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Removal of Nickel by sorption on anaerobic sludge. Effects on methane production

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Biosorption of Ni (II) on industrial anaerobic sludge was investigated at 308.1 K and 7.5 pH in a batch reactor. The effective metal sorption capacity was of 10.25 mgNi/gTSS. Equilibrium data were fitted using Langmuir and Freundlinch models and the results compared by non-linear regression. A better agreement with experimental data was shown by Freundlich isotherm. Effects on methane production were also studied with the purpose of investigate if the biosorption process could occur without any variation in the ability of the anaerobic sludge to produce biogas. The results reveal that methane production rapidly drops for low metal concentration and that it can be partially recovered with further metal addition.

1. Introduction

Some heavy metals, at very low concentrations, are crucial for many physiological and biochemical processes. At higher concentrations they can become, however, hazardous to human health and environment: thus heavy metals can accumulate in the food-chain and may present increasing long-term toxic effects. The industrial development has increased the concentrations of such pollutants in the wastewater and, at the same time, legislative standards have become stricter. For these reasons, an economic water treatment for heavy metals removal is of interest. Biosorption is an innovative cost-effective heavy metals removal process and it is based on the metal binding capacities of various biological materials. Mechanisms involved in biosorption process are mainly non-metabolism dependent (Veglio' and Beolchini, 1997), then biosorption is considered to be a physico-chemical process. Equilibrium is often described using classical adsorption models: Langmuir and Freundlich isotherms are the most widely used equations (Aksu et al., 2002; Kim et al., 2002; van Hullebusch et al., 2004). pH, metal concentration and biomass characteristics are the most important factors which can influence the biosorption process. Studies on biosorptive ability of several biomass were carried out (Bakkaloglu et al., 1998). Anaerobically digested sludge has been selected as the most suitable for heavy metal biosorption (Artola and Rigola, 1992).
In this study, the adsorption of Ni on anaerobic sludge was analysed. Equilibrium data were fitted using Langmuir and Freundlich isotherms in order to determine which of them can better represents metal biosorption on the sludge. Effects on methane production were also investigated to check if the biosorption process can take place

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without change in the biogas production capacity of the anaerobic sludge. A reactor without metal was assembled in order to compare biogas production of the metal contaminated reactor. Stability of anaerobic digestion requires a balanced activity of the mixed population of bacteria: many studies have shown that methanogenic bacteria are the most sensitive to heavy metals (Wong and Cheung, 1995; Lin and Chen, 1999). Once more, Nickel can be toxic to biological processes at very low concentrations. Eckenfelder (1980) revealed that anaerobic process is inhibited at Ni concentrations of 2 mg/L. However, several authors found other values of toxic limits: Wong and Cheung (1995) demonstrated Nickel effects on anaerobic sludge at concentrations of 338 mg/L; Lin and Chen (1999) carried out their experiments in a laboratory UASB reactor, testing the Ni concentrations of 1 – 3000 mg/L. These different values are obtained because heavy metals effect on the digestion process depends on several factors, such as the properties of the metallic salt added into the system, the feed concentration, the temperature and the detention time in the system (Al-Qodah, 2006). In this study, a batch reactor was fed with Nickel solution adding a metal amount of 10 mg per day. Biogas generated by reactor was collected and determined in a plastic gas-meter and the pressure was continuously monitored by a piezoelectric pressure transducer.

2. Materials and methods

2.1 Anaerobic sludge and Nickel solution

Anaerobic sludge was collected from a full-scale UASB reactor treating wastewater from a brewery. Biomass had not been selected before the beginning of the tests. The characteristics of the sludge used are reported in table 1. Metal solution was prepared by dissolving $NiCl_2.6H_2O$ in deionized water.

2.2 Analytical methods

Total solids (TS), total suspended solids (TSS) and volatile suspended solids (VS) were measured according to APHA, AWWA, WEF (1998). COD measure was performed according to Reactor Digestion Method (Jirka and Carter, 1975), approved by USEPA. COD analyses were carried out using a HACH COD Reactor and a HACH Spectrometer. Nickel concentrations in the liquid and solid samples were determined by a mass spectrometer (ICP-MS Agilent 7500), with standard deviations less of 4.0%. Liquid samples were obtained after filtration of sludge samples. Solid samples were obtained by the ashes originated from incineration of filters paper (pore 0.45 μm) containing suspended solids. Acid digestion was carried out with a mixture 3:1 of HCl and HNO_3 (aqua regia) to solubilize Nickel ions from the ashes (McGrath and Cunliffe, 1985). Known solid sample amounts in the range of 0.03 ÷ 0.05 g were digested under reflux with 15 ml of aqua regia for 2 hours at 100°C. The same procedure was applied for measuring the metal content in the original sludge, with 30 ml of aqua regia in a 50 ml sludge sample. The pH was measured using a portable pH-meter (Hanna, HI 98150).

Table 1. Characteristics of anaerobic sludge

Total Solids (TS)	16.39 g/L	COD	255 mg/L
Volatile Solids (VS)	6.06 g/L	Nickel	10.31 μg/gTS

2.3 Experimental apparatus

Batch experiments were performed in two glass bottles with a volume of 1L (figure 1). Average sludge content in the reactors was of 1L with the concentrations of 16.39gTS/L and 6.06gVS/L. One reactor was daily fed with a Nickel solution, in order to add a metal amount of 10mg/day. The second reactor was a blank working without metal. 8ml of nutrients solution (NH_4Cl, $FeCl_3$ and K_2HPO_4, 170 gCOD/L) were daily supplied to both reactors. The bottles were placed in a thermostatic water-bath at 308.1K. Magnetic stirrers were used to maintain well-mixed conditions. Biogas generated by each reactor was collected in a 0.6L plastic calibrated gas-meter. The CO_2 capture was assured by caustic soda filled into the gas-meters. CH_4 volumes were determined by the liquid level inside the gas-meters and pressure values were continuously monitored by piezoelectric P-transducers. The experiments were carried out 34 days long. From day 1 to day 18, anaerobic sludge was fed only with a nutrient solution in order to achieve the stationary state. Metal contaminant was fed starting from day 19. Every day a sample of 20ml was taken from each reactor to determine the concentration of solids, COD and Nickel. This volume was replaced with nutrients and metal solution, in order to maintain constant volume into the bottles. At the same time, pH and biogas production were detected.

2.4 Isotherm models

Equilibrium data obtained for Ni (II) in the adsorption tests are reported in figure 2. These data have been analysed using Langmuir and Freundlich isotherms. The Langmuir isotherm is a non-linear model and provides the mass of metal adsorbed per mass of biomass q (mg/g), related to the metal ion concentration in solution Ceq (mg/l):

$$q = \frac{q_{max} b C_{eq}}{\left(1 + b C_{eq}\right)} \tag{1}$$

the constant q_{max} is the maximum amount of metal ion (mg) per gram of sorbent to form a complete monolayer on the surface bound at high C_{eq} and represents the maximum specific uptake corresponding to sites saturation; whereas b (L/mg) indicates the metal ions affinity for binding.

The Freundlich model is also a non-linear model that suggests a monolayer sorption of the metal on the biomass. Differing from the Langmuir, the Freundlich model assumes a

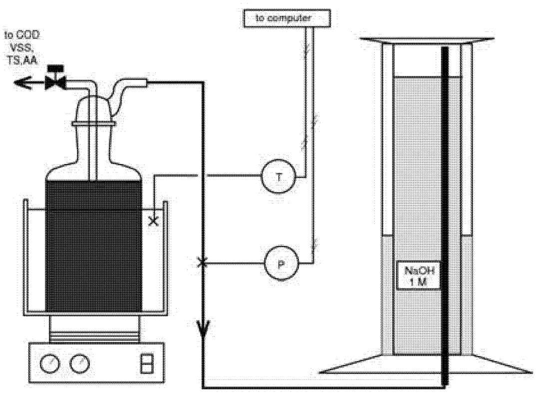

Figure 1. *Batch reactor scheme.*

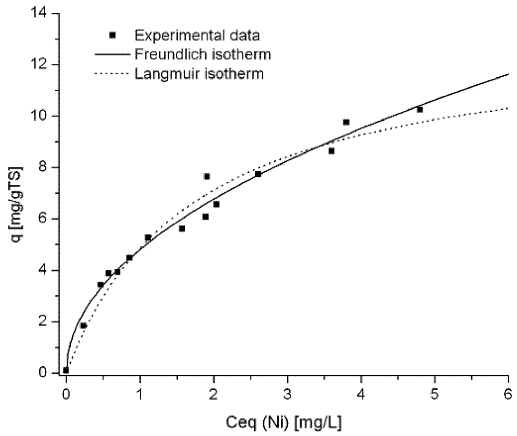

Figure 2. *Equilibrium adsorption isotherm for Ni (II) on anaerobic sludge.*

heterogeneous energetic distribution of the active binding sites on the sorbate surface with interactions between the adsorbed molecules and, consequently, the sites with stronger affinity are occupied first. For this reason, the model is considered to be more applicable for describing adsorption process by organic matter (Aksu et al., 2002).
The general equation for the Freundlich isotherm is expressed as:

$$q = KC_{eq}^{1/n} \tag{2}$$

in which K reflects the affinity of the adsorbent for a metal (maximum adsorption capacity) and n is the adsorption intensity related to the affinity or binding strength.

3. Results and discussion

3.1 Biosorption process

In all the performed biosorption tests pH value of the sludge was about 7.5. The effectiveness of biosorption process was verified by the 98.3% of Ni adsorbed onto sludge particles. Isotherm parameters were determined by non-linear regression (Levenberg-Marquardt). This method is more rigorous than linear regression, because it uses the original form of the isotherm equation (Ho et al. 2002). The parameters obtained from fitting the models onto the equilibrium data (figure 2) are reported in table 2. As it can be seen, Freundlich isotherm gives the best fit for data. Langmuir and Freundlich parameters for different nickel-sorbent systems are reported in table 3.

3.2 Effects on methane production

The experimental outcomes established that the addition of certain metals can reduce biomass methanogenic activity. As shown in figure 3, methane production rapidly drops

Table 2:Langmuir and Freundlich parameter

Model	**q_{max}** [mg/gTS]	**b** [L/mg]	**K** [(mg gTS^{-1}) (mg L^{-1})^n]	**n**	**R^2**
Langmuir	13.26	0.58			0.967
Freundlich			4.81	2.03	0.978

Table 3. Ni Langmuir (q_{max}) and Freundlich (K) parameters in different sorbents

Sorbent	q_{max} [mg/g]	K	pH	Ref.
anaerobic sludge	25.24	0.21[a]	---	Artola et al., 2000
Nocardia amarae	6.4	---	---	Kim et al., 2002
activated sludge	2.5	---	---	
dried activated sludge	106.4	3.21[b]	1.0	Aksu et al., 2002
dried activated sludge	238.1	3.80[b]	4.5	
anaerobic granular sludge	11.55	156.13[c]	8	van Hullebusch et al., 2004
anaerobic granular sludge	9.41	54.54[c]	7	
anaerobic granular sludge	7.90	16.69[c]	6	
NaOH treated activated sludge	58.8	4.85[d]	---	Al-Qodah, 2006
activated sludge	40.6	4.19[d]	---	
HCl treated activated sludge	37.3	2.96[d]	---	

K unit: (a) [(mmol g^{-1})(mmol L^{-1})^n]; (b) [(mg g^{-1})(mg L^{-1})^n]; (c) [dm^3 g^{-1}]; (d) [mg g^{-1}]

for low Nickel concentration: at 50 mg/L of metal concentration, methane volume reduction is of 41%. The increase of metal concentration inside the reactor provides a partial recovery of methane generation: at the end of experiment, methane volume reduction of 30% was measured for 150 mgNi/L. This result is probably due to biomass acclimatisation (Wong,and Cheung, 1995): microbial tolerance to heavy metals can be enhanced due to the dosage strategy, which resulted in low and constant increases in metal concentration. Lin and Chen (1999) found that the heavy metal concentration causing a decrease of 50% in methanogenic activity of the sludge were of 2000 mg/L of Ni(II) for a HRT of 1 day, and 1600 mg/L of Ni(II) for a HRT of 2 days.

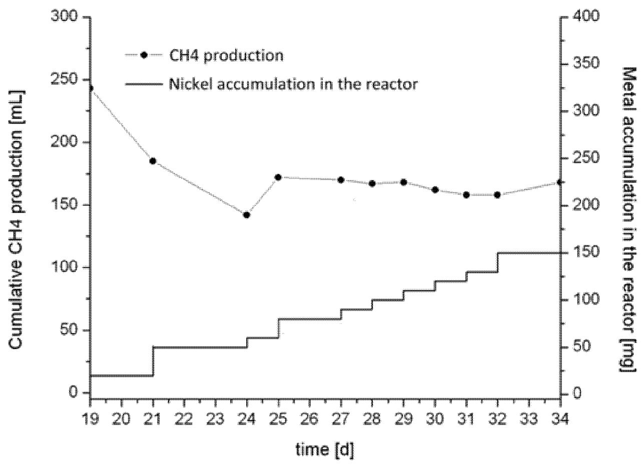

Figure 3: *Metal addition effects on methane production*

Conclusions

The biosorption of Ni (II) on anaerobic sludge was investigated. A laboratory apparatus was assembled to perform the batch anaerobic experiments. The study demonstrates the effectiveness of biosorption process with a percentage of Ni adsorbed onto sludge of 98.3%. Experimental data were fitted using Langmuir and Freundlich models: Freundlich isotherm shown a better agreement with experimental data. Effects on methanogenic activity were also investigated. Results demonstrate that methane production rapidly falls for low Nickel concentrations, and it can be partially recovered with further metal additions.

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