

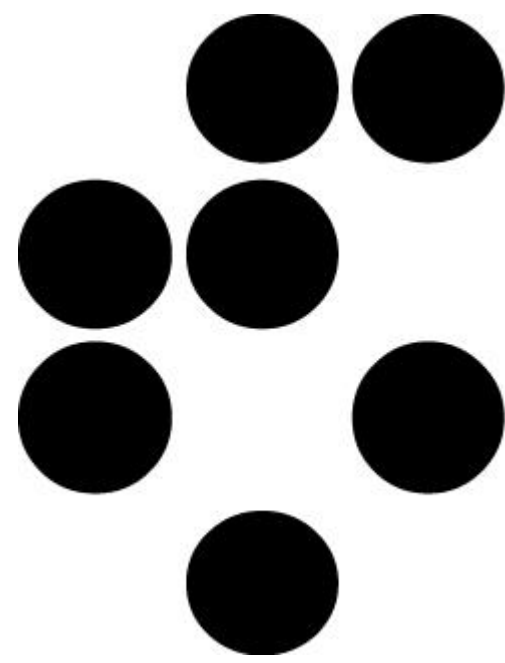
INVESTIGATION OF THE SORPTION PROPERTIES OF ZEOLITE WITH IRON OXYHYDROXIDES FOR APPLICATIONS IN REMOVAL OF Sr, U AND Th



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INTRODUCTION

Activities related to nuclear energy production such as ore mining and milling, fuel fabrication, or fallout accidents can lead to the release of (radio)toxic elements in the environment, which contaminate surface- and groundwater sources and pose threat to human health and the biosphere. Among all of those released, Sr-90, and isotopes of U or Th are of special importance due to their long half-lives and/or their high concentrations.

Among the processes employed for the removal of the elements in aqueous media, sorption by natural materials has proven to be effective, flexible, and low-cost. Naturally abundant aluminosilicates like zeolites are useful for having both a porous structure and advantageous physicochemical characteristics. Iron oxyhydroxides, such as ferrihydrite or goethite, commonly present in the environment provide additional active sites and can influence the mobility of radioisotopes.

In this study, a natural zeolite from Greece was modified with iron(III) oxyhydroxides and used to explore the sorption of Sr, U and Th in aqueous media under varying conditions. The materials were characterized before and after sorption with techniques such as FTIR, pXRD, BET and SEM, and their pH_{pzc} and CEC were calculated. Metal concentrations were determined by mass spectrometry in the case of Sr, or by optical photometry with the Arsenazo(III) method in the case of U and Th.

MATERIALS & METHODS

Sorbents

Natural zeolitic rock from Petrolia in Evros region, Greece (**Zeolite**) containing 89% clinoptilolite was ground to particle size of < 50 μm. Modification with iron(III) oxyhydroxides (**FeZ**) was carried out according to a precipitation method using FeCl₃·6H₂O and NaOH.



Fig. 1 : Raw and modified zeolites

Reagents

Sorption experiments were undertaken using the batch method. Stock solutions of increasing metal concentrations were prepared:

- Sr(NO₃)₂ : 1 to 250 mg/L at pH=5.
- UO₂(NO₃)₂·6H₂O : 25 to 1000 mg/L at pH=4 and 7.5.
- Th(NO₃)₄·5H₂O : 5 to 250 mg/L at pH=3.
- Background electrolytes NaNO₃ 0.1 mol/L and Ca(NO₃)₂ 0.05 mol/L for the effect of competing ions.



Fig. 2 : Uranyl nitrate hexahydrate

- [Cu(trien)]²⁺ 0.1 mol/L : determination of CEC.
- KNO₃ 0.1 mol/L : determination of pH_{pzc}.

Analytical Techniques

- Optical spectroscopy (UV-vis) with the Arsenazo(III) reagent at 660 nm for U and Th determination.
- ICP-MS Triple Quad (mass 88, He gas) for Sr determination.

CONCLUSIONS

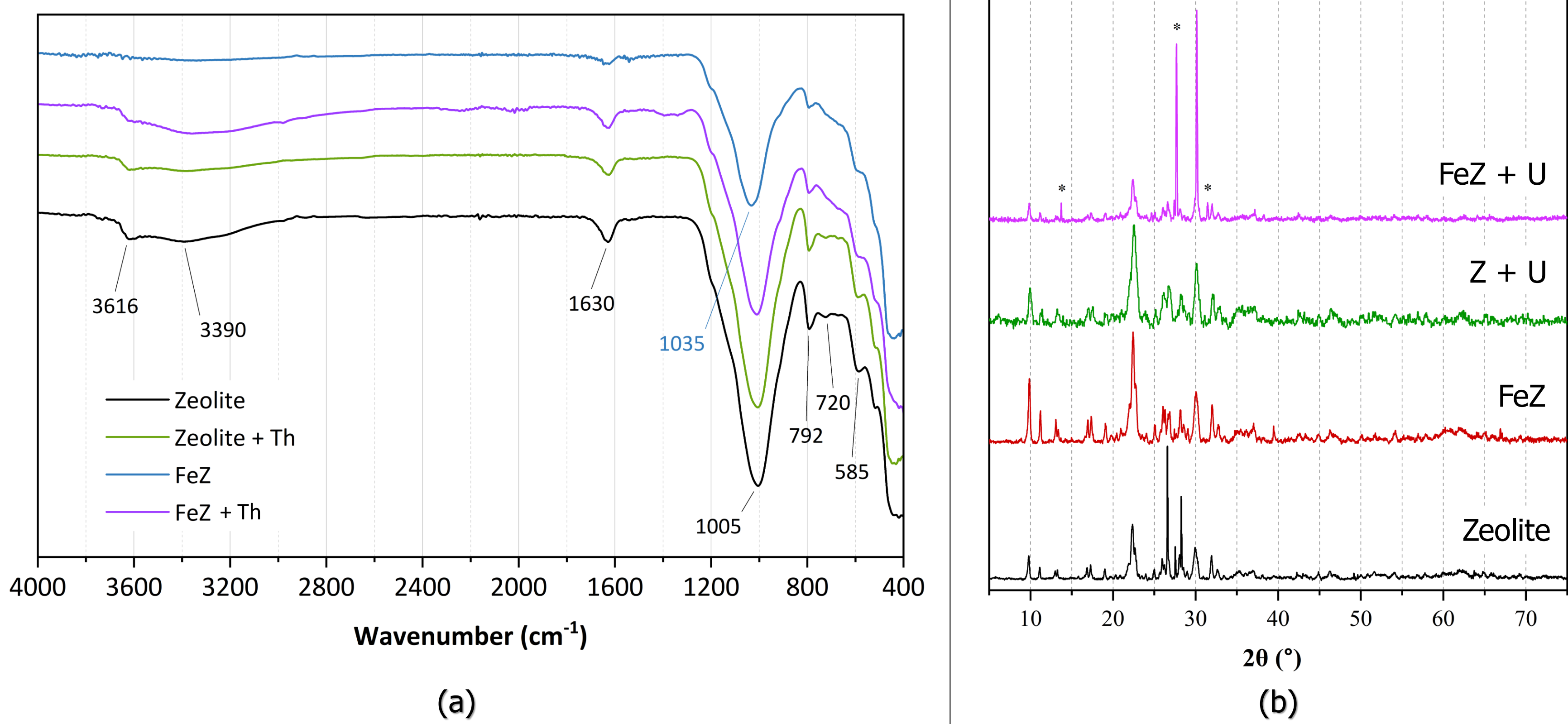
- A natural zeolite was successfully modified with iron oxyhydroxides.
- The iron compounds were found to be an amorphous mixture of low crystallinity ferrihydrite and goethite.
- Iron oxyhydroxide presence affects significantly surface area, surface charge and cation exchange properties as shown by the BET, pH_{pzc} and CEC values respectively.
- Iron oxyhydroxide presence had different effect on the sorption properties of different metals. Enhanced, equal, or lowered uptake values were calculated for U, Sr, and Th sorption respectively.
- The presence of Na⁺ and Ca²⁺ cations, which compete with for the binding to the zeolite active sites, leads to significantly reduced sorption capacities.
- Equilibrium is achieved fast (< 40 min for U-sorption and < 10 min for Sr-sorption)
- As shown by characterization techniques (FTIR, pXRD, SEM) sorption led to minor changes in the structural characteristics of the materials.
- All evaluated materials are potential candidates for environmental applications and radioactive waste remediation.

LITERATURE

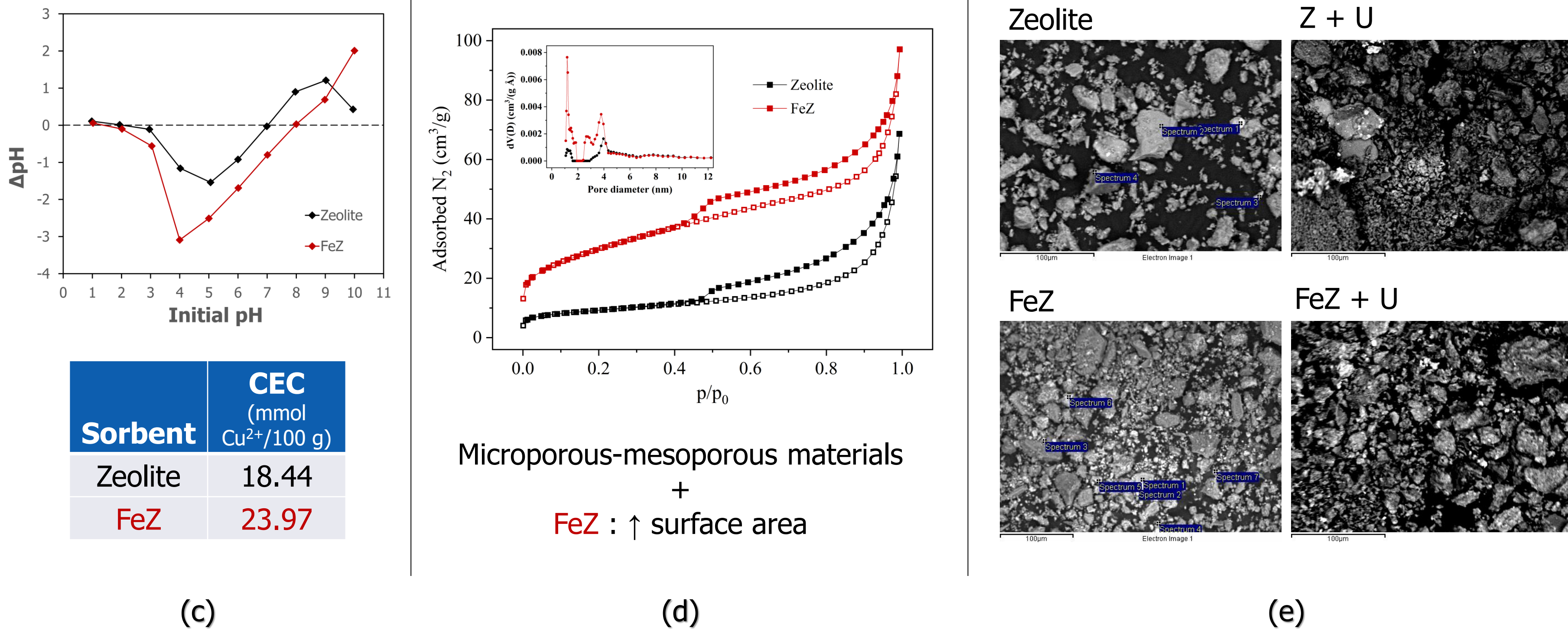
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RESULTS & DISCUSSION

Characterization

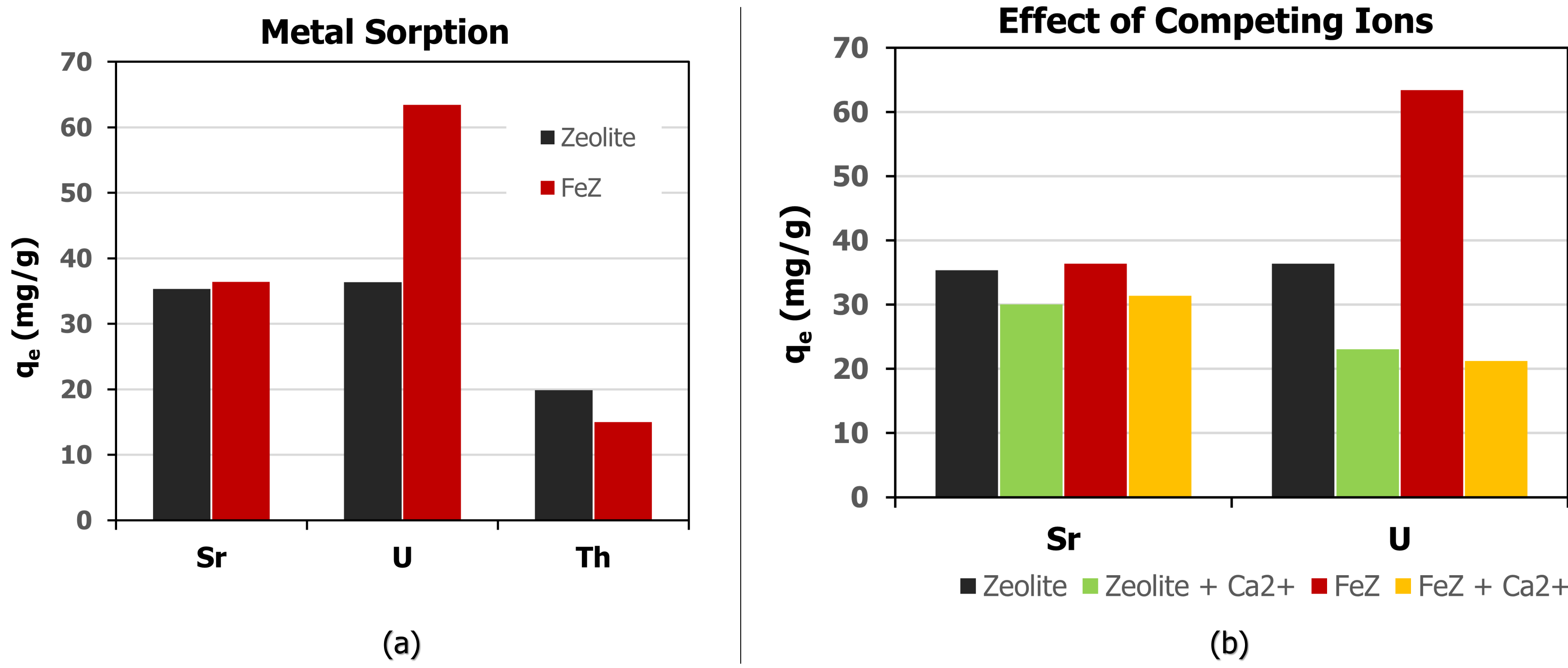


FTIR spectra (a), and pXRD diagrams (b) of the raw and modified zeolites before and after metal sorption

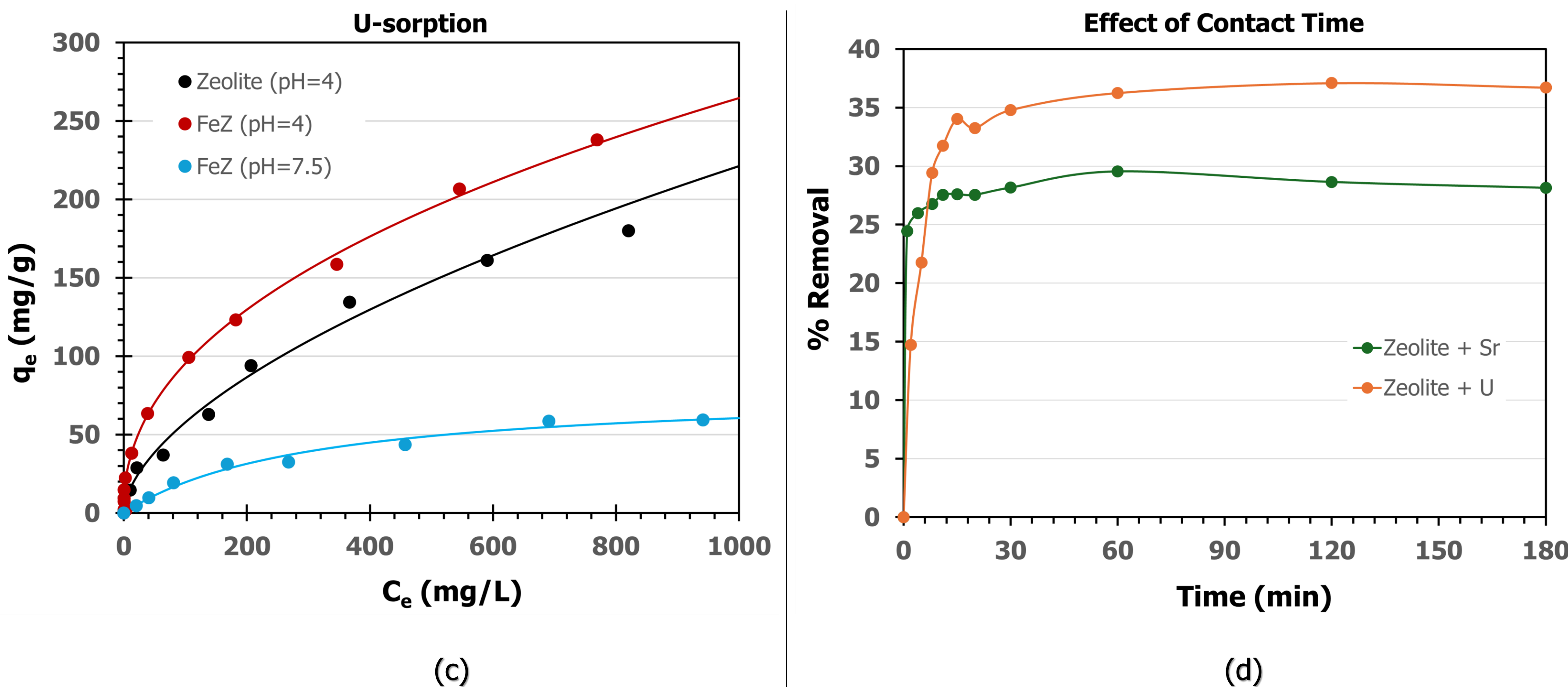


pHpzc and CEC measurements (c), BET surface area (d) and SEM images (e) for the materials examined

Sorption Experiments



Sr, U and Th sorption capacities on the natural and iron-modified zeolites in the absence (a) and presence (b) of competing ions (C₀=100 mg/L, dosage 1 g/L, T=298 K)



The effect of solution pH and initial metal concentration on U-sorption (c) (C₀=25–1000 mg/L, dosage 1 g/L, T=298 K) and the effect of contact time on U- and Sr-sorption (d) (C₀=100 mg/L, dosage 1 g/L, T=298 K)