Nanoporous polyanilines as sorbents for dyes and heavy metals abatement from water

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Introduction

Every year, from 300 to 500 millions of tons of solvents, heavy metals, toxic sewage sludges and others industrial waste are released in water [1]. The most employed approach for waste abatement is based on the use of activated carbon thanks to its high surface area, high porosity and low selectivity. The main disadvantage of this material is the necessity to activate and regenerate it through thermic treatment at high temperature or using solvents, causing additional costs. In this regard, the necessity to develop innovative materials is crucial. The present study is focused on the "green" synthesis and characterization [2] of porous polyanilines (PANI), characterized by specific features that make them useful for the removal of two classes of wastewater pollutants: organic dyes (methylene blue, MB, and acid green, AG) and heavy metals (Pb^{+2}, Cd^{+2} and Cr^{+6}).

Methods

PANIs synthesis and characterization

PANI1/HCl and PANI1/H_2SO_4 were synthesized by a traditional method [3] using aniline in the presence of $NH_4S_2O_8$ as the oxidant and both HCl and H_2SO_4. as the dopants. PANI2/HCl and PANI2/H_2SO_4 were produced by a green protocol [2] replacing aniline with *N*-(4-aminopheyl)aniline in the presence of H_2O_2 as the oxidant and both HCl and H_2SO_4. as the dopants

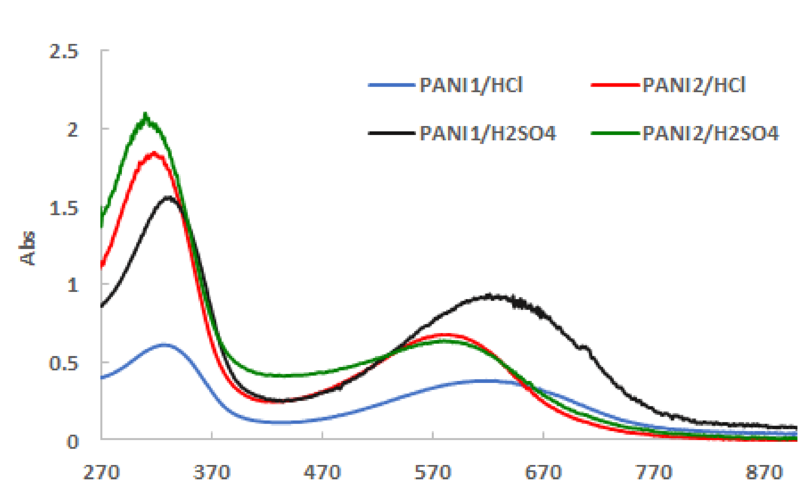
All materials were characterized by UV-Vis and FT-IR spectroscopy and SEM.

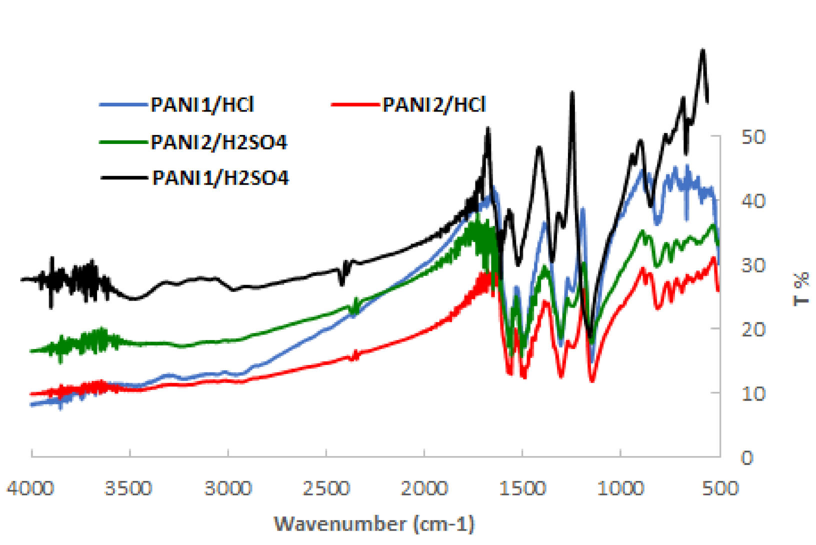
Pollutants removal and recycle studies

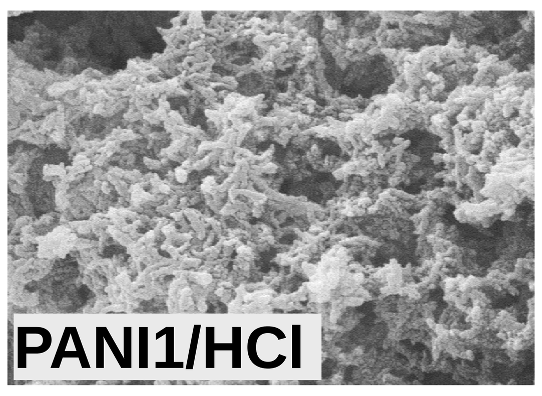
50 mg of each PANI were dispersed in 20 mL 10mg/L of each pollutant (MB, AG, Pb^{+2}, Cd^{+2} and Cr^{+6}) or of a mixture of them (Pb^{+2} and Cd^{+2} , MB and Pb^{+2}) for: 30 minutes, maintaining the spontaneous pH of the solution or modifying it (pH 2-10) depending on the treated pollutant. Then, PANI was recovered by centrifugation, washed by water and acetone, dried and reused up to 4 recycle tests. Here, the best results are reported.

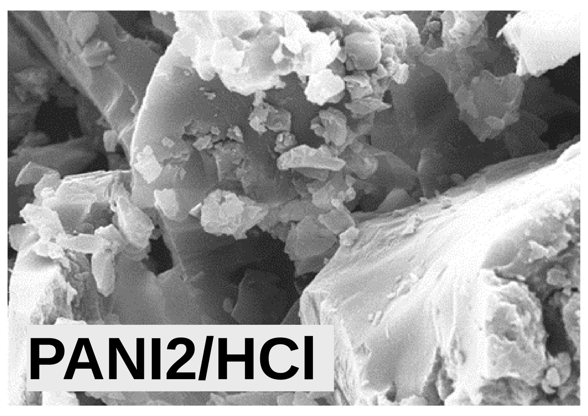
Characterization

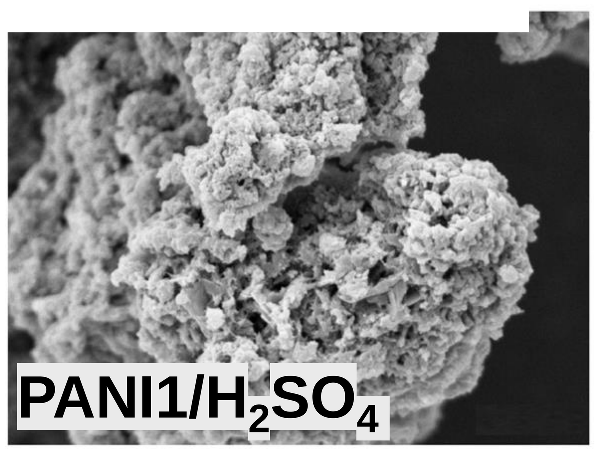
UV-vis and FT-IR spectra of all the PANIs show that the polymer is always obtained in form of emeraldine.

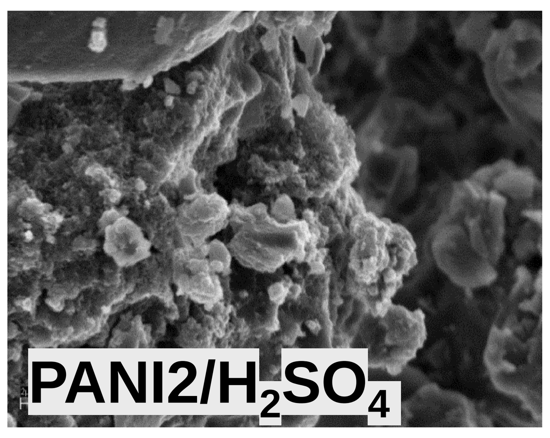








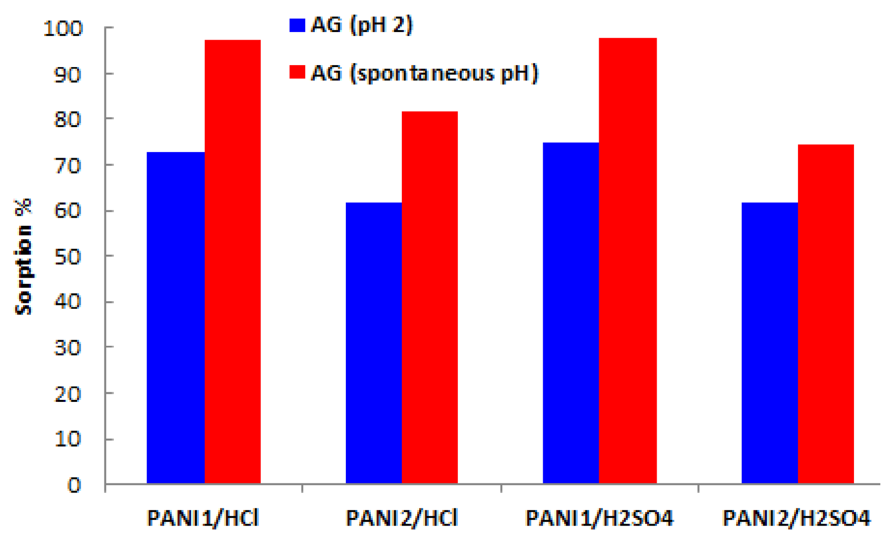


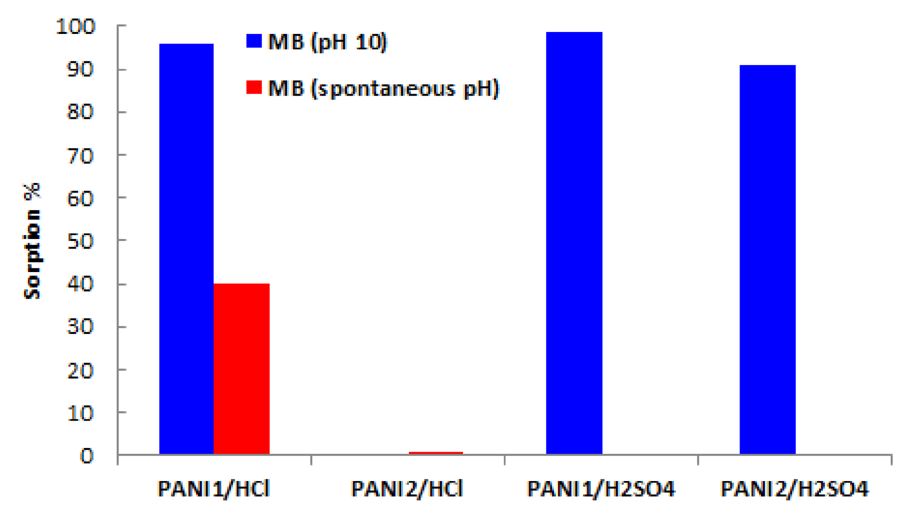


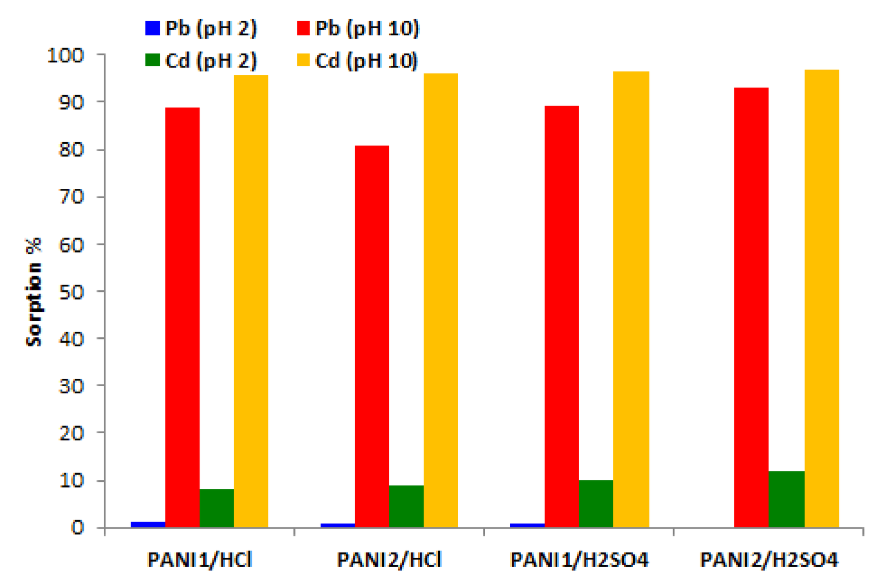
PANI1/HCl exhibits a nanoporous structure characterized by microsized nanorods, whereas PANI2/HCl is compact and smooth. However, when H_2SO_4 is used as the dopant, PANI1 maintains its porosity, whereas PANI2 strongly reduces its compactness showing a morphology more similar to that of PANI1.

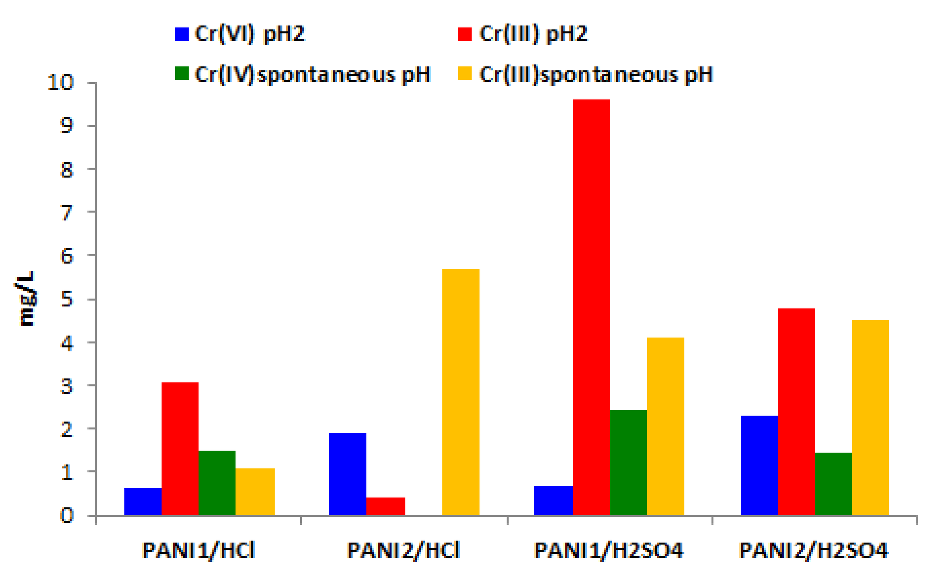
1. http://www.unesco.it/it/News/Detail/510
2. C. Della Pina et al., Materials 13, 2020, 2161.
3. J.C. Chang et al., Synth. Met. 13, 1986, 193.

Sorption tests



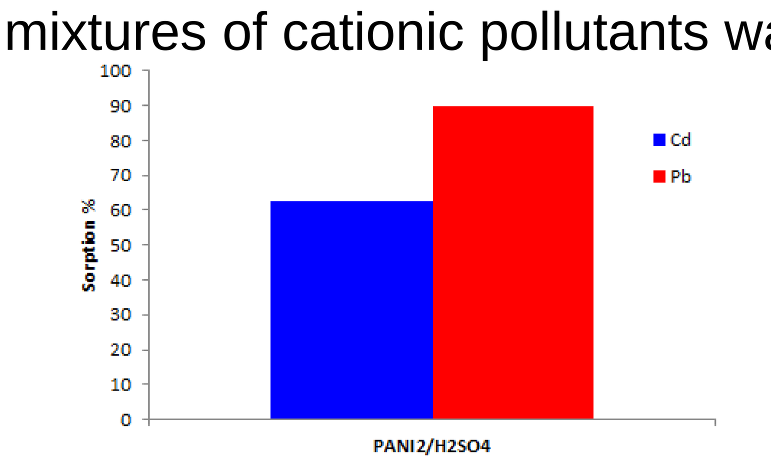


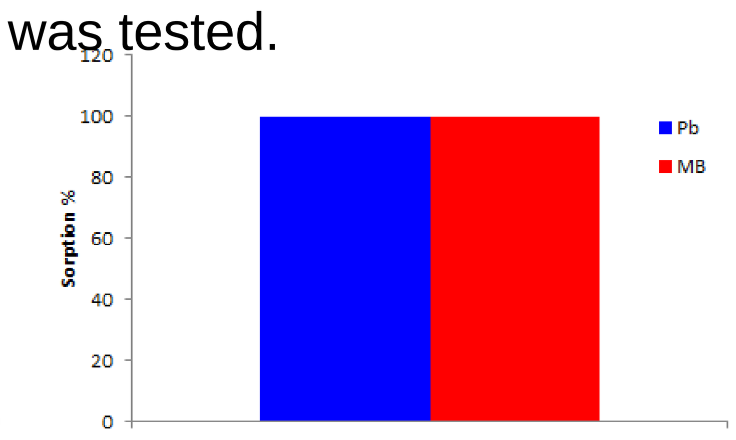




All the PANIs show extrardinary sorption ability towards all the investigated pollutants. The mechanisms involved in pollutants removal by PANI can be numerous and different and strictly related to the porosity of the sorber and to the matrix conditions. Concerning the pollutants removal here investigated, the sortpion mechanism seems to be strongly and mainly pH dependent. In fact, alkaline pHs promote the sorption of cationic pollutants (Pb^{+2}, Cd^{+2} and MB) exploiting the interaction between deprotonated amine/imine sites of the polymer and the cations, whereas acidic pH levels are required for the removal of anionic pollutants (MB, chromate) by the interaction between the positive charges on imino groups of the polymer and the pollutants. Unexpectedly, PANIs/H_2SO_4 show higher Cr(VI) reduction ability than PANIs/HCl suggesting a modification of the redox potential of the polymer when H_2O_4 is used as the dopant. Among all sorbents investigated, PANI2/H_2SO_4 was selected for further investigations and was subjected to 4 recycle tests maintaining good performances.

On the basis of the obtained results, it is clear that PANI-based sorbents cannot be used simultaneously for the removal of both cationic and anionic pollutants. Therefore, the ability of PANI2/H_2SO_4 to absorb mixtures of cationic pollutants was tested.





PANI2/H_2SO_4 maintains excellent sorption ability also in the presence of mixtures of pollutants and its low selectivity makes it a good candidate for real applications.

Conclusions

In the present work different types of polyanilines were synthesized using different approaches and tested as sorbents for the removal of cationic and anionic pollutants in water demonstrating that the mechanism of abatement is strongly pH dependent. Concerning Cr^{+6} removal the dopant H_2SO_4 seems playing a role in the redox ability of the polymer. The possibility to reuse PANI2/H_2SO_4 for many cycles and its low selectivity towards the removal of mixture of pollutants could lead to important economic and environmental advantages in the sector of wastewater treatment.

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