Combined application of induced MAP (Magnesium-Ammonium-Phosphate) precipitation and adsorption through natural zeolites for reducing NH_4^+ and PO_4^{3-} in swine wastewaters

Tescaro N., Galamini G., Ferretti G., Faccini B., Eftekhari N., Coltorti M.

Department of Physics and Earth Science, University of Ferrara, Italy

Introduction

The increasing needs of crop productions leads modern agriculture to apply increasingly quantities of fertilizers to soil and the demand of meat is increasing with the global population.

One of the most used organic fertilizer consists in animal slurry, or zootechnical wastewater (ZW). These materials are very rich in nutrients like **ammonium** (NH_4^+) and **phosphates** (PO_4^{3-}) and often are applied in strong excess in order to assure high crop yield. The main problem is that about 50% of introduced N and P are not exploited by crops, impairing the environmental quality through nitrogen losses in atmosphere (emission of harmful and GHG gasses like N_2O, NO_x, NH_3, and others) and eutrophication of water bodies.

It is thus necessary to develop techniques for the treatment of ZW in order to reduce their nutrient content. Two important techniques were efficiently proposed, the first involves the use of natural zeolitites (rocks containing > 50% of zeolites, ZEO) as sorbent for the reduction of NH_4^+, while the second consists in the precipitation of a mineral phase (magnesium-ammonium-phosphate, MAP) induced directly in ZW, in order to sieve NH_4^+ and PO_4^{3-}.

The aim of this work is to **study the removal of N and P by the combination of MAP precipitation and natural zeolites adsorption** from a synthetic solution with a NH_4^+ and PO_4^{3-} content comparable to a common zootechnical wastewater.

Materials and methods

Two synthetic solutions with different $Mg^{2+}:NH_4^+:PO_4^{3-}$ molar ratio (MR) were tested: **MR1** (1:1,5:1) and **MR2** (2:1:1). The reagents used were $MgSO_4$, NH_4Cl and K_2HPO_4. In order to obtain MAP precipitation pH was buffered at 9 using KOH.

The adsorbent used was a **natural chabazite-rich ZEO** quarried in Italy.

The NH_4^+, PO_4^{3-} and K^+ concentrations were respectively determined with an ion-selective electrode (ISE), an UV/VIS spectrophotometer and an ICP-MS.

The solid material obtained (MAP precipitates in combination with ZEO) were collected, dried at room temperature and subsequently analyzed using a Scanning Electron Microscope (SEM) by carrying out a series of chemical mappings.
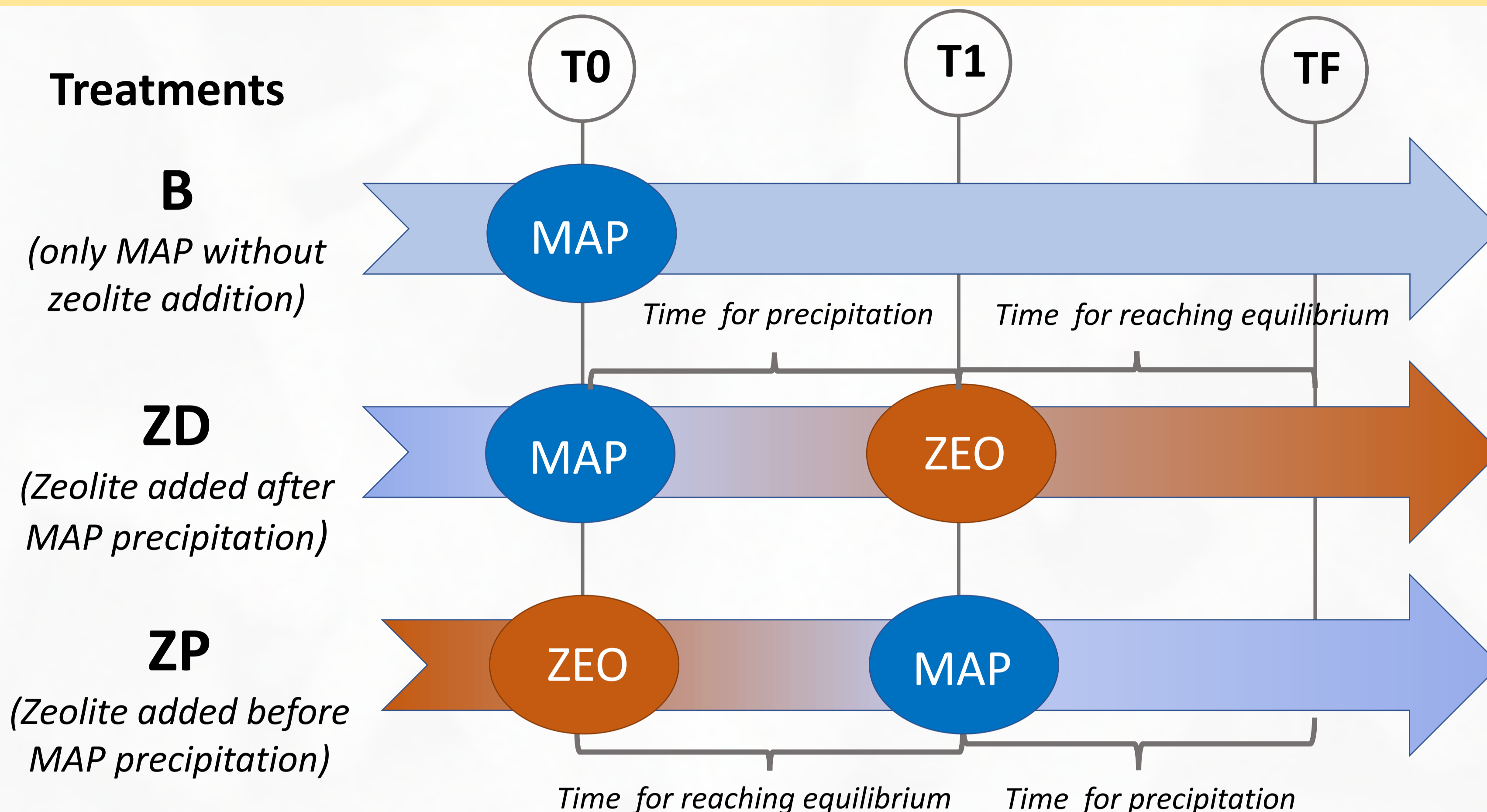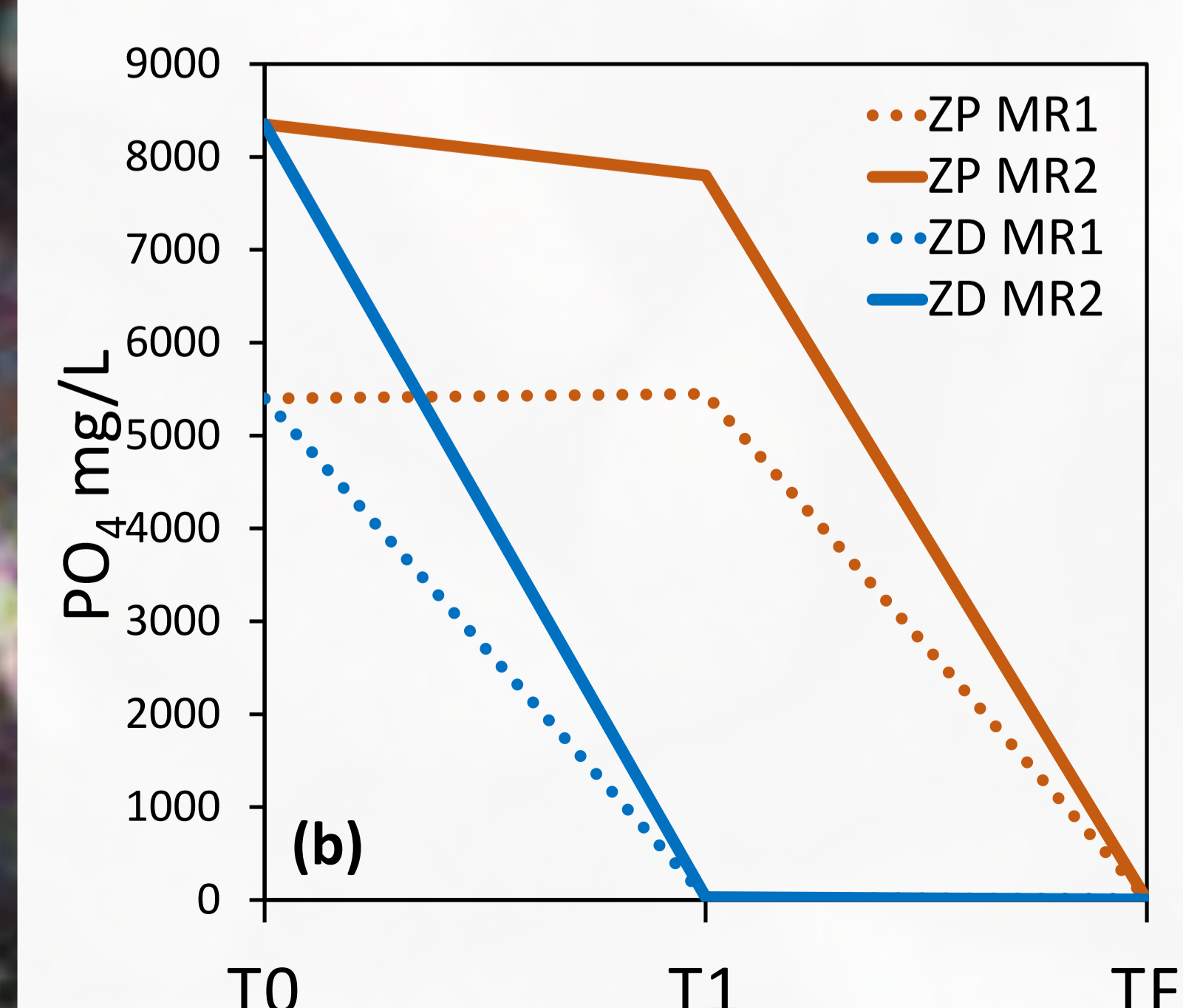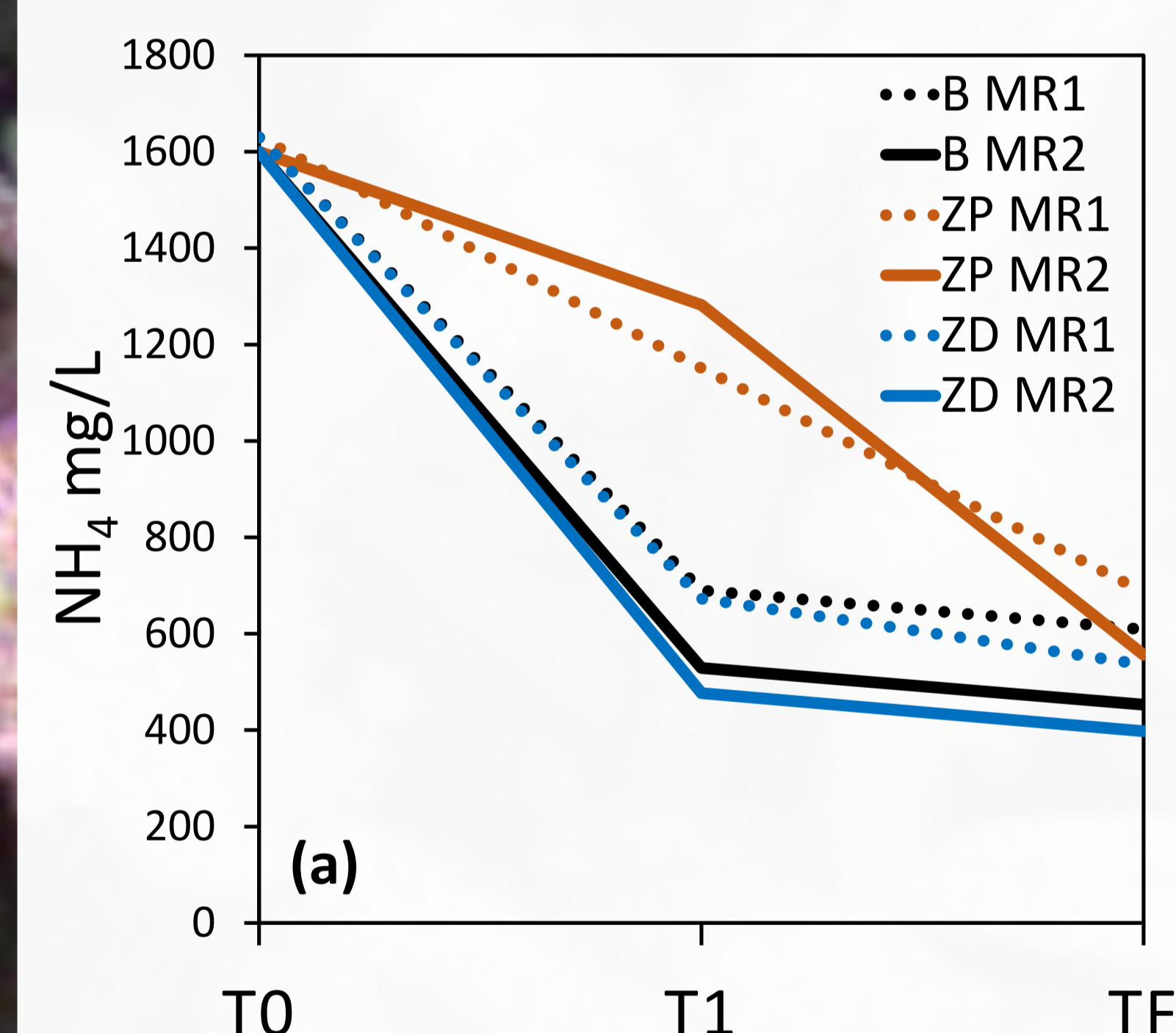
Experimental set-up

Figure 1. *The Experimental set-up included three treatments: B, ZP and ZD, where T0 is the start point. For B MAP precipitation was achieved at T1 without adding any zeolite; for ZD the MAP precipitation was archived at T1, then a quantity of zeolite was added and let reaching equilibrium (TF); for ZP a quantity of zeolite was added and let reaching equilibrium (T1), then MAP precipitation was induced at T1. NH_4^+ and PO_4^{3-} were measured at all the time points. The experiment were carried out in 3 replicates both for MR1 and MR2.*

Results

Figure 2. NH_4^+ *(a) and* PO_4^{3-} *(b) concentrations for T0, T1 and TF. In (b) B treatments for MR1 overlaps ZD MR1 and B for MR2 overlap ZD MR2.*
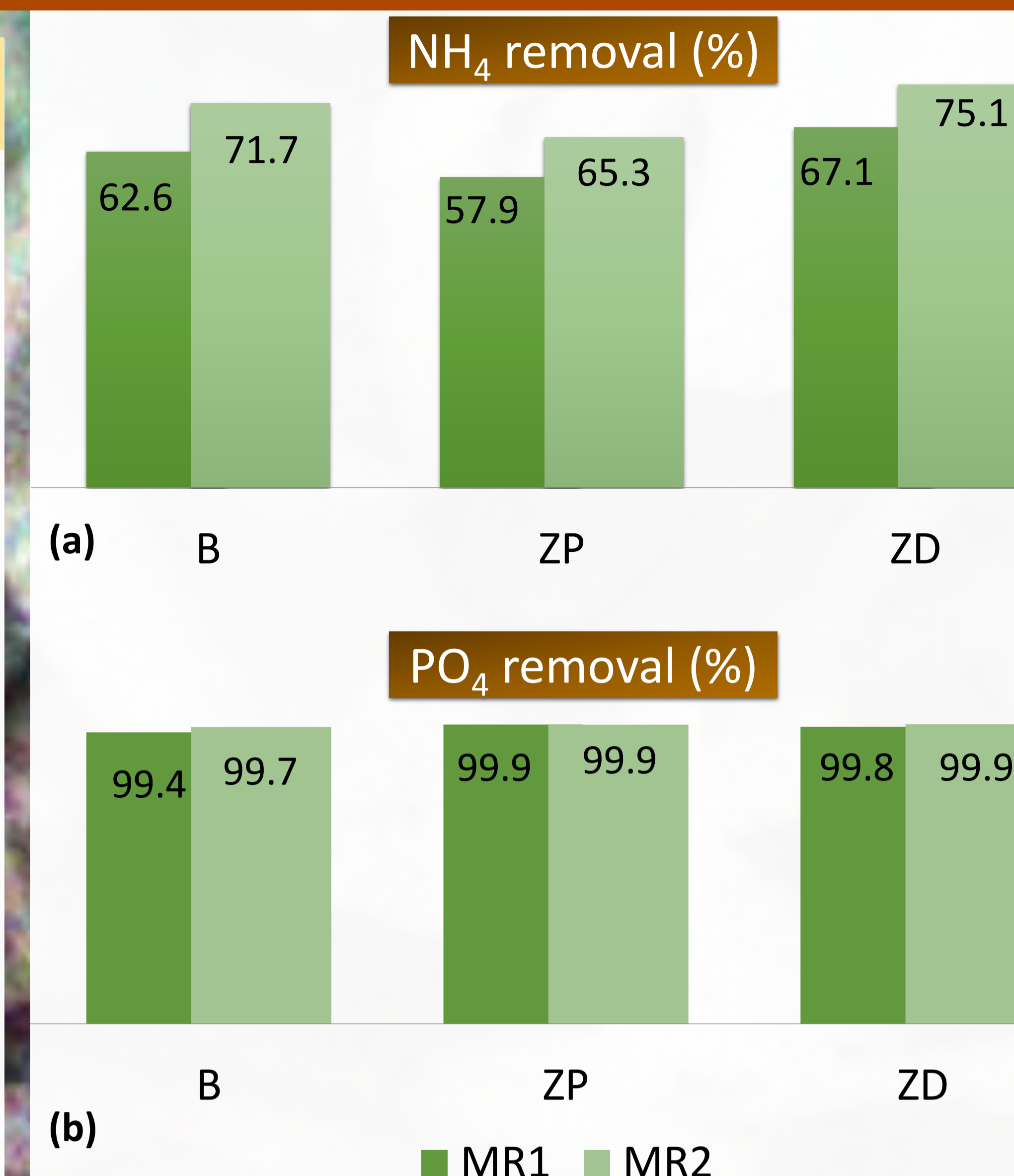
NH_4^+ and PO_4^{3-} concentrations in T0, T1 and TF are showed in figure 2. It is observed that the process that reduces the major part of NH_4^+ and all the PO_4^{3-} in solution is MAP precipitation. For both MR1 and MR2 adding zeolite before MAP precipitation (ZP) is less efficient because the adsorption of NH_4^+ subtracts ammonium ions from the solution, changing the optimal molar ratio between Mg^{2+}, NH_4^+ and PO_4^{3-} for MAP precipitation.

It is also noted that the reductions in MR2 are greater than those of MR1, thus MR2 is considered the most efficient molar ratio.

Figure 3. NH_4^+ *and* PO_4^{3-} *total removals (%) of the three treatments in MR1 and MR2.*

NH_4^+ and PO_4^{3-} total removal efficiency is shown in figure 3. MR2 Reductions are greater than those of MR1 for all treatments.

The addition of ZEO before MAP precipitation (ZP) introduces interfering ions (Ca^{2+} and Mg^{2+}) that precipitates as Calcium - magnesium phosphates reducing the overall MAP production.

From ESEM chemical mappings (figure 4a) it is clear the difference between MAP and the zeolites since the MAP is detected by magnesium and phosphorous, while the zeolite tuff is detected by silicon, aluminum and potassium.
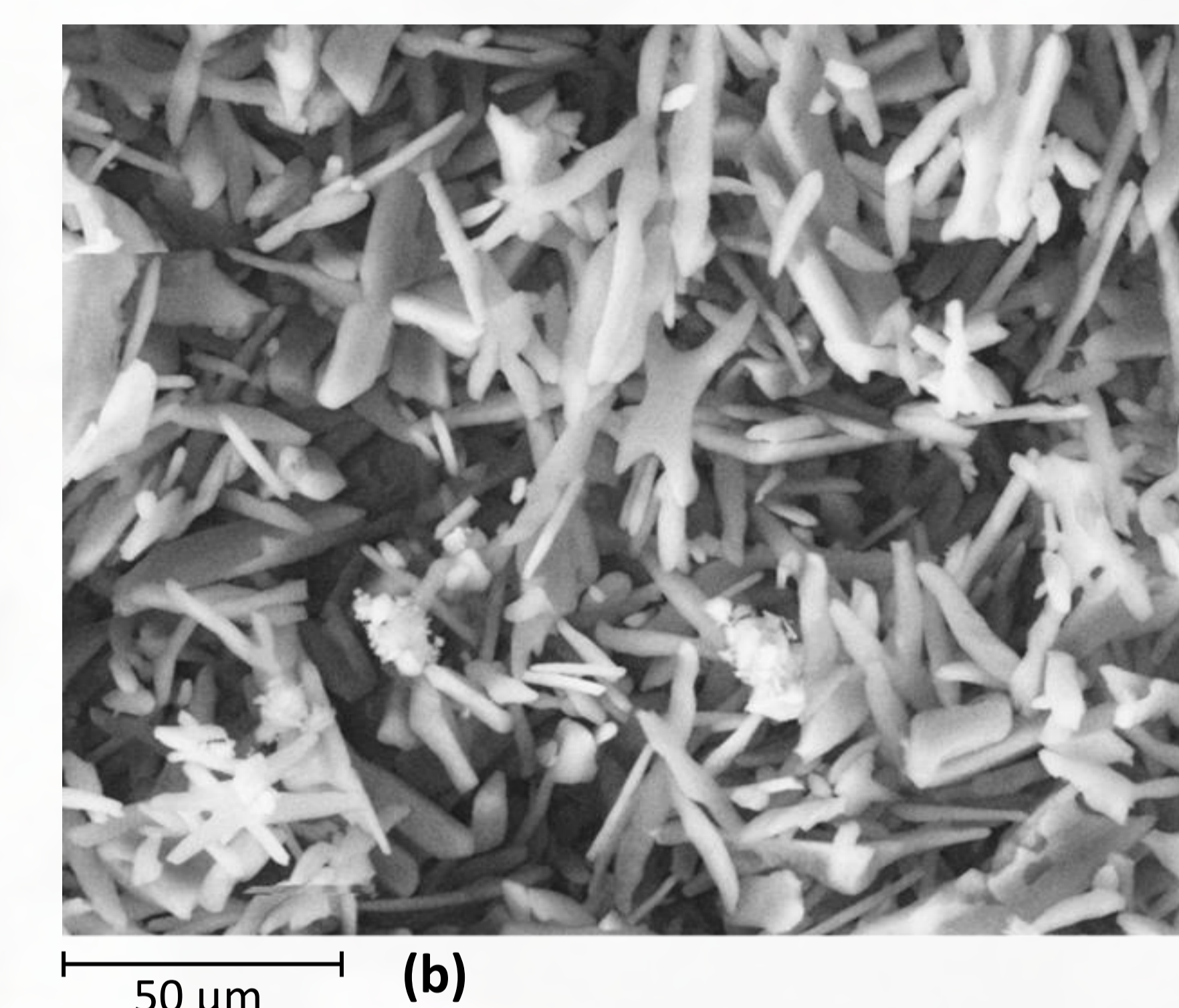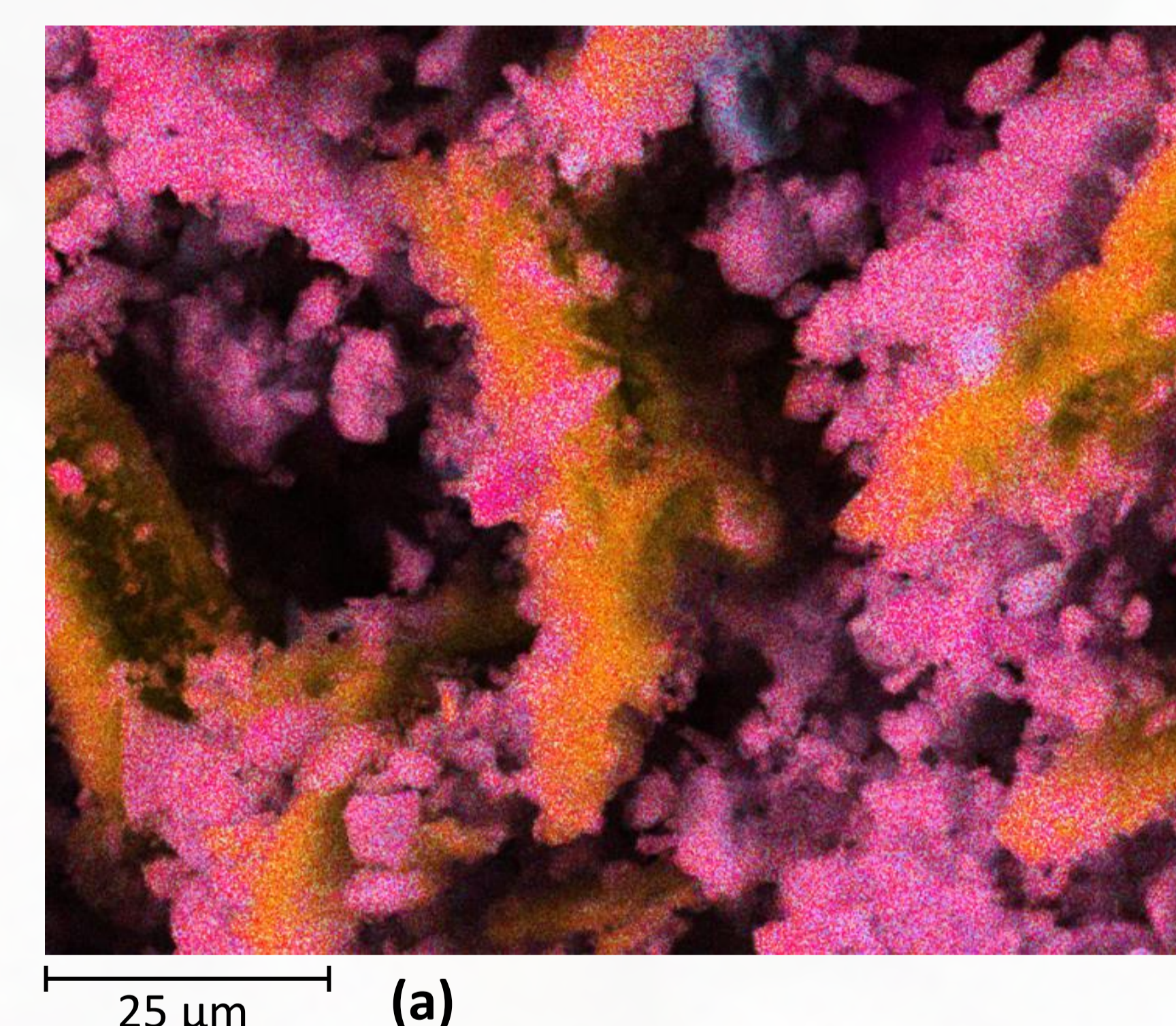

Figure 4. *ESEM images of the materials obtained from the experiments (a) chemical mapping of ZD MR2, MAP corresponds to the orange zones, zeolite tuff is flash pink, while other precipitates are visible (light blue). (b) MAP crystals obtained from MR2 batch, with their characteristic «X-shape» gemination, acicular forms approximately 30-40 µm long.*

Conclusions

In the experimental conditions used in this work, natural zeolites better performed when added after MAP precipitation, in particular higher quantities of MAP were obtained using the MR2 molar ratio. The addition of natural zeolite before MAP precipitation unbalances the molar ratios between $Mg^{2+}:NH_4^+:PO_4^{3-}$ and leads to the introduction of elements as Ca^{2+} that interferes with MAP precipitation.

Further experiments are needed to further improve the efficiency of this technique.

The material produced could therefore constitute an interesting fertilizer that combines both good concentrations of N and P and fundamental properties such as slow and gradual release.