leads to the generation of tannery sludge with environmental concerns (Abreu and Toffoli, 2009). The sludge, containing chromium, sulfides, organic pollutants, metals, and microorganisms, is usually disposed of in landfills, contributing to environmental impact (Zhao et al., 2022).
To address this issue, anaerobic digestion (AD) is proposed as a sustainable method to manage tannery sludge. AD involves four stages (hydrolysis, acidogenesis, acetogenesis, and methanogenesis) and can produce valuable by-products, such as short-chain fatty acids (SCFAs) and biogas.
However, tannery sludge, being solid-rich, faces challenges in hydrolysis, affecting subsequent stages (Achouri et al., 2021). To enhance organic matter solubilization, a mild thermal pretreatment is applied, known for its effectiveness in solubilizing the organic matter as shown on similar substrates (Zhen et al., 2017).
Moreover, tannery sludge contains high levels of ammonia and chromium, which can inhibit AD (Montalvo et al., 2020), thus zeolites, crystalline aluminosilicates, are chosen for their ability to absorb these compounds, promoting a more favorable environment for anaerobic microorganisms (Montalvo et al., 2012). The properties of zeolites are influenced by various factors, with the ratio of silica to aluminum content, referred to as the Si/Al ratio, being among the key determinants. Zeolites with a low silica content, specifically those with a Si/Al ratio below 2, exhibit outstanding ion exchange capacity (Jiang et al., 2018). Chabazite and Clinoptilolite were selected for their absorption properties for ammonia and heavy metals, as well as their low cost and easy availability.

Paper Received: 06 April 2024; Revised: 28 March 2024; Accepted: 12 May 2024
Please cite this article as: Tuci G.A., Gottardo M., Trevisanato G., Pavan P., Valentino F., 2024, Optimizing SCFAs Production from Tannery Sludge: Insights from Zeolite-Assisted Fermentation with Mild Thermal Pretreatment, Chemical Engineering Transactions, 110, 175-180 DOI:10.3303/CET24110030

The study focuses on analyzing tannery sludge as an AD substrate, considering the combined effects of zeolites and mild thermal pretreatment on fermentation parameters. In particular, the focus is on the absorption of ammonia and Cr operated by the added zeolites and the potential impact that this material has on the fermentation, in terms of SCFAs production. Semi-continuous fermentation tests are conducted in continuously stirred tank reactors (CSTR) with two hydraulic retention times (HRT) and compared to a "blank" condition without zeolite addition to assess the material's impact. The goal is to find sustainable ways to reduce the environmental impact and volume of tannery waste while producing valuable by-products through anaerobic fermentation.

2. Materials and methods

2.1 Substrates' characteristics

The tannery sludge employed in this investigation is a mixture of primary and secondary sludge obtained from the Montebello Vicentino wastewater treatment plant (WWTP) in northeast Italy. The WWTP handles wastewater from 23 tannery plants, subjecting it to both primary and secondary biological treatment.
The resulting dried sludge exhibits specific chemical and physical characteristics, including 830 ± 14 g of total solids (TS)/kg and 590 ± 4 g volatile solids (VS)/kg. The chemical oxygen demand (COD) is 793 ± 18 g COD/kg TS, while total phosphorus (TP) and total Kjeldahl nitrogen (TKN) are 8 ± 1 g P/kg TS and 32 ± 1 g N/kg TS, respectively. The total chromium content is determined to be 19155 ± 310 mg Cr/kg TS.
Two natural zeolites, Clinoptilolite (CL) and Chabazite (CH), are utilized in this study. Clinoptilolite, with a Clinoptilolite content of 70%-80% and water retention of 33.7%, required grinding due to 90% of the material having a granulometry >1mm. Chabazite, composed of 64% Chabazite and a water retention of 37.8%, was used as-is since 98% of the material measured less than 0.15 mm. The Si/Al molar ratio is approximately 3.3 for Chabazite and 4.3 for Clinoptilolite.

2.2 Experimental setup and parameters

A zeolite dosage of 0.26 g/gVS was chosen based on successful outcomes reported by Silva et al. (2021) and Zorpas et al. (2002). The tannery sludge underwent mild thermal pretreatment, involving heating diluted sludge and tap water with a S/I ratio of 7.0 w/w VS basis at 70°C for 20 hours, and was then employed as feedstock for the three cycles of semi-continuous tests.
Each cycle involved two parallel reactors with a working volume of 1.5 L, inoculated with tannery sludge at a concentration of 70 g TS/L. The reactors were maintained under thermophilic conditions (50 ± 2 °C) with water recirculation, and after a one-week lag phase, feeding occurred once per day based on selected HRTs of 4.0 and 8.0 days. Reactors RA4 and RA8 received only thermally pretreated tannery sludge, while zeolite-amended runs (RB4, RB8, RC4, and RC8) had the same sludge with the addition of Chabazite or Clinoptilolite. The working conditions are summarized in Table 1.
The effluent from the reactors was used for the characterization in terms of sCOD, $N\text{-}NH_4^+$, SCFAs, pH, and Cr.

Table 1: Operating conditions of the six runs of acidogenic fermentation. Clinoptilolite (CL) and Chabazite (CH).

CSTR run	HRT (d)	OLR (g VS/l d)	Zeolite
RA4	4	12.6	No
RA8	8	6.05	No
RB4	4	12.6	CH
RB8	8	6.05	CH
RC4	4	12.6	CL
RC8	8	6.05	CL

2.3 Analytical methods and calculations

The analyses were performed according to the Standard Methods (Apha Awwa, 2012), including total and volatile solids (TS, VS), total Kjeldahl Nitrogen (TKN), $N\text{-}NH_4^+$, total phosphorus, and both forms of chromium (Cr(III) and Cr(VI)). For the determination of SCFAs, an Agilent 6890 N gas chromatograph equipped with a flame ionization detector (FID) was utilized, employing an Agilent J&W DB-FFAP fused silica capillary column. The total Cr quantification was carried out with an inductively coupled plasma-mass spectrometry (ICP-MS) NexION 350X (Perkin Elmer) coupled with the autosampler seaFAST (ESI). The Cr(VI) analyses were performed with the direct spectrophotometric determination Cr(VI) by diphenylcarbazide (Apha Awwa, 2012); the absorption measurements were carried out at 540 nm wavelength.

An assessment of acidogenic fermentation involved the evaluation of different parameters such as SCFA concentration, SCFAs/sCOD, the fermentation yield (Y_{SCFA}^{CSTR}) according to equation 1, and rate (q_{SCFA}^{CSTR}) according to equation 2.

$$Y_{SCFA}^{CSTR} = [COD_{SCFA}]_t/VS_0; \quad (1)$$

$$q_{SCFA}^{CSTR} = [COD_{SCFA}]_t/(VS_0 \cdot HRT); \quad (2)$$

The release of ammonia was determined by calculating its percentages based on final concentrations in the liquid phase and initial substrate content, using the equation: $N\text{-}NH_4^+$ release (%) = $[N\text{-}NH_4^+]_t/TKN_0$.

3. Results and discussion

The study involved six experimental runs, each featuring parallel reactors with HRTs of 4 and 8 days, selected based on Tuci et al., (2022). The acclimation time for achieving steady SCFA production was short and consistent across all tests, facilitated by the pH stability of around 7 maintained by the tannery sludge itself.
The pH regulation performed by tannery sludge has been well-established, demonstrating resilience due to the substantial lime content introduced during both the tanning process and wastewater treatment, effectively maintaining a neutral pH (Tuci et al., 2022). However, in the absence of zeolite addition in our experiments, a notable deviation towards more alkaline values was observed. Notably, this shift was mitigated by the inclusion of zeolites, except for run B4, which exhibited a pH deviation, likely attributable to the short retention time, which didn’t allow the Chabazite to exert this buffering action. Namely, the pH values in RA4 changed from 7.0 ± 0.2 to 7.5 ± 0.2, and in RA8 from 6.9 ± 0.0 to 7.4 ± 0.0. Similarly, RB4 presented a shift from a pH of 7.2 ± 0.2 to 7.8 ± 0.1. In contrast, runs with clinoptilolite maintained a consistent pH value of 7.6 ± 0.1 throughout the entire test duration, as observed in RB8 as well. This pH regulatory phenomenon associated with zeolites has been previously documented, with ion exchange capacity proposed as a contributing factor (Castellar et al., 1998).

Table 2: Main parameters of the six runs of acidogenic fermentation.

Parameter	Unit	RA4	RA8	RB4	RB8	RC4	RC8
sCOD	g/L	23.1 ± 0.4	28.2 ± 0.5	19.4 ± 0.2	22.1 ± 0.3	20.4 ± 0.4	23.0 ± 0.2
COD_{SCFA}	g/L	16.7 ± 0.2	20.3 ± 0.2	17.03 ± 0.17	20.2 ± 0.2	14.6 ± 0.2	17.0 ± 0.1
COD_{SCFA}/sCOD	g/g	0.72 ± 0.01	0.72 ± 0.01	0.87 ± 0.01	0.92 ± 0.01	0.71 ± 0.01	0.75 ± 0.01
N-NH4+ release	mgN-NH4+/g TKN	48 ± 1 %	46 ± 1 %	47 ± 2 %	55 ± 2 %	63 ± 2 %	64 ± 2 %

3.1 SCFA production in the semi-continuous tests

HRT strongly influenced SCFA production, with higher HRTs leading to increased SCFA values. Tests without zeolite addition demonstrated higher productivity, surpassing mesophilic equivalents (Tuci et al., 2023), highlighting the effectiveness of the mild thermal pretreatment as well, which is also confirmed by the high sCOD. However, zeolite addition resulted in lower sCOD, as they absorbed a considerable portion of soluble organic matter (OM) as reported in Table 2.
However, this positively impacted the efficiency of sCOD conversion into SCFAs, notably in runs with added Chabazite converting over 90% of dissolved COD into SCFAs. This efficiency can be also attributed to biomass immobilization by zeolite, enhancing process efficiency (Montalvo et al., 2012).
Zeolite addition also resulted in lower SCFA content as shown in Figure 1, attributed to zeolites' absorption ability which has been shown to also include SCFAs (Tang et al., 2023), impacting parameters evaluating SCFA production efficiency, such as yield and rate. These parameters remained consistent between zeolite-amended runs and run A, primarily attributed to the heightened efficiency of the zeolite-amended runs related to the immobilized biomass, while simultaneously the absorption of a percentage of SCFAs by the zeolites played a counterbalancing role, diminishing their presence in the effluent.
Comparisons with literature data highlighted tannery sludge's higher profitability for SCFA production compared to sewage sludge. For instance, yields for runs RA4, RB4, and RC4 were 0.33 ± 0.01, 0.34 ± 0.01, and 0.29 ± 0.01 g COD_{SCFA}/(g VS_0), respectively, and for runs RA8, RB8, and RC8 were 0.40 ± 0.01, 0.40 ± 0.01, and 0.34 ± 0.01 g COD_{SCFA}/(g VS_0), respectively. In contrast, Zhang et al. (2019) achieved yields of 0.19 and 0.17 g COD_{SCFA}/g VS_0 for thermally pretreated and raw sewage sludge, emphasizing tannery sludge's promise as a substrate, with zeolites showing no significant influence on this parameter at the employed dosage.

Overall, for what concerns SCFAs production zeolite addition did not manage to improve the reactors' performances, as the highest productivity was obtained from RA8 (average of 20.3 ± 0.2 gCOD/L), with the exception of the sCOD conversion efficiency which showed a 20% improvement with Chabazite addition.

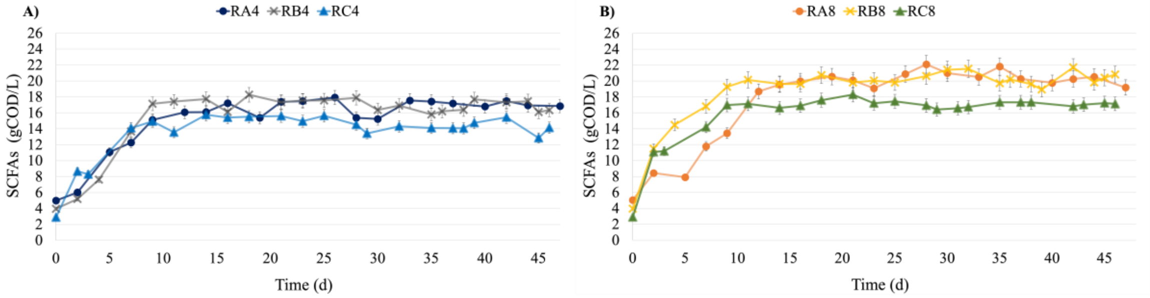

Figure 1: Trends of SCFA production in the three runs with HRT = 4 days (A) and with HRT = 8 days (B).

3.2 Ammonia release

In assessing ammonia concentration, steady periods revealed comparable levels between tests RA and RB for both HRTs (1127 ± 23 mg/L and 1098 ± 45 mg/L for HRT 4, and 1078 ± 33 mg/L, and 1291 ± 45 mg/L for HRT 8, respectively). In contrast, RC demonstrated notably higher values of 1478 ± 47 mg/L and 1518 ± 47 mg/L for RC4 and RC8, respectively, equating to an ammonia release percentage exceeding 60% for test RC, in contrast to approximately 55-45% for the other tests (Table 2). Tang et al. (2023) proposed that zeolite addition might enhance the solubilization of organic matter, resulting in increased ammonia release in the liquid fraction, explaining the higher ammonia concentration in RC.

Contrary to expectations based on existing literature, ammonia did not appear to be absorbed by the zeolites in these tests, as its concentration remained consistent across all runs. This unexpected result, given the documented effectiveness of zeolites in NH_4^+ absorption (Montalvo et al., 2012), may be attributed to the substantial presence of cations, particularly calcium ions (Ca^+) and sodium ions (Na^+), in tannery sludge originating from tanning processes and primary wastewater treatments. Past studies have indicated that these ions play a significant role in cation exchange and decrease in the liquid medium after zeolite addition (Rodríguez-Iznaga et al., 2022). The interaction of these cations could potentially diminish the capacity for NH_4^+ absorption.

Notably, as RC presented a higher ammonia concentration than RB, it can be hypothesized that Clinoptilolite was less effective than chabazite in absorbing ammonia, likely linked to its higher Si/Al molar ratio (4.3 compared to Chabazite's 3.3). However, the zeolites' remarkable ability to absorb chromium, the interaction of cations, along their observed absorption of the organic matter, contributing to reduced sCOD values, potentially contributing to this outcome.

Overall, while zeolites enhanced organic matter solubilization and NH_4^+ release, only Chabazite effectively absorbed some released ammonia, whereas Clinoptilolite did not. Importantly, the observed NH_4^+ concentration did not hinder the fermentation process.

3.3 Chromium release

Chromium (Cr) presence in both pretreated sludge and reactor liquid fractions was assessed, focusing on Cr(III) as Chromium (VI) was not observed. Mild thermal pretreatment allowed for a high Cr release in the liquid fraction, reaching 335 mg/L. The concentration trend showed an initial peak followed by a progressive decrease for all tests.

As shown in Figure 2, both tests without zeolite (RA) show a similar behavior characterized by a steady decrease in Cr concentration until they both reach a plateau achieving a 60% reduction.

In contrast, zeolite-containing tests showed continuous reduction until no Cr was detected in the liquid effluent. This result was achieved with different velocities according to the HRT, with the lower HRT allowing for a quicker Cr removal, as expected. Moreover, both run B and C showed a very consistent behavior between each other, both exhibiting an impressive absorption capacity for Cr.

This capacity allows for the utilization of the SCFA-rich effluent without additional treatment for Cr removal, emphasizing the effectiveness of zeolites in mitigating the presence of this toxic metal.

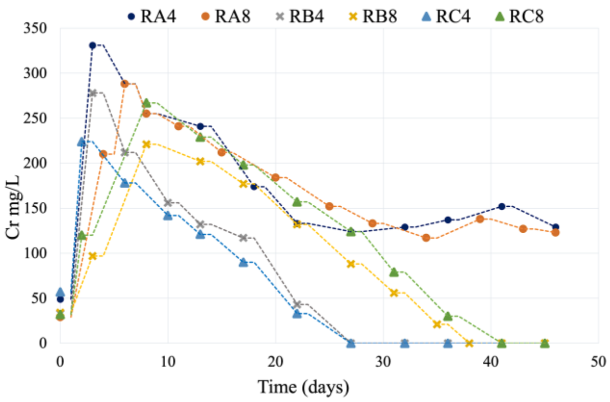

Figure 2: Trends of Cr in the liquid fraction in the six runs.

4. Conclusions

An exploration of SCFA production from thermally pretreated tannery sludge in CSTRs was performed, with a specific focus on the impact of zeolite addition. Notably, zeolite addition did not reduce ammonia concentration, as RA and RB displayed uniformity, while RC exhibited increased ammonia release. Conversely, runs with zeolites exhibited consistent differences in sCOD values, showcasing zeolites' efficacy in organic matter absorption and contributing to lower sCOD values. SCFA production reached its peak in tests without zeolite addition, particularly at higher HRT, reaching a mean value of 20.3 gCOD/L, corresponding to an acidification yield of 0.4 g COD_{SCFA}/g VS_0. Additionally, Chabazite addition substantially improved acidification efficiency, achieving a SCFA to sCOD ratio of 0.92 COD/COD.

Zeolites demonstrated a notable ability to absorb chromium from the fermentation broth, achieving complete removal over time, while tests without zeolites only achieved a 60% reduction in Cr concentration.

These findings provide valuable insights for optimizing SCFA production from tannery sludge and underscore the potential of zeolites in heavy metal removal within waste treatment processes. Further research is needed to investigate microbial dynamics and substrate interactions.

Acknowledgments

This research was financially supported by the European Union - Next Generation EU: PON “Ricerca e Innovazione”. This study was also carried out within the "Interconnected Nord-Est Innovation Ecosystem (iNEST)" project and received funding from the European Union Next- GenerationEU - National Recovery and Resilience Plan (NRRP) – MISSION 4 COMPONENT 2, INVESTIMENT N. ECS00000043 – CUP N. H43C22000540006.

References

Abreu, M.A., Toffoli, S.M., 2009. Characterization of a chromium-rich tannery waste and its potential use in ceramics. Ceram Int 35, 2225–2234. https://doi.org/10.1016/j.ceramint.2008.12.011

Achouri, O., Panico, A., Bencheikh-Lehocine, M., Derbal, K., Arias, D., Iasimone, F., Padulano, R., Bouteraa, M., Rebahi, A., Pirozzi, F., 2021. Role of H2O2 dosage on methane production from tannery wastewater: experimental and kinetic study. Journal of Water Process Engineering 43, 102313. https://doi.org/10.1016/j.jwpe.2021.102313

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

Apha Awwa, W.E.F., 2012. Stand. Methods Exam. Water Wastewater. American Public Health Association, American Water Works Association, and Water Environment Federation.

Castellar, M.R., Aires-Barros, M.R., Cabral, J.M.S., Iborra, J.L., 1998. Effect of zeolite addition on ethanol production from glucose by Saccharomyces bayanus. Journal of Chemical Technology and Biotechnology 73, 377–384. https://doi.org/10.1002/(SICI)1097- 4660(199812)73:4<377::AID-JCTB973>3.0.CO;2-I

Jiang, N., Shang, R., Heijman, S.G.J., Rietveld, L.C., 2018. High-silica zeolites for adsorption of organic micro-pollutants in water treatment: A review. Water Res 144, 145–161. https://doi.org/10.1016/J.WATRES.2018.07.017

Montalvo, S., Guerrero, L., Borja, R., Sánchez, E., Milán, Z., Cortés, I., Angeles de la la Rubia, M., 2012. Application of natural zeolites in anaerobic digestion processes: A review. Appl Clay Sci 58, 125–133. https://doi.org/10.1016/j.clay.2012.01.013

Montalvo, S., Huiliñir, C., Borja, R., Sánchez, E., Herrmann, C., 2020. Application of zeolites for biological treatment processes of solid wastes and wastewaters – A review. Bioresour Technol 301, 122808. https://doi.org/10.1016/j.biortech.2020.122808

Rodríguez-Iznaga, I., Shelyapina, M.G., Petranovskii, V., 2022. Ion Exchange in Natural Clinoptilolite: Aspects Related to Its Structure and Applications. Minerals 2022, Vol. 12, Page 1628 12, 1628. https://doi.org/10.3390/MIN12121628

Silva, R.M., Abreu, A.A., Salvador, A.F., Alves, M.M., Neves, I.C., Pereira, M.A., 2021. Zeolite addition to improve biohydrogen production from dark fermentation of C5/C6-sugars and Sargassum sp. biomass. Sci Rep 11, 1–14. https://doi.org/10.1038/s41598-021-95615-1

Tang, C.C., Zhang, B.C., Yao, X.Y., Zhou, A.J., Liu, W., Ren, Y.X., Li, Z., Wang, A., He, Z.W., 2023. Insights into response mechanism of anaerobic digestion of waste activated sludge to particle sizes of zeolite. Bioresour Technol 385, 129348. https://doi.org/10.1016/j.biortech.2023.129348

Tuci, G.A., Valentino, F., Bonato, E., Pavan, P., Gottardo, M., 2022. Microwave-Hydrogen Peroxide Assisted Anaerobic Treatment as an Effective Method for Short-Chain Fatty Acids Production from Tannery Sludge. Processes 10, 1–3. https://doi.org/10.3390/pr10112167

Tuci, G.A., Valentino, F., Parmar, A.C., Pavan, P., Gottardo, M., 2023. Minimizing tannery sludge in landfilling through a mixed microbial culture approach: Effect of oxidizing pretreatment, temperature and hydraulic retention time on process performances and chromium fate. Biochem Eng J 200, 109073. https://doi.org/10.1016/j.bej.2023.109073

Zhang, D., Jiang, H., Chang, J., Sun, J., Tu, W., Wang, H., 2019. Effect of thermal hydrolysis pretreatment on volatile fatty acids production in sludge acidification and subsequent polyhydroxyalkanoates production. Bioresour Technol 279, 92–100. https://doi.org/10.1016/j.biortech.2019.01.077

Zhao, J., Wu, Q., Tang, Y., Zhou, J., Guo, H., 2022. Tannery wastewater treatment: conventional and promising processes, an updated 20-year review. Journal of Leather Science and Engineering 4. https://doi.org/10.1186/s42825-022-00082-7

Zhen, G., Lu, X., Kato, H., Zhao, Y., Li, Y.Y., 2017. Overview of pretreatment strategies for enhancing sewage sludge disintegration and subsequent anaerobic digestion: Current advances, full-scale application and future perspectives. Renewable and Sustainable Energy Reviews 69, 559–577. https://doi.org/10.1016/j.rser.2016.11.187

Zorpas, A.A., Inglezakis, V., Loizidou, M., Grigoropoulou, H., 2002. Particle size effects on uptake of heavy metals from sewage sludge compost using natural zeolite clinoptilolite. J Colloid Interface Sci 250, 1–4. https://doi.org/10.1006/jcis.2002.8246