# REMOVAL OF AMMONIUM FROM WASTEWATER WITH METAKAOLIN BASED-GEOPOLYMER SORBENTS

**M. Otero*, L. Freire, S. Gómez-Cuervo, P. Villar**

AIMEN Technology Centre, O Porriño, SPAIN
(E-mail: miguel.otero@aimen.es; lorena.freire@aimen.es; santiago.cuervo@aimen.es; pvillar@aimen.es)

## HIGHLIGHTS

- Metakaolin based geopolymer was manufactured as ammonium adsorbent.
- Characterization through batch and continuous tests.
- Implementation of a wastewater treatment plant with adsorbent geopolymer.

**Keywords: geopolymer, sorbent material, metakaolin, $NH_4^+$ removal**

## INTRODUCTION

Ammonium ($NH_4^+$) is the most dominant form of nitrogen pollution in the aquatic environment. Elevated $NH_4^+$ concentrations in untreated waterways contribute to eutrophication and dissolved oxygen depletion, which causes severe degradation of water quality. Untreated wastewater containing high organic and nitrogen contents poses serious environmental problems if those pollutants are improperly managed. Anaerobic treatment technology is commonly adopted to treat piggery wastewater especially in developing countries with only emphasis on removing organic matter. However, the $NH_4^+$removal in anaerobic systems were limited.

The commonly methods used for $NH_4^+$ removal include microbial nitrification–denitrification reactions, breakpoint chlorination, air extraction, reverse osmosis, ionic exchange and sorption. The most widely used method to remove nitrogen from wastewater is microbial nitrification–denitrification reactions. However, nitrification rate drops sharply as temperature of wastewater decreases(1). Adsorption or ion-exchange-based approaches offer a more robust alternative method for $NH_4^+$ removal. It was demonstrated by a simulation that anaerobic digestion followed by zeolite-based ion-exchange had lower operational costs and better nitrogen-removal(2).

One of the main problems with zeolites is in their production, which requires high synthesis temperatures. Geopolymers have emerged as a promising alternative. Geopolymer is an inorganic polymer with excellent mechanical and physical properties and can be synthesized by alkaline activation of aluminosilicate materials from natural minerals or inorganic waste. Like zeolite, geopolymer has negative charges on the aluminosilicate structure where the exchangeable cations are located in the voids. The geopolymer could be synthesized at room temperature, resulting in lower energy consumption. To reduce the consumption of non-renewable resources in line with the circular economy principle, attempts have been made to convert industrial waste into useful products, including geopolymer. These materials do not require high synthesis temperatures, and their raw materials are available locally and at a relatively low cost. In addition, its adsorption capacities are even slightly higher than zeolites(1).

In our study, a porous metakaolin based-geopolymer was manufactured. Batch and continuous experiments were carried out to study ammonium removal capacity. After laboratory tests, the produced geopolymer with optimal characteristics is taken to a real industrial wastewater, located in Spain in order to validate the capacity adsorption.

Metakaolin geopolymers were manufactured at room temperature using waste from the granite industry. Commercial sodium silicate solution ($Na_2SiO_3$) containing 25,6 wt% $SiO_2$, 7,9 wt% $Na_2O$ and 66,5 wt% $H_2O$; and sodium hydroxide solution (NaOH) were used as alkaline activator with different silicate modulus (Ms). $H_2O_2$ was added as foaming agent in a range between 0.5% - 3%. The material was crushed and sieved to obtain particle sizes of 4 - 8 mm.

The adsorbent characteristics play an essential role in the adsorption process. This research characterized and compared the physical properties (e.g., bulk density, apparent porosity) of the synthesized geopolymer adsorbents. Batch experiments were carried out in 250 mL Erlenmeyer flasks using deionized water with known ammonium concentrations and geopolymer weights (generally for 24 h, pH = 6,50 mg $NH_4^+$/L and 5 g/L of geopolymer). The effect of variables was measured, including initial water pH, adsorbent dose, contact time and initial concentration. The experimental data will be adjusted to the isotherm model and kinetic equation that present a greater goodness. Column tests were also carried out with a pollutant flow of 6ml/min to determine the adsorbent capacity of ammonium of the produced material.
As a final validation, the optimal formulation obtained from the laboratory results was taken to a Spanish landfill, where two wastewater systems were designed and data on the decrease in ammonium concentration, pH and conductivity were collected.

## RESULT & DISCUSSION

Several geopolymer formulations were studied, being the following one, the most promising as adsorbent material (Table 1).

**Table 1: Most promising geopolymer formulation**

| Silicate modulus | NaOH (M) | $Si_2O_3$/NaOH (molar ratio) | Granite waste substitution | % $H_2O_2$ | Setting time (h) | Curing T (°C) |
|---|---|---|---|---|---|---|
| 1,5 | 10 | 1,2 | 20 | 1 | 24 | Room temperature |

The effect of pH was examined, and it was observed that the adsorption increased slightly the more acid. Regarding the dose of adsorbent, the highest was found at 5g/L with similar results at higher doses. The 1h contact time is when the highest slope of elimination occurs. At longer times the slope becomes smaller. Finally, the initial ammonium concentration tests show that the maximum adsorbent capacity ($q_m$) is 23mg of ammonium per gram of geopolymer.
The isotherm that best fits the data is the Redlich–Peterson isotherm (Figure 1). The rate equation with the best fit is the Weber-Morris equation (Figure 2).

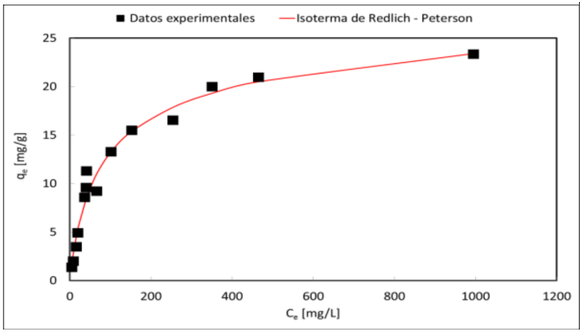


**Figure 1:** Redlich–Peterson isotherm

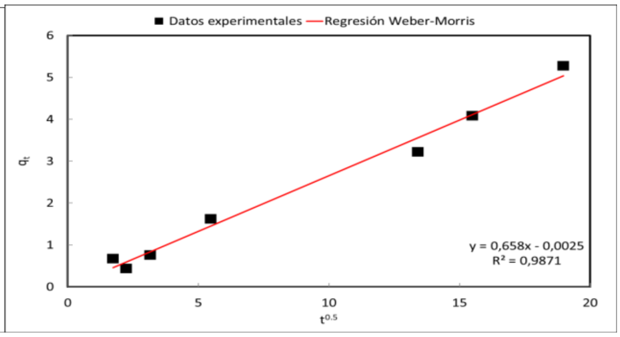


**Figure 2:** Linear regression fit of the WM equation

The results of continuous tests performed in columns show how at short times the $NH_4^+$ elimination is maximum, but from 120h the geopolymer becomes saturated and the contaminant concentration does not decrease (Figure 3).

Once the laboratory tests were finished, the selected geopolymer were conformed in form of cylinders (3cm diameter, 5 cm height) and in form of gravel (4mm-8mm sizes) as shown in Figures 4 and 5. These pieces were located at the wastewater plant in order to test the adsorbent material in real operating conditions. The results obtained for the ammonium removal in this industrial wastewater plant was up to 80%. However, the pH of the effluent increased from 9 to almost 12 at the outlet of the treatment. This issue needs to be studied in future works.

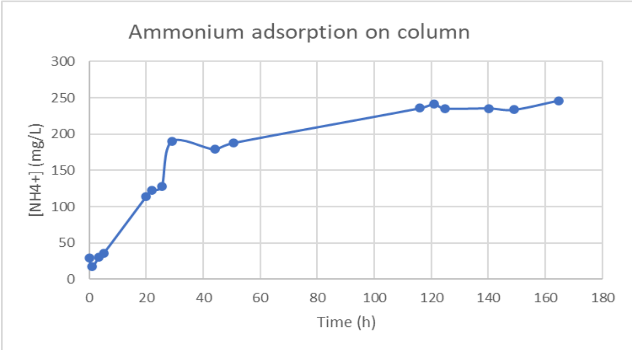


**Figure 3:** Continuous column tests

**Figure 4:** Geopolymer in cilynder format

**Figure 5:** Geopolymer in gravel format

## CONCLUSIONS

Preliminary results have shown a high sorption capacity of the geopolymer, obtaining removal efficiencies up to 80% and a maximum adsorption capacity ($q_m$) of about 23 mg/g. This value is similar to that reported for natural and synthetic zeolite(1). When the geopolymer is implemented in a wastewater treatment plant, the adsorption capacity maintains above 80%.

According to these results, this material can be an alternative adsorbent due to its simple synthesis conditions and low operational costs. In addition, it shows good workability in different climates.

However, more studies are required to increase the $NH_4^+$ removal. It is priority to control the adsorption mechanism and the alkali leachate in order to implement the material at industrial scale.

## ACKNOWLEDGEMENT

The project **LIFE GREENADAPT** has received funding from the LIFE Programme of the European Union under the Grant Agreement no LIFE20 CCA/ES/001795.

## REFERENCES

1. Giorgia, F., Janne, P., Tero, L., Chengying, B., Paolo, S., Renata, B., Sara, C., Murilo, I. and Paolo, C. Removal of Ammonium from Wastewater with Geopolymer Sorbents Fabricated via Additive Manufacturing. *Materials and Mechanics* 195 (2020), 109006.
2. Lin Y, Guo M, Shah N, et al. Economic and environmental evaluation of nitrogen removal and recovery methods from wastewater. *Bioresour Technol*. 215 (2016), 227–238.