

Water Treatment Applications of Eco-Friendly Cationic Maltodextrin-Based Adsorbents

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Research Article

Keywords: Water treatments, environmental applications, green processes, maltodextrin-based polymers, cationic adsorbents

Posted Date: July 29th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-678834/v1>

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Abstract

The anthropogenic environmental pollution generated during the last decades led to significant consequences for the aquatic ecosystems and to potential risks for human health. For this reason, the research has been focused on studying and develop pollutants-removing technologies. Nowadays, despite the presence of performing techniques applied in e.g. the potabilization and waste-water treatments, new strategies aimed to better meet the industrial needs and the environmental requirements are still widely investigated. In this frame, the pollution caused by the presence of anionic species in water, is still not completely solved. For this reason, this work is focused on studying novel cationic maltodextrin-based adsorbents obtained via sustainable approach, for water treatment applications. The adsorption performances towards nitrates-, sulphates- and phosphates-polluted water solutions have been tested and discussed.

Highlights

- Maltodextrins are water-soluble starch hydrolysis products which can be exploited to develop biobased polymers
- Employing amines in the polymerization reaction of maltodextrins with diglycidyl ethers can impart the final product cationic features
- The cationic features can be exploited to study the obtained polymers as novel adsorbents for water treatment applications

Introduction

Since the second half of the twentieth century, one of the most important scientific achievements has been the explicit realization that human activities have changed the chemistry of the environment (Laborde et al. 2015). In this context, the eutrophication resulting from the presence of nitrogen, phosphorus and the toxicity associated with nitrates are considered the main cause of degradation of rivers, lakes and marine compartments throughout the planet (Gakstatter et al. 1978; Correll 1998; Morse et al. 1998; Smith 2003; Azam et al. 2019). Besides, in recent decades a significant increase of nitrates concentration in surface water, groundwater and agricultural areas especially when associated with intensive livestock activities, has been reported (Costamagna et al. 2020a).

Alongside animal farming, the agricultural sector is one of the most hydro-demanding production field. Furthermore, the employment of fertilizers and plant protection products determined a significant impact on the territory and water resources (Carpenter et al. 1998; De La Torre et al. 2011). In addition, high contents of sulfates due to natural soil composition, industrial processes or atmosphere emissions represent a threat for the ecosystem. As instance, in a carbon enriched environment sulphates can be easily involved in anaerobic bacterial reduction processes, generating H_2S as a result (Geurts et al. 2009; Baldwin and Mitchell 2012). Besides, acid sulfate soils can also be generated starting from compounds

naturally present in soils, such as mackinawite or pyrite. Once these kind of sediments are formed, water can take part to the oxidation and leaching processes, giving adverse consequences on the surrounding environment, such as acidification and deoxygenation (Zelano et al. 2006; Baldwin and Mitchell 2012). Eventually, phosphates are often the main cause of a poor-quality state of groundwater which are, by far, the primary source of drinking water production (Bowell et al. 1998; Peplow 1999; Călinescu et al. 2016; Azam et al. 2019; Volpi et al. 2019; Costamagna et al. 2020b).

Despite the development of specific water treatments currently applied in the industrial scale, such as chemical denitrification, electrodialysis, reverse osmosis and nanofiltration, new technologies necessary to meet industrial needs and more strict environmental requirements are still widely investigated (Chopra et al. 2011; Archana et al. 2012). In this framework, being bio-based materials more sustainable if compared to conventional petrochemical ones, the development of adsorbent materials obtained from renewable sources such as polysaccharides, has gained scientific and industrial attention, being also in harmony with the aims of the Green Chemistry (Anastas and Kirchhoff 2002; Álvarez-Chávez et al. 2012; Hu et al. 2014; Ma et al. 2014; Musa et al. 2020). Nevertheless, the good water solubility displayed by most polysaccharides represent a limit when specific mechanical properties are required, especially for aqueous media applications. For this reason, several studies have been attempted to cross-link soluble polysaccharides to get cross-linked polymers. In this regard, the use of suitable functional molecules such as epichlorohydrin, isocyanates, polyamines, carbodiimide, glutaraldehyde, and poly-carboxylic acids has been extensively reported, however, often in combination with organic solvents (Hovgaard and Brøndsted 1995; Kuijpers et al. 2000; Gyawali et al. 2010; Hennink and van Nostrum 2012; O'Connor et al. 2015; Reddy et al. 2015; Castro-Cabado et al. 2016). Among others, water-soluble diglycidyl ethers have shown good performances, thanks to their low toxicity and the possibility to be exploited in aqueous media, avoiding the use of organic solvents (Komiyama and Hirai 1987; Nobuhiko et al. 1993; Huang et al. 1998; Suye and Mizusawa 1999; Crini and Morcellet 2002; Rodriguez-Tenreiro et al. 2006; Concheiro and Alvarez-Lorenzo 2013).

Maltodextrins are defined as water-soluble starch hydrolysis products which can be obtained either enzymatically or via thermal treatment, mostly applied as food and pharma additives (Anceschi et al. 2017; Pycia et al. 2017). They are D-glucose polymers α -(1,4) and α -(1,6) linked, characterized by a dextrose equivalent (DE) < 20 (Lumdubwong and Seib 2001; Pycia et al. 2017; Ananya et al. 2020).

Said so, with the aim of producing polysaccharide-based adsorbents, in awareness of the role of amines in the epoxy-based polymers production starting from maltodextrins, as reported by a previous work of this group,(Ceccone et al. 2021) amine-mediated ring-opening reactions of three different suitable di- and tri-glycidyl ethers were exploited to cross-link a commercial maltodextrin, employing water as unique solvent. The resulting polymers were subsequently tested as suitable adsorbent for the treatment of nitrate-, sulphate- and phosphate-polluted water samples.

Experimental

2.1 Materials

Glucidex 2® (GLU2) was provided by Roquette Freres (Lestrem, France), while 1,4-diazabicyclo [2.2.2] octane (DABCO), 1,4 butanediol diglycidyl ether (BDE), neopentyl glycol diglycidyl ether (NGDE) and trimethylolpropane triglycidyl ether (TTE) were purchased from Sigma-Aldrich (Darmstadt, Germany). GLU2 was dried in an oven at 75°C up to constant weight before use.

2.2 Polymers synthesis

In a typical procedure, the synthesis of the polymer was carried out by dissolving 3.5 g of Glucidex 2® in 10 mL of 0.2M NaOH sodium hydroxide distilled water solution, using a round-bottom flask. Afterwards, while keeping the solution under stirring 0.25 g of DABCO was added. Eventually, the linker (0.79 g in case of BDE, 0.84 g for NGDE, and 1.35 g for TTE) was added, and the temperature was increased at 70°C, using a hotplate stirrer equipped with thermoregulation and a metal hemispheric bowl to get a homogeneous heating of the flask. The reaction was then allowed to occur for 90 minutes, obtaining a monolith block as the product. Later, the product was recovered from the flask with a spatula and subsequently purified with distilled water, to remove any non-reacted reagents. At the end of the purification step, the product was dried in oven at 70°C up to constant weight and grinded in a mortar to homogenize the grain size. It was possible to obtain a polymer product from all the chosen cross-linkers (BDE, NGDE and TTE), thus obtaining three different materials which will be identified as GLU_BDE, GLU_NGDE and GLU_TTE accordingly to the cross-linker used during the synthesis. Also, the amount of polymer resulting after the purification step was described as mass balance and consisted of approximately the 85% of the initial weight (Fig. 1). All these details are discussed in the results and discussion section.

2.3 TGA characterization

Thermogravimetric analyses (TGA) were carried out using a TA Instruments Q500 TGA (New Castle, DE, USA), from 50°C to 700°C, under nitrogen flow, with a heating rate of 10°C/min.

2.4 FTIR-ATR analysis

A Perkin Elmer Spectrum 100 FT-IR Spectrometer (Waltham, MA, USA) equipped with a Universal ATR Sampling Accessory was used for FTIR-ATR (Attenuated Total Reflection) characterization. All the spectra were collected in the wavenumber range of 650–4000 cm^{-1} at room temperature, with a resolution of 4 cm^{-1} and 8 scans/spectrum.

2.5 Elemental analysis characterization

The samples chemical composition was studied using a Thermo Fisher FlashEA 1112 Series elemental analyser (Waltham, MA, USA).

2.6 Swelling tests

The swelling tests were performed by adding 200 mg of polymer to 10 mL distilled water. The samples were subsequently allowed to swell for 24 hours. After the removal of the liquid phase by centrifugation, the swelling percentage was calculated as follow:

$$\text{Swelling \%} = \frac{\text{grams of swelled polymers} - \text{grams of dry polymer}}{\text{grams of dry polymers}} * 100 \quad (1)$$

2.7 ζ -potential analysis

A Malvern Zetasizer Nano – ZS (Malvern, UK) was used to measure the zeta potential. All the tests were performed using ultrapure water at room temperature.

2.8 Adsorption tests

All the adsorption tests were performed using 1 gram of cationic adsorbent for 100 mL pollutant solution. The adsorption performances towards nitrates and sulphates have been tested at different concentrations. Potassium nitrate and sodium sulphate (Sigma Aldrich ACS \geq 99%) were used to prepare 100, 200, 300, 400, 500, and 1000 mg/L solutions of each anion. In the case of phosphates, the adsorption was studied at different pH values. Sodium orthophosphate, sodium mono-hydrogen phosphate and sodium di-hydrogen phosphate (Suprapur® Supelco) were used to obtain phosphates-containing water solutions characterized by pH values of 11.88, 8.49, 7.04, and 5.25, by keeping the concentration of phosphorous constant at 32 mg/L. The salts were kept in oven up to constant weight before use. Concentrations of pollutants lower than 400 mg/L were chosen with the aim to simulate the treatment of different grade of polluted waters, in awareness of the Italian Environmental Law Limits (D. Lgs. 152/06 - Appendix 3), while concentration higher than 400 mg/L were aimed to evaluate the saturation grade of each adsorbent.

Each adsorption test was carried out by stirring the solution containing the adsorbent for 24 hours at room temperature, using an orbital shaker. Afterwards, the solution was filtered and analysed with ion chromatography technique using a Metrohm 883 Basic IC plus, with 1 mM NaHCO₃ and 3,2 mM Na₂CO₃ as eluent, Metrosep A Supp 5 250/4.0, 250 x 0,4 mm as column. Three replicates were carried out for each test.

Results And Discussion

3.1 Material design and characterization

As mentioned, with the purpose to obtain bio-derived adsorbents, the amine mediated ring opening reaction of di- and tri-glycidyl ethers has been exploited to cross-link a commercial maltodextrin, giving cationic polymer structures as product. Even though the epoxy ring-opening reaction is reported to occur already at 50°C in alkaline water solutions, the addition of tertiary amine during the synthetic step allows to obtain polymers characterized by the presence of positively charged pendants, since the nucleophilicity displayed by amines allows the latter to be kinetically favoured compared to hydroxyl species (Rodriguez-

Tenreiro et al. 2006). This approach allows also to decrease the polymerization reaction time, since the amine introduced let a faster production of alkoxide intermediates, responsible of the subsequent generation of polymer chains. An initial interaction, occurring between DABCO and the linker (Figure 1A), was reported to generate alkoxides species, which subsequently led to the actual growth of polymer chains (Figure 1B-E) (Cecone et al. 2021). Once formed, the alkoxides could react with either other epoxide rings belonging to the linker or hydroxyl functions from GLU2. In the first case, the reaction was associated mostly with a propagation of the alkoxide species, but a negligible molecular weight increase if related to unreacted linker molecules. On the other hand, the alkoxides generated on the backbone of GLU2 molecules which could further react with other epoxides rings, were considered to be of great impact to the increase of the molecular weight, being GLU2 characterized by molecular weight of approximately 300k Da (Stijnman et al. 2011). As a result of the reactive path described, a cationic polymer network was reported as product. As a confirmation of that, it was possible to recover a polymer product from all the synthetic conditions chosen for this work. Said so, the first characterization was carried out by comparing the amount of product recovered from each synthesis. The amount of polymer obtained after the purification and drying process was expressed as mass balance, considering the weight of the final product with respect to the theoretical weight, equal to the sum of GLU2, DABCO and the cross-linker. The highest mass balance was observed for GLU_TTE which was equal to 88.1 %, followed by GLU_NGDE and finally by GLU_BDE, 86.3 % and 85.8 % respectively. As reported in Figure 2, the polymer products were characterized by the presence of polydisperse granules whose size was approximately between a few tens to twohundred microns. The morphological characterisation also revealed the presence of smooth external surfaces. Further, to evaluate the thermal stability, a thermogravimetric analysis was carried out for each sample. As reported in Figure 3A, the thermogravimetric profiles of all samples were characterized by a first weight loss occurring approximately up to 150°C which was related to the volatilization of the water adsorbed on the samples. Subsequently, between 250°C and 450°C GLU_BDE profile displayed a single step decomposition process, whereas GLU_NGDE and GLU_TTE profiles indicated a multistep decomposition process. Subsequently, a carbon residue stable up to 700°C was obtained, corresponding roughly the 20% of the initial weight. Also, the highest T_{onset} was displayed by GLU_BDE which was equal to 302°C, while GLU_NGDE and GLU_TTE displayed a T_{onset} equal to 287°C and 282°C, respectively. Afterwards, the presence of quaternary ammonium functions within the polymers structure was studied via FTIR-ATR. As reported in Figure 3A, all the samples display a peak centered approximately at 1590 cm^{-1} , suggesting how the aforementioned functions were displayed over the network. The presence of nitrogen atom composing the polymer structure was further confirmed by the elemental analysis of the samples. The highest amount of nitrogen was detected in GLU_TTE and resulted equal to 1.1%, followed by GLU_BDE corresponding to 0.8% and by GLU_NGDE equal to 0.6%. Furthermore, what obtained was supported by ζ -potential analysis where GLU_TTE displayed a ζ -potential equal to $13.8 \pm 1.7\%$, GLU_NGDE a value of $11.4 \pm 1.3\%$ and GLU_BDE a value of $10.4 \pm 1.2\%$. What observed so far, allowed to demonstrate how the presence of tri-functional linkers such as TTE, compared to di-functional ones like BDE and NGDE, resulted in higher amounts of product characterized by higher cationic features. This aspect has been related to the capability of tri-functional linkers to act both as a linker between two GLU2 molecules, and

as cationic pendant via reaction with DABCO, by exploiting the remaining epoxy function. On the contrary, di-functional linkers can be present only as a linker or as a pendant. What hypothesized was also supported by the swelling capability which resulted approximately 1400 % in the case of GLU_BDE, 1300 % for GLU_NGDE, and 1100 % in the case of GLU_TTE. Being TTE capable to generate a higher number of cross-links, its structure resulted less prone to adsorb solvents, in this case water.

3.2 Evaluation of adsorption performances

The obtained cationic polymers were subsequently studied as novel adsorbents for the removal of anionic pollutants from water solutions. The study has been performed by choosing nitrates, sulphates, and phosphates as case-study and by testing the adsorption features against each anion at different concentration and pH values. The adsorption tests have been performed starting from 100, 200, 300, 400, 500 and 1000 mg/L solutions in the case of nitrates and sulphates, while in the case of phosphate the adsorption has been carried out by varying the pH value (11.88, 8.49, 7.04, and 5.25), keeping constant the concentration of phosphorous at 32 mg/L. In the case of nitrates (Figure 4A and 4B), it is possible to observe how the adsorption efficiency changed with the variation of the initial concentration of the pollutant. GLU_TTE displayed higher adsorption performances if compared to GLU_BDE and GLU_NGDE, which gave similar behaviours. By looking at Figure 4A, an overall decrease in the percentage of removal efficiency as the nitrate concentration increases was observed. The reason behind this trend was hypothesized to be related to the number of cationic sites displayed by the adsorbent, which can electrostatically interact with the pollutant resulting in a retention of the latter. Once these sites are saturated by the presence of the corresponding number of anions, the adsorption capacity of the adsorbent will be lower, causing an overall decreasing of the adsorption performances at increasing pollutant concentration. In fact, all the adsorbents displayed the higher percent adsorption capability from 100 mg/L solutions, where the highest value was observed for GLU_TTE ($79.7 \pm 4.0\%$), followed by GLU_BDE and GLU_NGDE ($62.9 \pm 3.1\%$ and $59.4 \pm 3.0\%$, respectively). Furthermore, being the electrostatic interaction between the adsorbent and the pollutant occurring as equilibrium between the free anion and adsorbed anion, considering also that the reported adsorbents display swelling features in water media, the total amount of adsorbed pollutant was hypothesized to be higher starting from higher concentration. As a confirmation, the milligrams of nitrate retained per gram of material increased starting from higher concentration of pollutant, as reported in Figure 4B. In this regard, the higher adsorption performances in terms of milligrams of pollutant adsorbed per gram of adsorbent were observed from 1000 mg/L solutions. Again, GLU_TTE was the most performing system with 38.0 ± 0.6 mg/g, followed by GLU_BDE which resulted in 18.0 ± 0.3 mg/g and GLU_NGDE with 15.0 ± 0.3 mg/g. A similar trend was displayed also in the case of sulphates adsorption tests (Figure 4C). However, by looking at the lowest starting concentrations, higher adsorption capacities have been observed, if compared to nitrate tests. As reported before, also in this case GLU_TTE displayed the best performances with $94.6 \pm 4.7\%$ from 100 mg/L solution, while GLU_BDE displayed a value of $64.2 \pm 3.2\%$ and GLU_NGDE a value corresponding to $59.4 \pm 3.0\%$. This feature demonstrated how the adsorption efficiency and the adsorption mechanisms in general are affected by the nature of the anion. What observed was related firstly to the higher charge of sulphates if compared to nitrates, allowing the first to be more prone to electrostatically interact with the

adsorbent. Also, sulphates display higher molecular weight if compared to nitrates, this second aspect could be the cause of a higher retention of the anion within the polymer network. What described was hypothesized as main reason behind the differences observed. Furthermore, by considering the electrostatic interactions the main phenomena behind the adsorption process, the total amount of sulphate adsorbed was hypothesized to be lower than that of nitrate. This because, given the number of cationic pendants displayed by the adsorbents, sulphates would saturate those sites before than nitrates, displaying four times the charge of the latter for each anion. As a confirmation of that, by looking at the adsorbed amount of pollutants from 1000 mg/L solution, the decrease of performances for GLU_TTE was equal to 23%, 14% for GLU_BDE, and 12% in the case of GLU_NGDE. Eventually, the reported adsorbents were also tested on four phosphate solutions at pH 11.88, pH 8.49, pH 7.04 and pH 5.25, in awareness that phosphates can be found in three different forms depending on the pH value. Between pH 4 and pH 6, phosphates are mostly found as di-hydrogen phosphate species, between pH 8 and pH 11 the predominant form is the mono-hydrogen phosphate, while above pH 12.5 the orthophosphate anion becomes the most represented form (Cantrell et al. 2008; Peng et al. 2018). Having said this, unlike the trends described above, the presence of a maximum centered at pH 8.49 was observed, by comparing the different removal efficiencies. At this pH value, the adsorption resulted quantitative ($99.0 \pm 0.2\%$) in the case of GLU_TTE, GLU_BDE resulted in $83.5 \pm 1.3\%$, while GLU_NGDE was equal $87.2 \pm 2.1\%$. This peculiar trend was hypothesized to be mostly affected by two different aspects. Firstly, since the different phosphates anions are characterized by different number of charges, they might display different electrostatic behavior towards the adsorbent. With the above in mind, the orthophosphate was hypothesized to be more prone to interact with the adsorbent if compared to the mono-hydrogen phosphate and to the di-hydrogen phosphate, since the higher the number of charges displayed by the anion, the stronger the interaction generated with the adsorbent. Second, at increasing alkaline condition the presence of hydroxyl anions together with the phosphates species would generate a competition for the interaction with the cationic sites, resulting in lower adsorption performances. As a proof of that, the lowest adsorption values were observed in the most alkaline conditions (pH 11.88). In this case, despite the presence of orthophosphate species, the concentration of hydroxyl anions resulted high enough to hinder the interaction of the pollutant with the adsorbent. On the other hand, in acidic (pH 5.25) and neutral (pH 7.04) conditions, the adsorption performances were affected by the presence of less charged species, if compared to the orthophosphate. However, in this pH range the presence of proton ions in solution did not result in a significant modification of the adsorption performances. The highest adsorption features displayed at pH 8.49 resulted the optimal trade-off between the concentration of hydroxyl ions such that did not hinder the adsorption of the pollutant and the presence of the less protonated ion forms, thus more negatively charged.

Conclusions

The amine-mediated epoxy ring-opening reaction was proven to be a suitable approach for achieving the cross-linking of water-soluble maltodextrins. It was possible to obtain a one-step synthesis of positive-charged cross-linked polymer networks by exploiting 1,4-Diazabicyclo [2.2.2] octane (DABCO), starting

from a commercial maltodextrin (Glucidex 2®). 1,4 butanediol diglycidyl ether (BDE), neopentyl glycol diglycidyl ether (NGDE), and trimethylolpropane triglycidyl ether (TTE) have been tested as suitable di- and tri-glycidyl linkers, allowing to perform the polymer synthesis in water media, without the use of any organic solvent. All studied synthetic conditions allowed to obtain a polymer product characterized by mass balance higher than 85 %, while the presence of nitrogen atoms within the polymer structure as cationic pendants, was confirmed by FTIR-ATR characterization, elemental analysis, and ζ -potential measurements. Subsequently, the polymer products were tested as novel bio-derived adsorbent for the treatment of nitrate- sulphate- and phosphate-polluted waters, starting from different concentration of the pollutant (nitrates and sulphates) and pH of the solution (phosphates). GLU-TTE resulted the most performing system by reaching, from 100 mg/L solutions, an adsorption percentage of approximately 80% and 94% towards nitrates and sulphates respectively, while a quantitative adsorption towards phosphates at pH 8.49 was observed. Also, the adsorption performances towards nitrates and sulphates resulted dependant on the starting concentration of the pollutant. The percentage of adsorbed anion was demonstrated to be higher at lower starting pollutant concentrations, while the grams of pollutant adsorbed per gram of adsorbent resulted higher from more concentrated starting solutions. On the other hand, phosphates removal efficiency showed a dependency on the pH value and a maximum adsorption percentage at pH 8.49. This pH value has been identified as the optimal trade-off condition between the presence of the most negatively charged phosphate form, and the competition of the pollutant with hydroxyl group taking place in alkaline conditions. In this work, we have been able to demonstrate how the combination of maltodextrins, di-/tri-glycidyl ethers and amines is a useful and sustainable approach for obtaining one-step syntheses of cationic polymers avoiding the use of organic solvents, while the high adsorbing feature displayed against nitrates sulphates and phosphates allows these materials to be further studied as bio-derived adsorbents for environmental applications.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

All data generated or analysed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

Funding

The authors received no financial support for the research, authorship, and/or publication of this article.

Authors contributions

Giulia Costamagna: Conceptualization, Methodology, Investigation, Validation, Formal analysis, Visualization, Writing - Original Draft, Writing - Review & Editing. Claudio Cecone: Conceptualization, Methodology, Investigation, Validation, Formal analysis, Visualization, Writing - Original Draft, Writing - Review & Editing. Paola Fini: Methodology, Writing - Review & Editing. Pinalysa Cosma: Methodology, Writing - Review & Editing. Marco Ginepro: Supervision, Methodology, Writing - Review & Editing. Francesco Trotta: Supervision, Project administration, Writing - Review & Editing.

Acknowledgements

We thank Roquette Frères (Lestrem, France) for providing Glucidex 2®.

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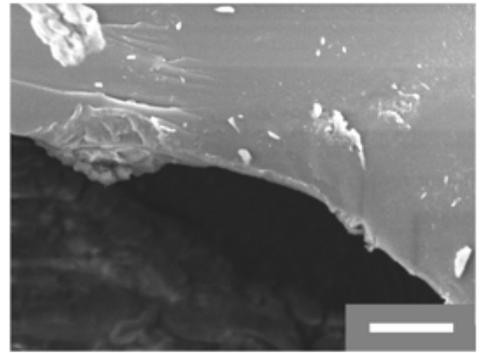
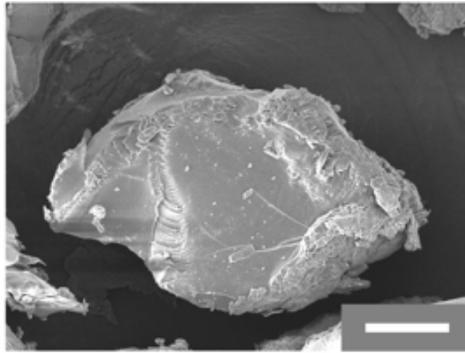
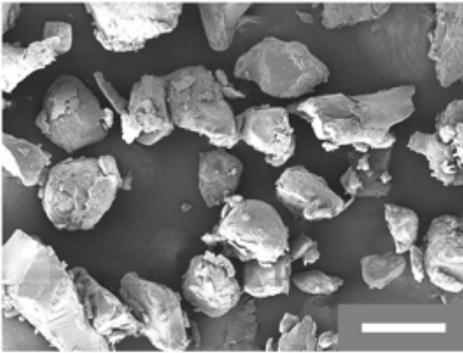
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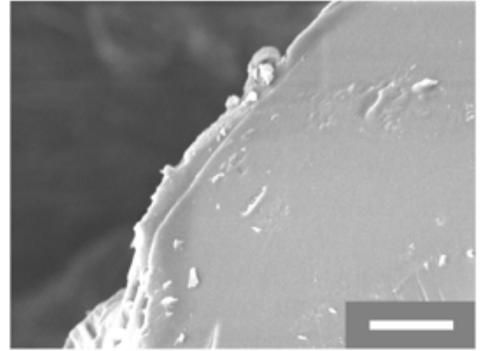
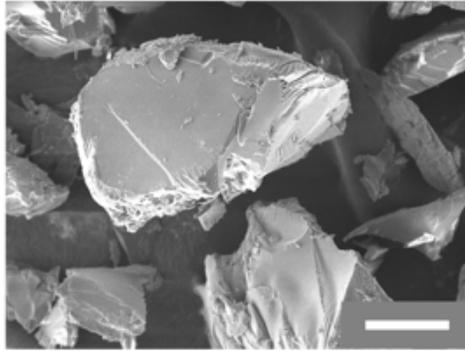
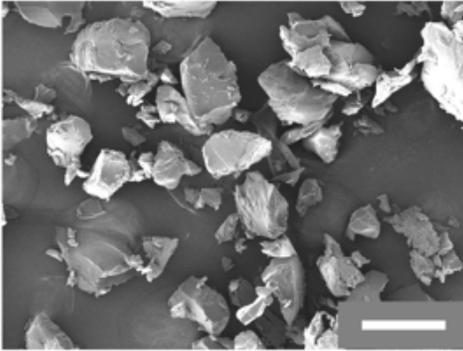
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Figures

GLU_BDE



GLU_NGDE



GLU_TTE

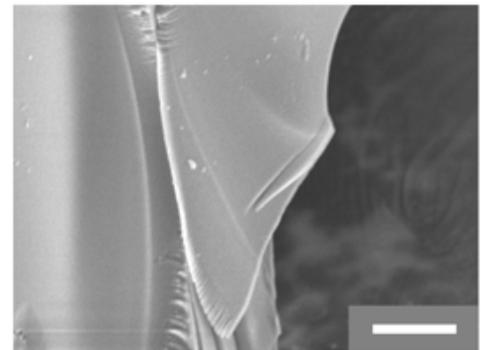
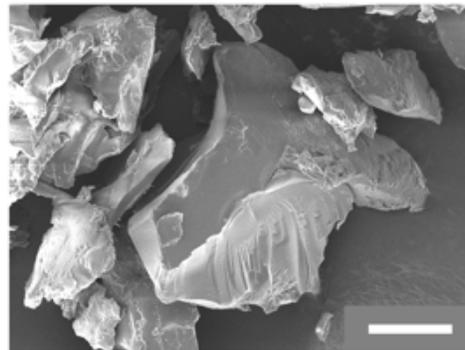
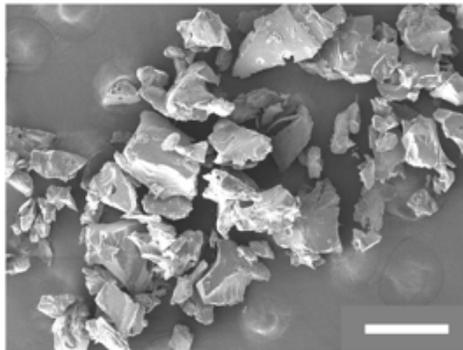


Figure 2

SEM images of GLU_BDE, GLU_NGDE, and GLU_TTE polymer granules. Scale bars: 200 μm (first column); 50 μm (second column); 5 μm (third column).

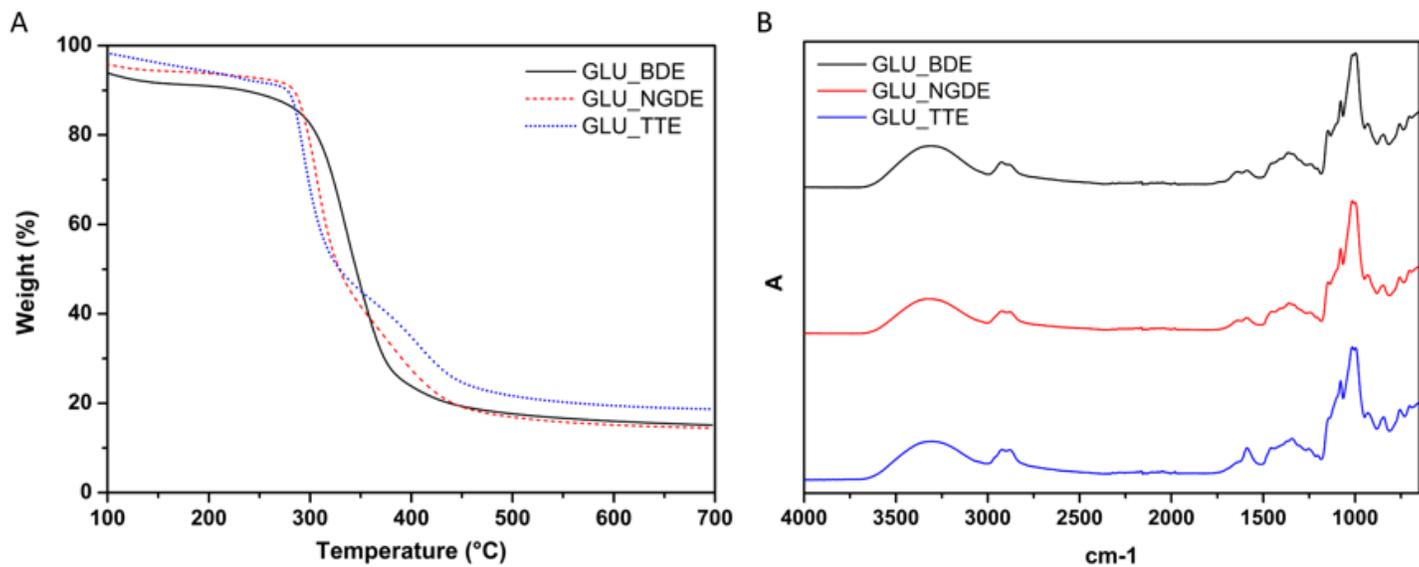


Figure 3

TGA analyses (A) and FTIR-ATR spectra (B)

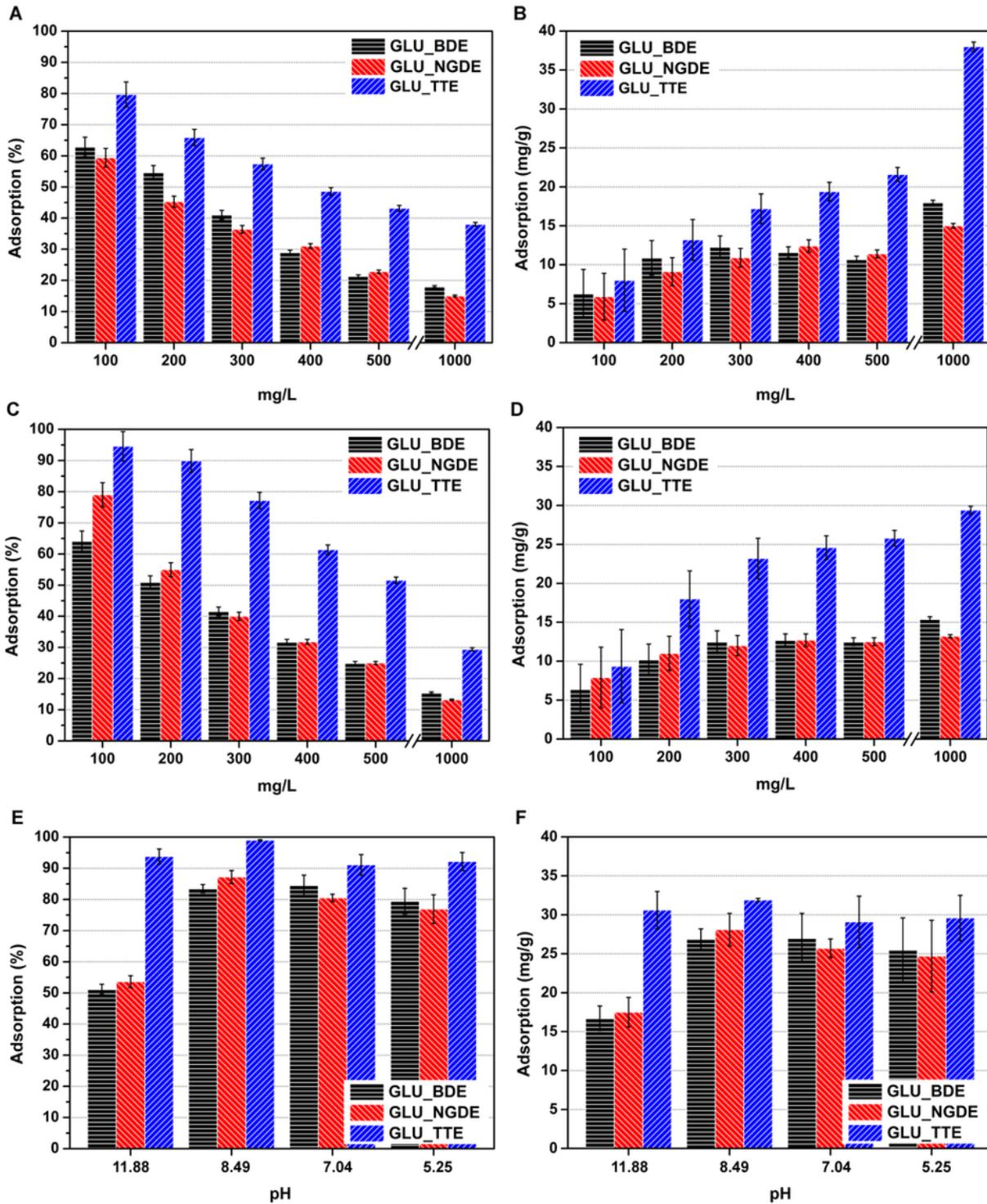


Figure 4

Results for (A-B) nitrates adsorption, (C-D) sulphates adsorption, and (E-F) phosphates adsorption tests. The first column shows the adsorptions as percent of adsorbed pollutant in function of the initial concentration, while the second column reports the adsorptions evaluated as milligrams of pollutant adsorbed per gram of adsorbent.

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