Application of membrane separation and adsorption for nutrient recovery from dairy waste waters

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Abstract

Among the current environmental challenges facing humanity is the protection of water in quantity and quality. The objective of reduce to zero the generation of waste in productive activities by applying the concept of circular economy has led to the emergence of proposals for the production of biomaterials capable of contributing to environmental protection and that do not imply huge investments of money. As a good example of these proposals, biochar had to be mentioned which is a material with excellent adsorbent properties, with low production costs and that is made with any type of organic matter such as agricultural waste. In this work a nanoparticle-modified ultrafiltration membrane was used as a pre-treatment method prior to ammonium adsorption. As adsorbent for ammonium removal alkaline modified biochar produced from banana leaves were used. The characterization of biochar and the research about kinetics models obtained after batch experiments. The general results obtained after the combination of membrane filtration and adsorption are promising and reflect a satisfactory ammonium removal percentage, and these results prove that biochar would be a good adsorbent for nutrient recovery from wastewaters.

Key words: ammonium removal, water treatment, membrane filtration, biochar, adsorption.

Introduction

Currently, humanity is facing important challenges regarding the protection of the environment and natural resources, within these challenges is the care of water quality. In this sense, water treatment has gained vital importance in recent years, ammonia and phosphates are among the biggest contaminants in water, their presence is a cause of eutrophication. One of the most used wastewater treatment methods is membrane filtration due to the advantages it offers such as high efficiency, low cost, simple operation, among others. On the other hand, circular economy means a waste recycling and reuse strategy to produce high-quality products, agricultural industrial waste offers great potential for recovery instead of going to landfills and can recover all untreated or treated biomass material one of a good example of this is the biochar, in the last decade the adsorption of water pollutants with biochar has gained strength and popularity in terms of environmentally friendly treatments.

Material and methods

Modified Biochar preparation

Banana leaves were collected, cut into small pieces and washed with distilled water to remove impurities and dust, then they were oven dried at 150ºC for two hours, the material was ground until reaching the desired particle size of less than 250µm, subsequently, the material was modified with alkaline sodium hydroxide solution 1M for 24 hours in a stirrer and finally the material was pyrolyzed in a muffle furnace at 300ºC for two hours in an oxygen depleted atmosphere.

Zeta Potential measurement

In order to know the surface chemistry of the biochar adsorbent material as well as its possible interactions with the adsorbate, the Zeta Potential was measured using 10 mg suspensions mixed in bottles containing 10 ml of sodium chloride (NaCl) 0,01 M solutions at different pH values. After mixing, equilibrium pH of samples was measured and adjusted then zeta potential was measured by zetasizer Nano Zs, (Malvern, UK) using electrophoretic light scattering (ELS).

Membrane Separation

Wastewater used for the present study was sampled from SOLE Company that is a milking parlour unit near the city of Szeged, Hungary. The initial ammonia concentration was measured with the spectrophotometer obtaining the value of 19mg/L, after that the water was filtered through modified fabrication membranes: polyvinylidene fluoride (PVDF), polyvinylidene fluoride with titanium dioxide TiO_2 (PT100) and polyvinylidene fluoride with bismuth vanadate (PB100). The ultrafiltration membranes were prepared with phase inversion method, the pore size was 30.04nm for PVDF, 33.43nm for PT100 and 47.33 for PB100.

Adsorption experiments

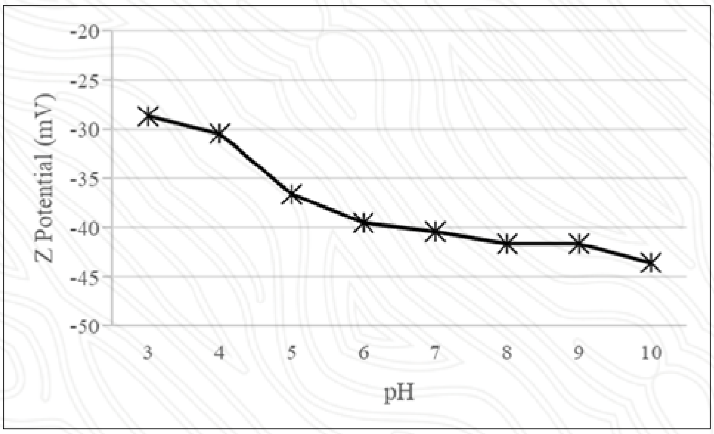
Batch experiments were carried out, 50mL of wastewater permeate was stirred at 250 rpm with different doses of biochar for two hours, then samples were taken and analyzed in the spectrophotometer to determine the final concentration of ammonium in the water. The variables that were modified and taken into account to carry out the adsorption experiments were pH, temperature and biochar dose.

Results and discussion

Regard to the zeta potential measurement showed that biochar surface is negatively charged in the studied range of pH. The value of zeta potential decreases from -28.7 mV to -43.6 mV when pH increased from 3 to 10 (Figure 1).

Figure 1

Zeta Potential of biochar as function of pH (NaCl Concentration=0,01M).



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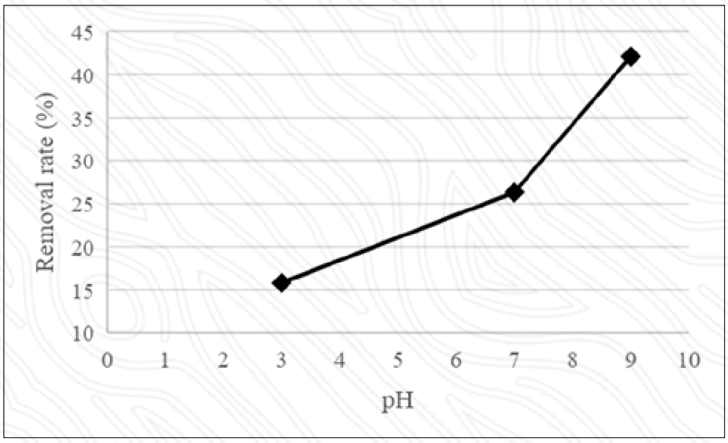
The results obtained in the experiments show that the combination of membrane filtration and biochar adsorption methods form an efficient system for removing ammonium present in wastewater. PVDF membrane removed 99% of chemical oxygen demand (COD) from wastewater, PT100 and PB100 removed 97% of COD.

The most significant ammonium removal was obtained in the adsorption process achieving up to 60% removal compared to the initial concentration. It was determined that the temperature is not one of the variables that greatly affect the removal of ammonium, however the pH is a determining factor, obtaining better results at high pH, in terms of the optimal dose of biochar, the best was 500mg/L.

To study the effect of pH, experiments were performed in solutions with different pH values (3, 7 and 9) and fixed values of other parameters (dose of biochar and temperature). The initial solution pH plays a critical role in the adsorption processes as it affects both adsorbate and adsorbent characteristics and behaviours. The highest amount of ammonium removed 42% was achieved with pH 9 with 500mg of biochar and at room temperature.

Figure 2

Effect of pH on removal ammonia rate.



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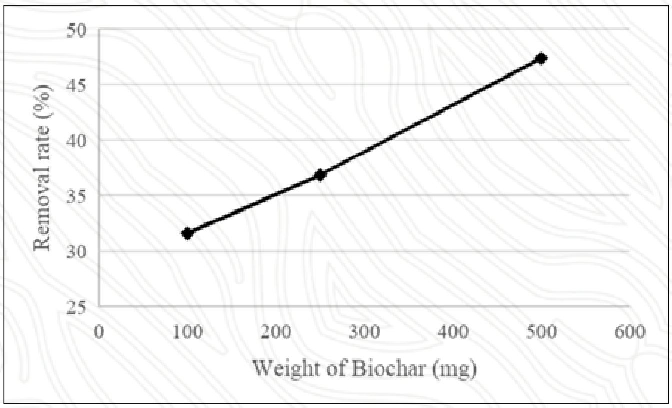
The effect of adsorbent dose was studied by varying the used mass of biochar and keeping other parameters constant (pH and temperature). Increasing biochar dose from 100 to 500 mg shows a remarkable increase in ammonia removal rate from 32% to 47%, respectively at pH 7 and room temperature.

Figure 3

Effect of dose of biochar on removal ammonia rate.



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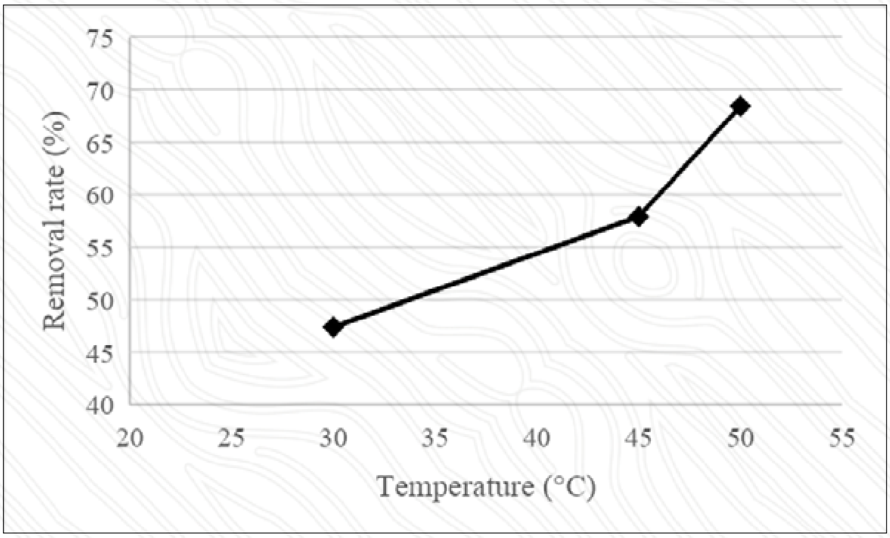
To study the effect of temperature, experiments were carried out with three different temperatures 30 ºC, 45 ºC and 50ºC and keeping other parameters constant (pH and dose of biochar). The results obtained show the maximum ammonia removal rate of 68% at 50 ºC, pH 9 and 500mg of biochar.

Figure 4

Effect of temperature on removal ammonia rate.



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Kinetics models were determined in order to know the required time to reach the state of equilibrium additionally, describe the mass transfer of NH4 from permeate to the active sites present in biochar surface. For the present study, pseudo first order and pseudo second order models were analyzed under conditions: pH 9, room temperature and 500mg of biochar. The equations and parameters of kinetics models are presented at Table 1, on the other hand, the Figures 5 and 6 show the linear form of pseudo first order and pseudo second order models respectively.

Table 1

Kinetic models, equations and parameters.

Name of kinetic model	Equation linear form	Parameters
Pseudo first order	$\frac{qt}{} + ln\ qe\ \ qt = ln\ qe - K\ t$	R^2=0.93 K1= -0.00014 (L/min) qe (cal)=0.61(mg/g)
Pseudo second order	$\frac{t}{} = \frac{1}{K\ q\ e} + \frac{t}{}$	R^2=0.98 K2=1.21 (L/min) qe (cal)=0.83 (mg/g)

Source: own authorship.

Figure 5

Pseudo first order kinetic model.

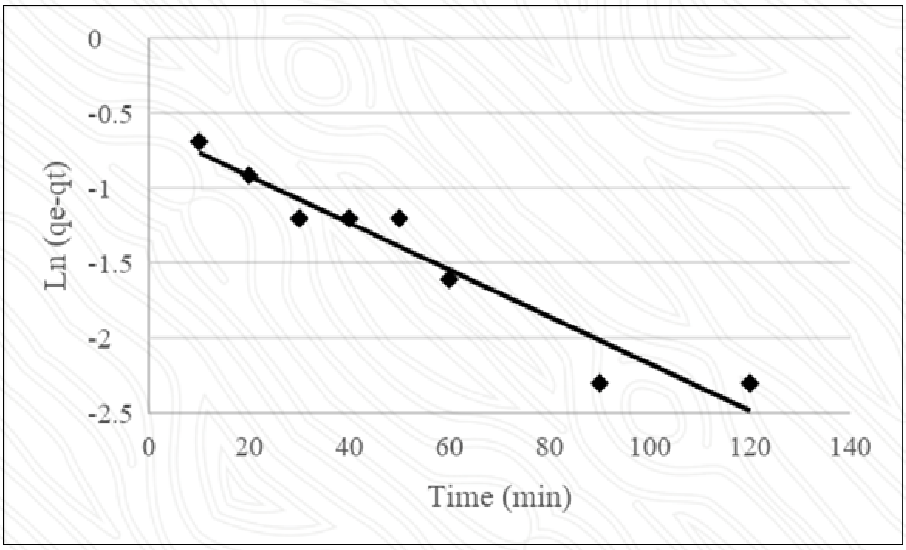

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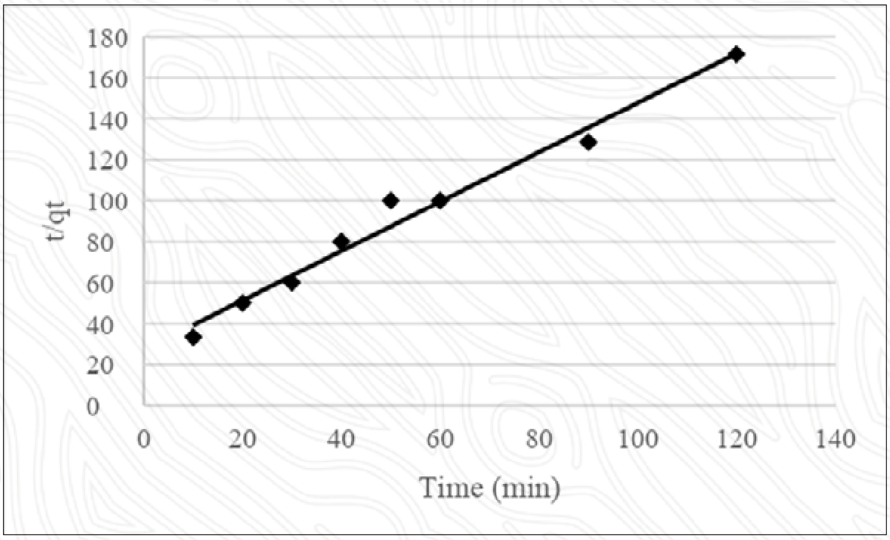
Figure 6

Pseudo second order kinetic model.



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Conclusions

The system made up of two unitary treatment operations consisting of membrane filtration and adsorption with biochar is efficient in terms of the main objective of removing ammonia from wastewater. The chosen membrane was effective in retaining suspended particles and was adapted as a first part of the treatment. Batch adsorption study of NH4+ with biochar showed that pH and adsorbent dose are parameters with the high effect on the process of ammonia removal of 60% was achieved within 120 min using 500 mg of biochar at initial NH4-N concentration of 19 mg/L, pH 9 and 50°C.

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