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Research article

COMPARISON BETWEEN BATCH AND CONTINUOUS REACTOR SYSTEMS FOR BIOSORPTION OF NEODYMIUM (ND) USING MICROALGAE

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ABSTRACT: Rare earth metals (REMs) are a series of 17 elements, for instance, neodymium is much less common than lanthanum or cerium and a very large amount of mining is needed for small amounts of neodymium. On the other hand, recovery of REMs is interesting due to its high market prices along with various industrial applications. Waste of electric and electronic equipment (WEEE), or electronic waste (e-waste) is a potential and important secondary source of base metal, precious metal and REMs. In the last decade, recovery of metals using bioprocess technology has been one of the most promising technologies. Biosorption represents a biotechnological innovation as well as a cost effective excellent tool for the recovery of REMs from aqueous solutions. In this study, Nd was removed from a mixed leachate solution derived from neodymium magnets in batch and continuous sorption systems by using dried green microalgae (*Chlorella vulgaris*). The maximum Nd uptake (q=157.21 mg/g) was determined at pH 5 with a biosorbent dosage of 0.5 g/L and an initial neodymium concentration in the mixed leachate solution was 250 mg/L at 35 °C in the batch test. Therefore *Chlorella vulgaris* was found to have a good potential in its role as a biosorbent for neodymium out of a mixed leachate solution derived from neodymium magnets. The use of the studied biosorbent in the removal of Nd in continuous mode was successful. Due to the slow kinetics of Nd sorption onto *Chlorella vulgaris*, the sorption capacity in batch assays was higher than that in continuous assays.
Keywords: Batch Test; Continuous Test; Biosorption; *Chlorella vulgaris*; Neodymium; Harddisk Magnets

INTRODUCTION

Rare earth elements (REEs) are often referred as the “seeds of technology” because of their uses in high-tech strength permanent magnets, lasers, automotive catalytic converters, fiber optics/superconductors, electronic devices, and green energy sectors [1]. Due to the ongoing development of new advanced technologies, there is an

over-increasing demand for REEs and Scandium in the international markets, with emphasis on identifying new resources to ensure adequate supply for present and future use [2]. The designation “rare earths” refers to the 15 elements of the periodic table known as “lanthanides” with yttrium and scandium.

Although relatively abundant in the earth’s crust, REEs rarely occur in concentrated forms, making them economically challenging to obtain. These elements constitute critical components of many important technologies and products, such as hybrid vehicles, wind turbines, and cell phones. Given this global demand for green and sustainable products in energy, military, and manufacturing industries, REE demand throughout the world is projected to increase [3]. In recent years, China has been providing 95 to 97 percent of REEs worldwide. Because China has demonstrated its ability to control and limit REE exports. Mining in the natural environment is the primary means of REE acquisition; however, it results in a large quantity (greater than 90 percent) of excess and unused materials and other environmental impacts.

Biosorption has emerged as promising technology as it is a combined effect of adsorption, ion exchange and micro precipitation onto functional groups of inactive cell walls of biological origin [4]. The study focuses on the investigation of biosorption process to recover Nd from aqueous solution using batch and continuous systems as well as the efficiency of the processes for recovery of Nd via biosorption is given in this study.

METHODS AND METHODOLOGY

Theory of Biosorption

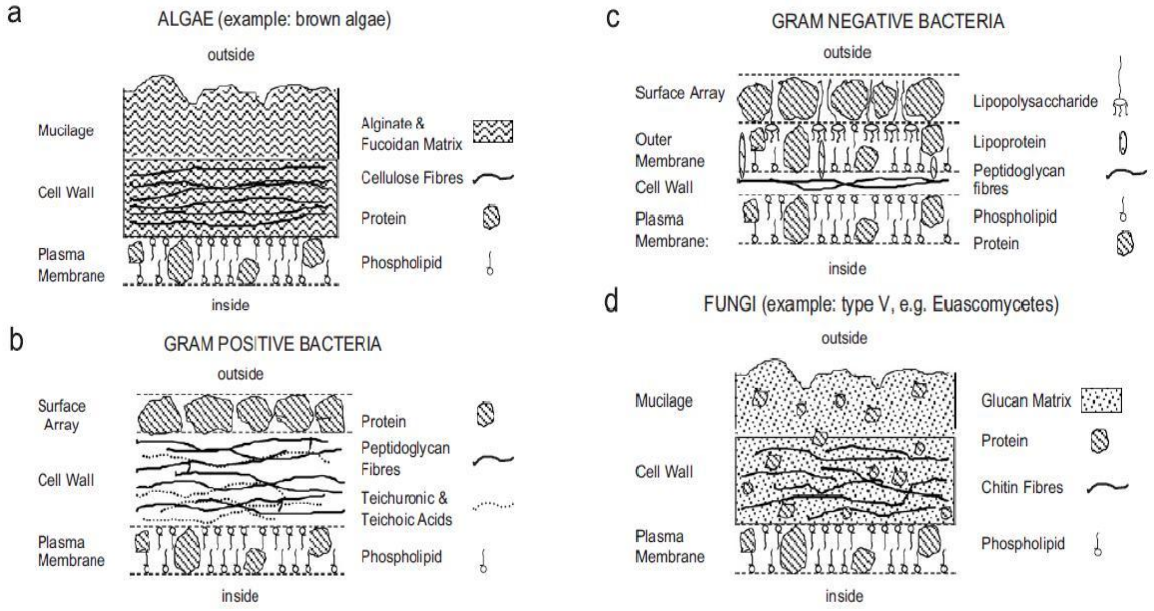
Biosorption has been defined as the property of certain biomolecules (or types of biomass) to bind and concentrate selected ions or other molecules from aqueous solutions [4]. When dead biomass is used, biosorption is a passive mechanism based on affinity between the biosorbent and the sorbate. Many biomasses can be used as sorbent for example algae, fungi, bacteria, crop residues [4].

In biomass chemical active sites have been identified, these have the property to show a pretention in holding the metal in the surrounding solution. The most common active sites, also called binding groups, are given as follows:

- Hydroxyl, Carbonyl (ketone), Carboxyl
- Sulfhydryl (thiol), Sulfonate
- Thioether, Amine, Secondary amine
- Imine, Imidazole
- Phosphonate
- Phosphodiester

The active sites are found among other in the cell wall of the biomass, which composition differs from one microbial type to the other. Molds have prominent chitin layers in their cell walls, bacteria have quantities of peptidoglycan (gram+) and teichoic acid (gram-) in their walls - all of these featuring important ion-exchange active groups in their structures [4]. Biopolymers in algae cell wall (e.g., alginate) show carboxylic group suitable in metal sorption. Furthermore some carboxylic groups sequester metals and others don't, which result in challenges to correctly identify the efficient active groups [4]. Figure 1 shows the composition of cell wall of different type of biomasses.

Figure 1: Schematic outline of the cell wall structures of (A) seaweeds; (B) gram +ve bacteria; (C) gram –ve bacteria; (D) fungi [4].



In the sorption process there is a solid phase (sorbent) and a mobile phase (solute). The contaminants in the solute bind onto the sorbent until equilibrium is achieved. This is called the equilibrium concentration (Ce).

Specific ion 'uptake' coefficient (q, mg/g sorbent) explains how much contaminant is adsorbed by the sorbent and can be found in Equation 1. In order to compare different ions in the solution, this unit is commonly written as mmol/g sorbent.

$$q = \frac{v(C_i - C_e)}{W} \qquad (1)$$

where q is the equilibrium uptake (mg/g); Ci and Ce are the initial ad equilibrium metal concentration in the solution (mg/g), respectively; V is the solution volume (L); and W is the dry weight of biosorbent (g).

Influencing Parameters

Many parameters or environmental conditions influence the biosorption processes. The most important parameters are listed as follows:

- Solution pH
- Process temperature
- Initial metal concentration
- Biosorbent dosage and size
- Presence of another metal

Batch and Continuous Biosorption Experiments

Metal Solution

Neodymium solution was prepared by dissolving Nd-Fe-B magnets in concentrated Nitric and Hydrochloric acid. For this purpose, magnets were extracted manually from the hard disk drives. Before leaching the magnets, the outer protective coatings were removed. The total of 20 gm of Nd-Fe-B magnets was used for experiments.

EPA Method 3050B was applied for the digestion of the magnets. Per 2 g (dry weight) of the sample 2.5 mL conc. HNO_3 and 7.5 mL conc. HCl were added in a flask and placed onto a heating source of exactly 95°C with constant stirring for 15 minutes. The digestate was filtered through Whatman No.41 filter paper and collected in a volumetric flask. The filter paper was washed with 5 ml HCl and 5 drops of concentrated HCl was added to the flask to prevent precipitation. After cooling the leachate was analyzed through atomic absorption spectroscope to analyze Nd concentration. The initial concentration of the leachate was used as a reference. Therefore, the leachate solution was standardized at 1000 mg/L neodymium. This stock solution was diluted according to the particular concentration that ranged from 50 to 100 mg/L Ci Nd (initial neodymium concentration).

Biosorbent preparation

The microalgae (*C. vulgaris*) used in the biosorption experiment was obtained from the Culture Collection of Algae (SAG) of the Georg-August-Universität Göttingen under the serial designation SAG 211-12 [5]. The final cultivation of algae was performed in a pilot plant of E. ON Hanse AG in Hamburg-Reitbrook. Before performing biosorption experiments, algae was dried overnight (24 hrs) at 55°C in oven (Figure 2). The particle size of the dried algae was determined using Retsch Sieving Systems and was found to be 250 µm.

For the batch biosorption experiments the dried biosorbent dosage ranged from 0.5 to 3 g/L was used.

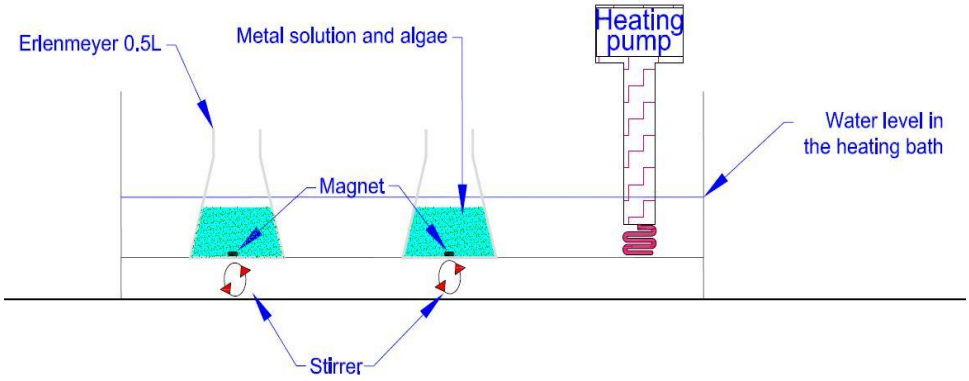
Figure 2: Dried microalgae *Chlorella vulgaris*.

Batch Biosorption Test

The experiments were carried out in 500 ml erlenmeyer flasks containing the respective amount of sorbent dosage and stock solution. A particular initial concentration of the solution was adjusted by dilution with deionized water. The appropriate pH was regulated and kept constant with ± 0.2 deviations by the use of 0.1 M HCl and 0.1 M NaOH. After pH adjustment, 2 ml of sample solution was taken in order to determine the starting metal concentrations. Following pH adjustments, the same solution has been used to perform a biosorption test with 0.5-3 g/L biosorbent *Chlorella vulgaris* dosage. The dry biosorbent was contacted with 0.2 L of known concentration solutions for 90 min and the suspension was agitated on a rotary shaker at 300 rpm at 21, 35 and 50°C (Figure 3).

In batch biosorption experiments, pH 3, 4 and 5 were adjusted in order to obtain the equilibrium isotherms. Samples were taken with an automatic pipette at pre-determined time intervals (0, 4, 8, 15, 45 and 90 min) for the residual metal ion concentrations in the solution. Each sample was at first filtered by Whatman 0.45 µm pore size membrane filters in order to analyze them using ICP-OES (Agilent).

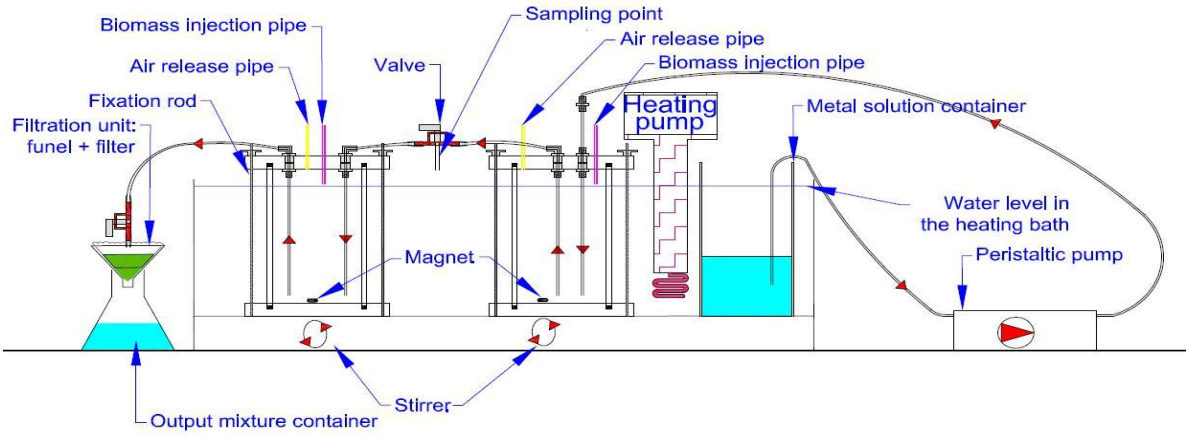
Figure 3: Experimental setup sketch for batch test.



Continuous Biosorption Test

The chosen setup consists of two 1 L cylindrical reactors in series fed by a peristaltic pump. The reactors and the metal solution are contained in a water bath heated by a pump at the optimal reaction temperature of 35°C (determined during batch test). Each cylinder was equipped with an air release pipe to flush the air out as the reactor is being filled, and a biomass injection pipe to inject the algae, this later can also serves as a sampling tube. A magnet and stirring system was used for mining the mixture. Figure 4 shows the setup as it was used. The experiment's conditions are explained as follows: pH 5, temperature 35°C, flow rate 20 ml/min, maximum contact time 100 min, total volume of solution=2.5 L and biosorbent dosage 2 g algae/L solution. The biosorbent (total 5 g) was fed at once at the beginning of the test.

Figure 4: Experimental setup sketch for continuous test.



RESULTS AND DISCUSSION

Batch Test Results for Neodymium

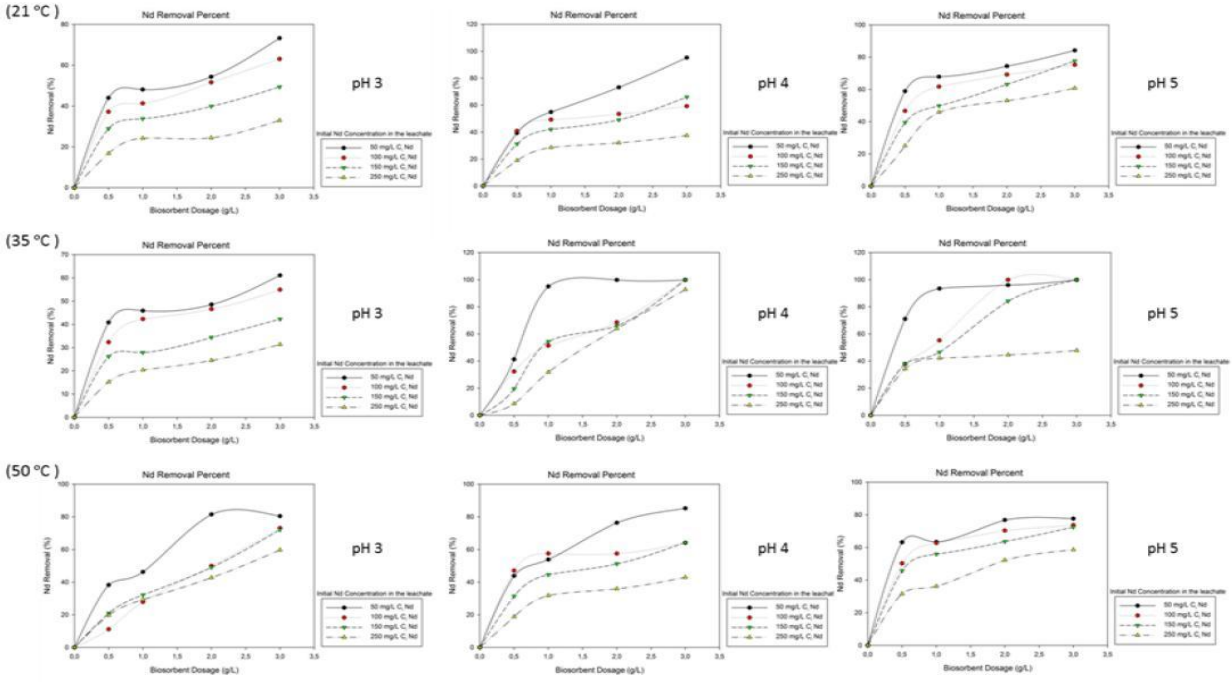
Biosorption experiments were (°C) performed at three different pH (3, 4 and 5) and temperature (21, 35 and 50 with different biosorbent concentration (0.5, 1, 2 and 3 g/L) and initial Nd concentration (50, 100, 150 and 250 mg/L). The experimental neodymium uptake values onto Chlorella vulgaris were plotted in function of biosorbent dosage and initial metal concentration.

The optimum °C pH was value pH °C, for the 5 (Figure Nd maximum biosorption 4). For 50 at 21 and 35 experimental uptake (q=123.82 mg/g) was obtained at pH 4, since, a higher pH coupled with increase in temperature leads to Nd precipitation. Therefore, the decrease of metal ion in solution resulted in low experimental Nd uptake by microalgae. A rising trend in neodymium uptake can be observed with an increase in pH at 35°C. A pH 5 has the best experimental uptake (q=157.40 mg/g) due to the fact that there is less competition of iron in the solution as well as less competition of H^+ protons and a more favorable pKa for the carboxylic acid groups. A pH of 4.8 has been determined as optimal for mono-metal uptake since this is the pKa of the carboxylic acid functional group, mainly responsible for the biosorption of Nd^{3+} and La^{3+} in general [6-9].

On the other hand, the leachate solution derived from harddisk permanent Nd-Fe-B magnets involves mainly Nd^{3+} and Fe^{3+}. Hence, there is a strong competition between Nd and Fe in order to bind negative functional group on the cell wall of microalgae during biosorption experiment. When the pH value increased from 2 to 5, iron ions started to precipitate which lead to decrease in the competition. In present study, at a pH between 4 and 5, about 98% of iron was precipitated in the leachate solution. Fe^{3+} is present at a pH between 0 and 3.8 as well as Fe^{2+} occurs between pH 0 and 9 [10]. Most Lanthanides including Nd are in their ionic form in a solution at an acidic to neutral pH and Nd will not form any hydroxide precipitation at a pH lower than 7 [10].

As it has been mentioned before that a high biosorbent dosage increase the removal rate, but lower the specific biosorption, in other word the utilization of the sorbent's mass in less optimized. According to isotherm experiments, the maximum Nd recovery was achieved at pH 5, 35°C with 50 mg/L initial metal concentration and 2 g/L biosorbent dosage. Therefore, the continuous biosorption test was conducted under those conditions.

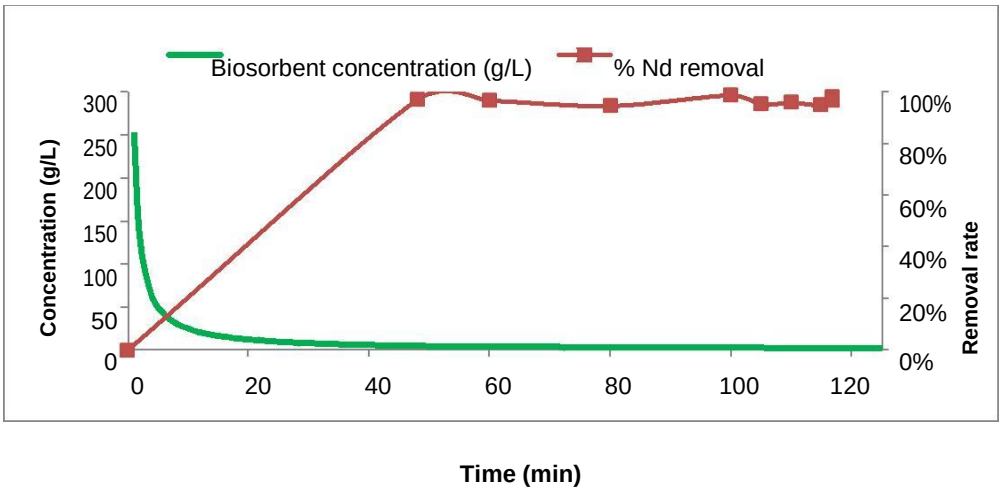
Figure 4: Removal percent of Nd at different temperature (°C) and (21, pH values 35 and (pH 50 3, 4 and 5).



Continuous Test Results for Neodymium

The Figure 5 shows the removal rate of Nd and the concentration of biosorbent in the reactor at different time. The time is the time since the beginning; the maximum retention time is 100 min, therefore for the Nd removal all values above time 100 min correspond to a retention time of 100 min. From 0 minute to 50 minutes the samples are done in reactor A, after 50 minutes the samples are taken in reactor B.

Figure 5: Neodymium removal rate and sorbent concentration evolution for 50 mg/L Nd solution, with single sorbent feeding at pH 5 and 35°C, flow rate 20 mL/min.



After 46 min the removal rate have reach 97% of Nd and the Nd concentration in reactor A is 2.15 mg/L. In the batch test at pH=5 and biosorbent dosage of 2 g algae/L the removal rate is about 50% for a Nd solution at 100 mg/L and 99% for a Nd solution of 50 mg/l. The reason for which the continuous system has higher removal rate can be explained by looking at the biosorbent concentration curve. At the beginning when the volume of solution in the reactor is small the biosorbent concentration is for a short time extremely high. For example during the first five minutes the biosorbent concentration is more than 50 g/L, in the first 20 min its concentration is more than 10 g/L and in the first 48 min the sorbent's concentration is more than 5 g/L. These extreme biosorbent concentrations lead to a very fast and effective removal rate.

Nevertheless, as the solution continues to flow in the reactor the Nd removal rate was stabilized at 96.5% ± 1.1% with is still high but certainly only influenced by the very high sorbent concentration during the process and the movement of the volume in reactor A to reactor B. If the metal solution would continue to be injected in the system all the algae would be progressively flushed out out and the biosorption process reduced, inducing a decreased of the removal rate. Plus no samples were taken in reactor A after 50 min, and not all the solution passed through both reactor.

By taking an average removal rate of 98% on the overall experiment a volume of 2.5 L solution and a total of 5 g algae, it is possible to calculate a specific biosorption of 34.3 mg Nd/g algae.

CONCLUSION

The results show that the applicability of batch and continuous biosorption process satisfactorily for Nd in this study which means that the biosorption for Nd by microalgae *Chlorella vulgaris* biomass is favorable. An increase in sorbent dosage is correlated with an increase in removal rates but also a decrease in removal efficiency. Neodymium biosorption was mainly influenced by the pH and temperature. A higher pH coupled with increase in temperature ≤ 2.5 cannot leads be analyzed to iron precipitation for. Whereas, a pH value of neodymium uptake due to strong acidic conditions that results in protonation of H+, while pH value >5 results in precipitation of lanthanides.

The experiments were performed in batch and continuous systems, and the obtained results confirm that maximum amount of metal removal (99.9%) was achieved at pH 5 and 35°C, after contact time of 30 minutes. Microalgae *Chlorella vulgaris* used in this study removed neodymium ions from a mixed leachate solution immobilizing up to 157.40 mg of metal per gram of dried biomass of 0.5 g/L with 250 mg/L initial neodymium concentration in the leachate. In the continuous test, the recovery rate of Nd was obtained by 96.5%. Due to the slow kinetics of Nd sorption onto *Chlorella vulgaris*, the sorption capacity in batch assays was higher than that in continuous assays.

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