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The effect of a joint clay-microorganism system to treat Ni and diethylketone solutions

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ABSTRACT: The capacity of a combined system using a *Streptococcus equisimilis* biofilm supported in vermiculite to treat aqueous solutions polluted with diethylketone and nickel was accessed. In order to evaluate the interaction between the sorbent matrices and the two adsorbates several batch experiments were performed exposing 1) different amounts of vermiculite to Ni and diethylketone (Singular Sorbent Systems – SSS) or 2) a biofilm supported in different amounts of vermiculite to both pollutants (Binary Sorbent Systems – BSS). Fed batch pilot scale experiments were also conducted. For the SSS experiments, the removal of 3 g/L of DEK was complete for all the assays, whereas the removal of 0.45 g/L of Ni ranged between 31% and 100%. For the BSS experiments, the removal percentages of DEK and Ni decreased (77% to 97%, 23% to 97% respectively). Maximum removal percentages of 87.3% of DEK and 57.6% of Ni were reached in the pilot scale experiments.

1 INTRODUCTION

Water and soil contamination with hazardous compounds has triggered and attracted increasing attention by researchers worldwide. Heavy metals, polycyclic aromatic hydrocarbons, dyes and ketones are examples of such hazardous substances. Although heavy metals and ketones exist in nature, their overuse in several anthropogenic activities and their subsequent release into the environment, lead to their accumulation in several environmental matrices.

Among the several metals known to exert several hazardous effects on the environment and on living beings, Ni stands out, not only due to its extensive use in numerous industries (mining operations, electronics, batteries and petrochemical industries), but also due to its carcinogenic, embryotoxic and nephrotoxic properties as well as its ability to cause several types of acute and chronic health disorders (Suazo-Madrid et al., 2011). Diethylketone, also known as DEK, is a simple, symmetrical dialkyl ketone that has been used in several activities (Quintelas et al., 2013) and it is known to cause dizziness, tachycardia, fainting and even cause coma or death in cases of prolonged exposure. Thus, taking into consideration the negative impact on the environment, it is urgent the development of green methods able to remove those substances from the environment and thus minimize their impact, as well as the development and implementation of stricter environmental legislation.

2 OBJECTIVES

The main objective of this work is the development of an environment-friendly technology able to treat aqueous solutions containing both Ni and DEK. This two pollutants are usually found together in wastewaters from different industries such as electronics, metal extraction and paint production. The simultaneous treatment of aqueous solutions contaminated with heavy metals and VOCs is still in a very preliminary state and in order to tackle with this specific pollution problem this work was divided in two stages. In a first stage two sets of batch adsorptions assays were conducted: one combining different doses of vermiculite and a specific concentration Ni and DEK. These assays aimed to determine the adsorption capacity of vermiculite towards these two pollutants.

In a second stage, batch adsorption experiments were conducted combining the use of concentrated biomass of *S. equisimilis* and different concentrations of sterilized vermiculite to remove and/or biodegrade, respectively, Ni and DEK from aqueous solutions. This experiments aimed 1) to determine the ability of this joint clay-microorganism system to simultaneously remove both pollutants from aqueous solutions, 2) to determine whether these two substances compete for the available adsorption sites either on the biomass or on the vermiculite and 3) to infer about the role of the biomass on the sorption and degradation process. The kinetic parameters were estimated using five growth kinetic models and four biodegradation kinetic models all reported in literature (Costa et al., 2012; Raghuvanshi and Babu 2010). The experimental equilibria data were analyzed using the BET, Dubinin-Radushkevich (D-R), Langmuir and Freundlich adsorption isotherms, also reported in literature (Khamis et al., 2009; Saravanan et al., 2009).

3 MATERIALS AND METHODS

Streptococcus equisimilis (CECT 926) obtained from the Spanish Type Culture Collection – University of Valencia was used in this work. Brain Heart Infusion (BHI, OXOID CM1135) was used for bacteria growth. The vermiculite was obtained from Sigma-Aldrich, and presented an average particle diameter of 8.45 mm, BET surface area of $39\,m^2/g$ and porosity of 10%. DEK was purchased from Acros Organics (98% pure) and it was diluted in sterilized distilled water. Stock solutions of nickel (1 g/L) were prepared by dissolving an appropriate amount of $NiCl_26H_2O$ (Carlo Erba Reagents, CAS number 7791-20-0) in 1 L of sterilized distilled water. The range of nickel concentrations (5 mg/L to 450 mg/L) was obtained by dilution of the stock solution. All glassware used for experimental purposes was washed in 60% HNO_3 and subsequently rinsed with deionised water to remove any possible interference by other metals.

3.1 *Adsorption assays – single sorbent systems (SSS)*

The singular sorbents systems adsorption assays were conducted with 1 L Erlenmeyer flasks containing 0.425 L of Ni (0.45 g/L) and DEK (3 g/L) solution and different amounts of sterilized vermiculite (5 g and 7.5 g). The flasks were kept at 150 rpm and 37°C until equilibrium was reached. Previous assays were made in order to determine the time required for equilibrium to be reached (circa 20 hours for Ni and DEK). Samples of 1 mL were collected, centrifuged at 13400 rpm for 10 minutes, and the supernatant was analyzed by GC or acidified with nitric acid to be analyzed by ICP-OES, respectively for the determination of DEK and Ni concentrations. The control consisted of aqueous solutions with Ni and DEK to determine any kind of Ni or DEK adsorption by the Erlenmeyer flasks.

3.2 *Adsorption assays – binary sorbent systems (BSS)*

The binary sorbents assays were performed with 2 L Erlenmeyer flasks containing 0.850 L of Ni (0.45 g/L), DEK (3 g/L) solution and biomass supported in vermiculite (0.1 g to 10 g). All the flasks were rotated at a constant rate of 150 rpm until equilibrium was reached. Previous assays were made to determine the time needed for equilibrium to be reached (5 to 7 days). Samples of 1 mL were collected, centrifuged at 13400 rpm for 10 minutes, and the supernatant was used for the determination of DEK and Ni concentrations. The samples were analyzed by GC and by ICP-OES, respectively for DEK and for Ni. A control with Ni, DEK and vermiculite was used to infer about the influence of the biomass on the sorption of both pollutants.

All the assays were conducted in duplicate and the results are an average of both duplicates. The relative standard deviation and relative error of the experiments measurements were less than 2 and 5%, respectively.

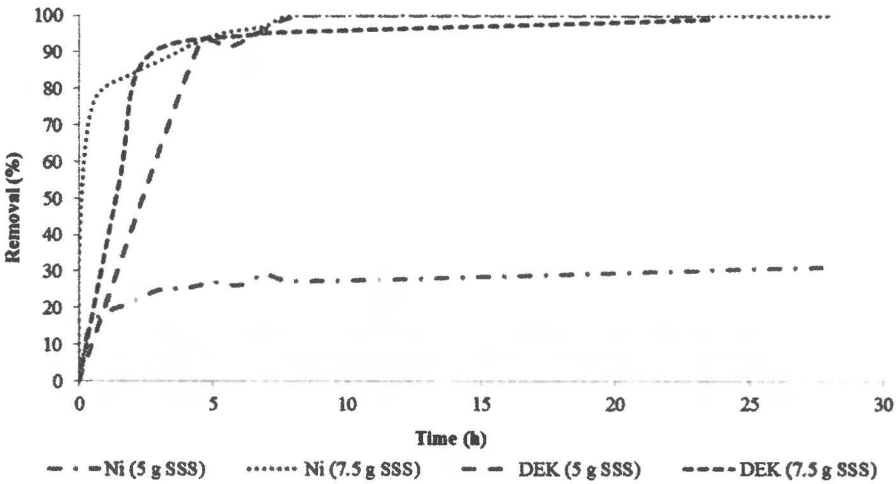

Figure 1. Ni and DEK sorption on different amounts of vermiculite on singular sorbent system (SSS).

3.3 *Adsorption assays – pilot scale*

The pilot adsorption assays were performed with a column with 16 dm^3 and can be divided in two stages. The first stage aimed the growth and development of the *S. equisimilis* biofilm on the vermiculite (700 g) and had the following conditions: 40 L of HBI culture medium with a flow of 125 mL/min at 25°C during 7 days. The second stage consisted in exposing the biofilm formed previously to an aqueous solution of DEK (7.5 g/L) and Ni (0.1 g/L) with a flow of 25 mL/min. This aqueous solution (S1) was subsequently replaced by a new solution (S2 and S3) containing DEK and Ni. At the end of the experiment only DEK was added to the S3 aqueous solution (S3 – DEK). Samples were collected and analyzed by GC and by ICP-OES, respectively for DEK and Ni concentration.

4 RESULTS AND DISCUSSION

4.1 *Adsorption assays – single sorbent systems (SSS)*

It is possible to conclude that for the SSS assays, the removal of DEK was always higher than 95%, reaching complete removal after about 8 hours for 5 g of vermiculite. For Ni, the removal percentage ranged between 31.13% and 100%, respectively for 5 g and 7.5 g of vermiculite (Figure 1).

Costa et al. (2015 a, b) studied the adsorption of DEK and/or Ni into vermiculite (single sorbate assays). According to these authors, the sorption of DEK (3 g/L) increase as the amount of vermiculite employed increased, reaching values of almost 100% for the assays using vermiculite doses equal and higher than 5 g. According to several authors this behavior can be explained as a result of an increased surface area, which is translated into a greater number of sites available for sorption (Quintelas et al., 2011). Regarding the sorption of Ni, these authors conclude that the percentage of initial Ni sorbed is similar (71% to 84%) for all assays conducted with different doses of vermiculite. When comparing these results it is possible to infer that the presence of Ni has a synergetic effect on the DEK's removal from aqueous solutions.

For both Ni and DEK, and for all the vermiculite doses tested, the kinetic model that best describes the obtained results is the pseudo-second order ($0.975 \leq R^2 \leq 0.999$ and $0.977 \leq R^2 \leq 0.999$, respectively).

The relationship between the pseudo-second order parameters and the adsorption performance was studied by several authors (Wu et al., 2009; Ofomaja, 2010). Wu et al. (2009) established

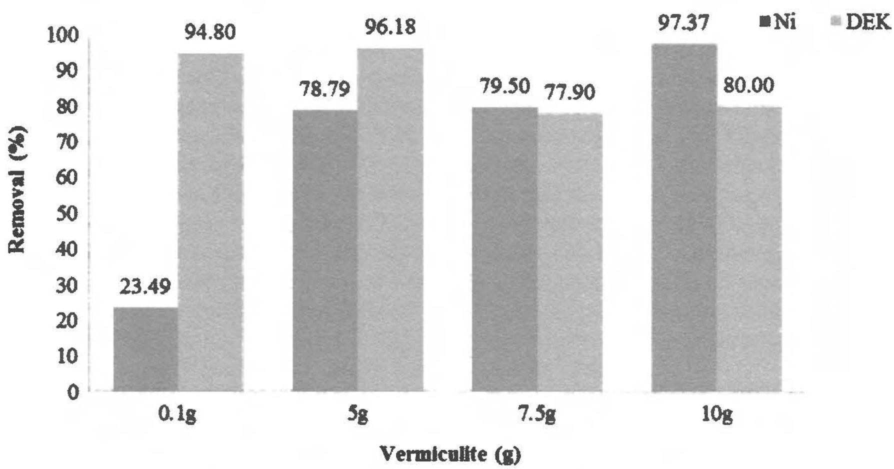

Figure 2. Removal percentage of Ni and of DEK using a biofilme of *S. equisimilis* supported into different doses of vermiculite.

an approaching equilibrium factor (R_w) which represents the characteristics of kinetic curve of an adsorption system using the pseudo-second order model. This approaching equilibrium factor (R_w) is defined as:

$$R_w = 1 / (1 + K_2 \cdot q_e \cdot t_{ref}) \quad (1)$$

In here t_{ref} is the longest operation time (based on kinetic experiments), q_e and K_2 correspond respectively to the uptake and to the pseudo-second order constant. For all the assays and for both pollutants the R_w factor was found to range between 0.006 and 0.120 which indicates that the kinetic curve is largely curved with a good approach to equilibrium, confirming the good performance of the system.

4.2 *Adsorption assays – Binary Sorbent Systems (BSS)*

Regarding the biosorption experiments it was possible to conclude that as the amount of vermiculite doses increases, the removal percentage of Ni also increases reaching its maximum removal value with 10 g of vermiculite (97.37%). For DEK, the maximum removal percentage was obtained for 5 g of vermiculite (96.18%) (Figure 2).

For vermiculite amounts higher than 5 g the removal percentage of DEK decreased significantly (about 16%) and may be justified by the decrease of the biomass concentration through time, which leads to the formation of a weaker and not fully developed biofilm.

For both Ni and DEK and for all the vermiculite amounts tested, the kinetic model that best describes the obtained results is the pseudo-second order ($R^2 > 0.986$ and $R^2 > 0.873$, respectively). The adsorption isotherm that best describe the results for the biosorption equilibrium of Ni was the BET isotherm ($R^2 = 0.997$). The high value obtained for Q_{max} (3.50×10^8) for the BET model and the fact that C_s is smaller than C_e suggest that the BET approaches the Langmuir isotherm.

The best fit for the biosorption of DEK was obtained with the Langmuir adsorption isotherm ($R^2 = 0.871$), followed by the Freundlich adsorption isotherm ($R^2 = 0.801$). These results suggest that the adsorption of DEK occurs in a monolayer and that all adsorption sites are equally probable (Costa et al., 2015a).

During the analyses of BSS samples experiments, it was possible to observe the appearance of several intermediates. These compounds were subsequently identified as 2-pentanone,

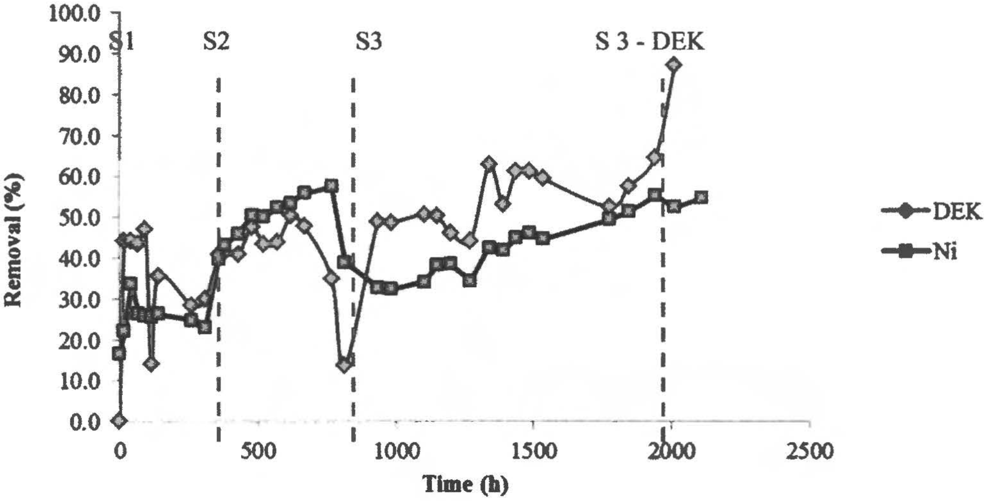

Figure 3. Removal percentage of DEK and Ni in the pilot scale assays, using a biofilme of *S. equisimilis* supported into different doses of vermiculite. S1 – Solution with Ni and DEK at time zero; S2 – replacement of the S1 solition, for a new Ni and DEK solution; S2 – replacement of the S2 solition, for a new Ni and DEK solution; S3 – DEK – addition of DEK to the S3 solution.

methyl-acetate and ethyl-acetate and did not appear at the end of the experiments, which means that they were also subjected to degradation by the *S. equisimilis* biofilm.

4.3 *Adsorption assays – pilot scale*

It was possible to infer that the removal of DEK was continuous through time, whereas the removal of Ni decreased significantly since the replacement of the S1 solution for the S2 solution (Figure 3).

These results can be explained by the increasing number of molecules competing for the active sites of the sorbent (not only Ni and DEK, but also DEK's metabolites), which can be translated by the decrease of removal percentages. Maximum removal percentages of 57.6 and 87.3% were obtained for Ni and DEK respectively.

Meena et al. (2005) studied the removal of several heavy metals from aqueous solutions using carbon aerogel as an adsorbent. These authors obtained Ni removal percentages of about 50%, 60%, 65% and 80% for carbon aerogel adsorbent doses of 5 g/L, 8 g/L, 10 g/L and 12 g/L respectively and an initial concentration of 3 mg/L. When comparing the results obtained by these authors, with the results obtained herein it seems that apart from the superior removal percentages, the initial concentration of Ni is also superior (150 times superior) obtained, which reveals and corroborate the good performance and capacity of these systems to decontaminate aqueous solutions conclusions.

5 CONCLUSIONS

From the results presented in this work it is possible to concluded that when Ni and DEK are mixed together in singular sorbent systems the maximum removal percentage of Ni decreases significantly to 30% for the assays conducted with 5 g of vermiculite, whereas the maximum removal percentages obtained for DEK were always higher than 71%, reaching a maximum value of almost 100%. It was also demonstrated that a joint system composed by a biofilm of *S. equisimilis* supported on vermiculite is able to efficiently remove Ni from aqueous solution and degrade and/or adsorb DEK. The presence of DEK does not affect negatively the removal of Ni and the presence of biofilm is a benefit in this type of systems, since it increases the removal of Ni and it degrades not only DEK but also its intermediates. The removal percentages obtained in the pilot scale experiments are lower than the ones obtained for the BSS system assays, but still it is possible to infer that the system can remove high concentration of Ni and DEK from aqueous solutions.

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