



HAL
open science

Template-Free Nanosized EMT Zeolite Grown on Natural Luffa Fibers for Water Purification

Hussein Awala, Mohamad El-Roz, Joumana Toufaily, Svetlana Mintova

► **To cite this version:**

Hussein Awala, Mohamad El-Roz, Joumana Toufaily, Svetlana Mintova. Template-Free Nanosized EMT Zeolite Grown on Natural Luffa Fibers for Water Purification. *Advanced Porous Materials*, 2014, 2 (2), pp.141-148. 10.1166/apm.2014.1055 . hal-01963780

HAL Id: hal-01963780

<https://hal.science/hal-01963780>

Submitted on 5 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Template free nanosized EMT zeolite grown on natural luffa fibers for water purification

Hussein Awala^a, Mohamad El-Roz^a, Joumana Toufaily^b, Svetlana Mintova^{a,*}

^aLaboratoire Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6, boulevard du Maréchal Juin, 14050 Caen, France.

^bLaboratoire de Matériaux, Catalyse, Environnement et Méthodes Analytiques, Université Libanaise, Rafik Hariri campus, Beyrouth-Hadath, Lebanon

Abstract

The purification of water using nanosized EMT-type zeolite grown on luffa (zeolite/luffa composite) has been carried out. The degree of crystallinity, porosity, and morphology of the pure zeolite, pure luffa and zeolite/luffa composite are characterized prior their use. It is found that the luffa fibers preserve the semi-crystalline structure under hydrothermal treatment thus resulting in the zeolite/luffa composite with enhance mechanical strength and long-term stability. The zeolite/luffa composite is used to remove heavy metals (Cu^{2+} , Co^{2+} , Fe^{3+} , and Mn^{2+}) from water; the sorption behavior is studied by UV-vis spectroscopy. Zeolite/luffa composite has shown high capacity for heavy metal removal from water, thus resulting in 85-95 % elimination of Cu^{2+} , Co^{2+} , Fe^{3+} and Mn^{2+} within 250 minutes. The performance of the zeolite/luffa composite is explained by enhance mechanical strength and long-term stability, fast diffusion, high contact area and high ion exchange and sorption capacity of both the zeolite nanocrystals and the natural luffa fibers.

Keywords: zeolite nanocrystals, zeolite/luffa composite, water purification, heavy metals, adsorption, ion exchange.

1. Introduction

The growing environmental awareness has stimulated the design of environmentally friendly materials for water, air, and soil purification. Since the 1990s, natural fibers are emerging as alternatives to synthetic fibrous supports (glass, aramid, carbon, etc.) for preparation of composites and membranes.[1-9] Consequently, in recent years, natural fibers have attracted more interest by providing a sub-complete solution to the demanding problems of industrial

society.[10-12] Moreover, the natural fibers are biodegradable, renewable, inexpensive and have good mechanical and chemical stabilities.[13,14] The fibrous vascular structure of natural fibers is associated with the organic polymers and thus can be used for preparation of new composites.[15-19] Besides, the natural fibers have been used, as support and/or as bio-template for deposition of porous materials including zeolites.[1,2,20-24] Due to their diverse structures, chemical compositions, porosity, morphology and degree of hydrophilicity/hydrophobicity, the zeolites have been applied in different fields including catalysis, ion exchange and sorption processes. The later processes are related with water and air purification.[25-27] There are 218 synthetic and 45 natural zeolites with diverse physicochemical properties.[28] Between the natural zeolites, the clinoptilolite is one of the most frequently studied due to the abundance and high selectivity toward heavy metals.[29] Clinoptilolite was used in the removal of Cs^+ and Sr^{2+} radioisotopes from waste water.[30] Besides, it has been shown that clinoptilolite has a high removal efficiency (>50%) for mixed heavy metal effluents (Pb^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , Cr^{3+} , Ni^{2+} , and Co^{2+}).[31,32] Moreover, the surface modified clinoptilolite with amorphous iron oxide species has improved exchange capacity and resulted in a simultaneous removal of Cu, Mn and Zn from drinking water.[33,34] On the other hand, synthetic zeolites are also widely used for purification of water. Zeolite A (LTA-type structure) is effectively used for elimination of Cr^{3+} ,[35] while zeolite Y (FAU-type structure) demonstrated a high capacity for removal of Cr^{3+} and Pb^{2+} . [36] Zeolite Y was also applied for selective elimination of different heavy metals (Fe, As, Pb, Zn, Cu, Ni, Cr) from waste water.[37] The other form of FAU-type zeolite (zeolite X) and zeolite A have shown a good efficiency for the removal of Cd^{2+} and Zn^{2+} from aqueous solutions.[38] The higher efficiency of zeolite Y for elimination of heavy metals with a selectivity in the order $\text{Fe} > \text{As} > \text{Pb} > \text{Zn} > \text{Cu} > \text{Ni} > \text{Cr}$ has been demonstrated, and a comparison with a natural PHI-type material (Na-Phillipsite) was reported. The results illustrated that the synthetic zeolite Y has a higher sorption capacity, *i.e.*, 10 times greater than the natural zeolites.[39]

In order to improve the performance of zeolites, not only the type of the crystalline structures is important, but also the morphology, surface properties, particle size and pre-shaping are of significant concerns. Once these properties are altered a significant improvements in the sorption kinetics and functioning of the materials are expected. In general, the decrease of the particle sizes results in an increase of the external surface area of zeolites, and thus fast diffusion of

molecules in the micro- and meso- pores is expected. However, processes using as prepared nanosized zeolite are difficult to be handle, and recycling of the nanosized materials after the sorption process is also a challenging task. Therefore, the immobilization of the nanosized zeolite crystals on supports is considered. Between numerous supports, natural fibrous materials have been widely used. The use of cellulose fibers as a support for high removal of heavy metals (Ni^{2+} and Cu^{2+}) from aqueous solutions has been demonstrated with a high capacity (82-98% vs 10% for non-supported zeolite).[40] More recently, LTL-type zeolite has been grown on natural hemp fibers, and the LTL/hemp composite presented a high ability for adsorbing aromatic derivatives from water; the removal degree reached is about 84%.[41]

Natural fibers such as cotton, hemp, flax, sisal, and luffa display diverse morphological and chemical characteristics. Between them, luffa fibers possess a netting-like fibrous vascular system characterized by microcellular architecture with continuous hollow microchannels. Therefore the luffa fibers have been used as biotemplate for preparation of hierarchical ZSM-5 zeolites.[42] The luffa fibers are also used as cell carriers in bioreactors,[43] scaffolds for tissue engineering,[40] and for development of biofiber-reinforced composites.[44]

In this work, luffa fibers were used as a natural support for the growth of template free nanosized EMT-type zeolite, and the resulted zeolite/luffa composite (ZLC) is further applied for removal of heavy metals (Cu^{2+} , Co^{2+} , Fe^{3+} , Mn^{2+}) from water. Luffa fibers (or luffa cylindrica fibers) are a tropical plant, which belongs to the family of curcubitacea. The fruit of luffa fiber has fibrous and vascular systems that form a natural mat when is dried. The luffa is composed mainly from cellulose, hemicelluloses and lignin. The fibrous vascular system is considered as an ideal support for the growth of zeolite nanocrystals where an increase of the contact surface area between the zeolites and the fiber surfaces is of favor for preparation of long-term stable composites. In addition, the three-dimensional (3D) structure of the luffa makes easier the preparation of composite and improves the water diffusion during the purification process. The results are compared with pure EMT-type zeolite, which is used as a reference. The water hardness effect is also taken into account during the purification process

2. Experimental Section

2.1. *Luffa fibers*

Luffa fibers purchased from Belo Horizonte (Brazil) were cleaned with acetone under ultrasonication for 7 minutes and then rinsed with water and dried at 60 °C. After drying, the fibers were treated twice with 0.1 M sodium hydroxide solution (NaOH) at 80 °C for 2 h and 12 h in order to purify the surface and to remove other constituents present in the fibers, and partially the lignin. The chemical composition of luffa fibers is given in Table 1. The density of the luffa fibers is 0.85 g/cm³. After each treatment the fibers were washed with distilled water.

2.2. *Heavy metals*

The heavy metals in the form of CuSO₄·5H₂O (98 %), Co(NO₃)₂·6H₂O (98 %), Fe(NO₃)₃·9H₂O (98 %), Mn(NO₃)₂·4H₂O (99.98 %) and Ca(NO₃)₂·4H₂O were supplied by Prolabo as analytical grade reagents. All experiments were performed with double distilled (dd) water, and the hardness of the water was controlled.

2.3. *Preparation of zeolite/luffa composite (ZLC)*

The synthesis procedure for pure EMT-type zeolite was reported elsewhere.[45] The nanosized EMT-type zeolite in the presence of luffa fibres was synthesized from a clear precursor suspension with a molar composition: 5.15SiO₂ : 1Al₂O₃ : 17.96Na₂O : 240.3H₂O. The synthesis was carried out at 30 °C for 36 h. The ratio luffa : precursor suspension of 4 : 96. was kept constant. After crystallization, the zeolite/luffa composites were purified with water under sonication, leading to removal of loosely attached zeolite nanocrystals from the fibers. After 15 min sonication, the fibers were rinsed with dd water and dried at room temperature.

2.4. *Characterization*

The phase purity and crystallinity of zeolites and luffa fibers were determined by X-ray diffraction using a PANalytical X'Pert-pro diffractometer in Debye-Scherrer geometry with Cu K α radiation (45 kV, 40mA) at a scanning speed of 0.00167 °/sec over a range 5-50 °2 θ .

The surface features and degree of coverage of luffa fibers with zeolite nanocrystals were determined by field-emission scanning electron microscope (SEM) using a JEOS JSM6700F with an accelerating voltage 30.0 kV.

The amount of zeolite crystals embedded in the luffa fibers were determined by thermo-

gravimetric analysis (TG) using a SETSYS evolution instrument (SETARAM). The samples were heated from 30 to 800 °C with a heating rate of 5 °C min⁻¹ in air.

The porosity of the samples was evaluated by recordering the nitrogen adsorption/desorption isotherms of the pure EMT-type zeolite, pure luffa fibers and ZLC using a Micromeritics ASAP 2020M volumetric adsorption analyzer. Samples were dehydrated at 170 °C under vacuum overnight prior to the measurements.

The inductively coupled plasma (ICP) spectroscopy is used to determine the chemical composition of the samples. The ICP results for pure EMT-type zeolite and ZLC are presented in Table 2.

2.5. Removal of heavy metals from water

The removal of heavy metals (Cu²⁺, Co²⁺, Fe³⁺, and Mn²⁺) from water using pure luffa fiber, pure nanosized EMT-type zeolite, and zeolite/luffa composite was carried out using a batch approach. Water samples (1000 ml) with 500 mg of heavy metal salts of Co²⁺, Fe³⁺, and Mn²⁺, where the pH was adjusted to 6.2, 5, and 5.4 by adding of HNO₃ and NaOH were prepared to avoid the precipitation and complex effect.[46] In the case of Cu²⁺, the precipitation occurred when the pH of the solution is higher than 5.5, so as the experiments were carried out without any further adjustment of the pH (pH = 4.8). Then 28 mg of zeolite powder or 100 mg of zeolite/luffa composite were added to 35 ml of the prepared solutions with salts of Co²⁺, Fe³⁺, and Mn²⁺, and kept on a shaker (speed of 150 rpm) from 5 to 250 min. Then the solid phase was separated from the water by centrifugation (20000 rpm for 10 min) prior characterization. While, the samples treated with zeolite/luffa composites were subjected to further characterization without additional centrifugation.

The water samples treated with pure zeolite, luffa and ZLC were characterized by UV spectroscopy using a UV-vis Hewlett Packard HP8453 spectrometer (the spectra were measured in the range 850 - 200 nm). The removal of heavy metals from solutions is determined using the following formula: metals removed (%) = $(C_o - C_e)/C_o \times 100$, where C_o and C_e are the initial and final metal concentrations (mg/l), respectively.

3. Results and discussion

3.1. General characterization

The crystallinity of pure zeolite, luffa and zeolite/luffa composite was determined by X-ray diffraction measurements (Fig. 1). The Bragg peaks at 16, 22.6, and 34.7 °2θ (Fig. 1a), confirm that the luffa fibers are semi-crystalline which is a base for moderate mechanical strength and stability. The XRD pattern of the ZLC (Fig. 1b) contains additional peaks at 5.9, 26.5, 29.2, 30.8, 40.8 °2θ that correspond to the crystalline EMT-type zeolite (Fig.1c). These results undoubtedly show that the ZLC is based on nanosized EMT-type zeolite grown on luffa fibers.

The zeolite nanoparticles on and embedded in the luffa fibers were further characterized by scanning electron microscopy. The surface features (morphology and size) of the initial luffa fibers, and the zeolite/luffa composite are shown in Fig. 2. The diameter of the luffa fibers is about 50 nm, and the length is determined from the preparation of the filaments prior to crystallization of zeolite crystals. The smooth surface of luffa fiber at high magnification is shown as insert in Fig. 2a. In contrast to the pure luffa fibers, the surface of the ZFC is more ridged and clearly contains zeolite nanocrystals on the surface and within the struts of luffa fibers. During the synthesis, the precursor suspensions penetrated well in the vascular system of the luffa fibers, and thus the crystallization takes place not only at the surface but also in the inner cellular network (Fig. 2 c,d). The EMT-type zeolite crystals are packed tightly and some are wrapped in a spiral mode due to the coiled textural structure of the luffa fibers (inset Fig. 2 c).

The amount of zeolite nanocrystals embedded in the composite is determined by thermogravimetry. The TG curves of pure luffa fibers, pure EMT-type zeolite and the ZLC are depicted in Fig. 3. The change in the weight (weight loss) of the pure luffa and zeolite samples under heating is observed in three steps: the first step is below 240 °C, the second step is in the range 240-330 °C, and the third one is above 330 °C. The first weight loss is due to removal of water from luffa fibers (3 %) and EMT-type zeolite (27.6 %). The second weight loss is related with the decomposition of pure luffa fibers (98 %), and the residue of 2 % is the extractive. Based on these results, the amount of zeolites embedded in the luffa fibers (ZLC) was determined using the difference in the weight loss between ZLC and pure luffa fibers. It is found that 24.7 % of EMT-type zeolite nanocrystals are embedded in the luffa fibers (see Fig. 3).

Prior using the pure zeolite and zeolite/luffa composite for water purification, their porosity was measured. The adsorption-desorption isotherms of the pure EMT-type zeolite as well as ZLC show a steep uptake at low relative pressures, followed by inclination with the increase in

the partial pressure, and terminated with a large hysteresis loop at high relative pressure. The latest is due to aggregation of nanosized zeolite crystals in the case of pure EMT-type zeolite and within the ZLC. The N₂ sorption isotherms show the combination between Type I and Type IV isotherms due to the presence of micro- and meso-pores in the materials (Fig. 4). The Brunauer-Emmet-Teller surface area (S_{BET}) and micropore volume of pure EMT-type zeolite is 560 m² g⁻¹ and 0.16 cm³ g⁻¹, respectively. These values correspond to a highly crystalline material, which is in good agreement with the X-ray diffraction data and SEM results. In the case of ZLC, the micropore volume is 0.015 cm³ g⁻¹, which is in agreement with the amount of zeolites embedded in luffa fibres (see TG results). The specific surface area, micropore, and mesopore volumes of ZLC are summarized in Table 3. The decrease of the microporosity of the ZLC with respect to the pure zeolite is expected and this corresponds to the amount of EMT-type nanosized crystallites embedded in the luffa fibers (24.7 %). The hysteresis loop at high relative pressure reveals the presence of mesopores in the zeolite and zeolite/luffa composite, which is expected to facilitate the diffusion as well as the ion exchange. The mesopores of the ZLC is similar to that of pure EMT-type zeolite (see insert in Fig. 4). The results reveal that the ZLC has a hierarchical structure containing a high amount of zeolite nanoparticles with well-developed micropores, inter-particle mesopores and hollow macro-channels originated from the luffa fibers.

3.2. Removal of heavy metals from water

The as-prepared EMT-type zeolite and zeolite/luffa composite are used for removal of Cu²⁺, Co²⁺, Fe³⁺, and Mn²⁺ from double distilled water. These experiments were performed for 250 minutes and compare with the performance of pure luffa fibers. The UV-vis spectra were collected from the water samples under treatment every 15 minutes and display in Figs. 5 and 6 (UV spectra of water samples treated with pure luffa are not shown). A faster decrease of the UV band at 510, 810, 320, and 300 nm which correspond to the removal Co²⁺, Cu²⁺, Fe³⁺, and Mn²⁺, respectively from water with pure EMT-type zeolite is measured and used as references. After the first five minutes of treatment, the intensity of the UV bands decreased considerably, then decline slowly with time, and after 250 min stays unchanged. Based on these results, the removal degree for the heavy metals is calculated and presented in Fig. 7. It is found that the sorption

capacity of pure EMT-type zeolite is decreased in the following order $\text{Co}^{2+} > \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Mn}^{2+}$ (Table 4).

The high removal degree is resulted from the high ion exchanged capacity of pure EMT-type zeolite with Si/Al ratio of 1.2, and a high concentration of Na (70 mg/l). The fast adsorption of the heavy metals with the EMT-type zeolite is explained with the small size of the crystallites (see Fig. 2). Moreover, the inter-crystalline mesoporosity (see Fig. 4, insert) of the EMT-type sample leads to an improvement of the performance of the zeolite since fast diffusion and exchange of the sodium for heavy metals is accomplished. The difference in the removal degree for Co^{2+} in comparison to Cu^{2+} and Mn^{2+} is explained by the different hydrated ion diameter of the cations (Table 5). The size of Co^{2+} and Fe^{3+} are similar (0.209 and 0.205 nm) but smaller than of Na^+ (0.235 nm). Therefore a fast exchange of sodium for cobalt and iron is achieved. Moreover, the high valence of Fe^{3+} cations leads to a stronger solvation effect, and the different solvation abilities result in different hydrated cations size. The results reveal that the pure EMT-type zeolite shows better adsorption capacity than natural zeolites (clinoptilolite and chabazite)[31-34]. Besides, the EMT-type zeolite performs better than the synthetic zeolites (NaP1, FAU-Y, FAU-X, MOR, LTA).[37,39] The use of clinoptilolite led to the removal of Ni^{2+} , Zn^{2+} , Cr^{3+} , Cd^{2+} and Cu^{2+} with 2, 3, 4, 4, 5 %, respectively, while the treatment with NaP resulted in 20, 30, 40, 44, 45 % purification of water, respectively.[39]

The performance of zeolite/luffa composite for water treatment under the same experimental conditions is studied, and the results are depicted in Fig. 6. After the first 5 minutes, a tremendous decrease of the UV-bands corresponding to Cu^{2+} , Fe^{3+} , Co^{2+} , and Mn^{2+} is observed. With further increase of the treatment up to 250 min, almost a complete vanishing of the band at 320 nm corresponding to Fe^{3+} is measured. The removal rate for heavy metals in water treated by zeolite/luffa composite is 85-95%, which is higher than pure zeolite powder (65-82 %). This can be explained by the presence of fibrous vascular system of the luffa fibers that contribute to the high porosity and accessibility of the composite. In addition to the high ion-exchange capacity of the EMT-type zeolite nanoparticles, the high sorption properties of the three-dimensional luffa structure lead to fast diffusion and high sorption. The capacity of pure luffa fibers in the purification of waste water has been demonstrated earlier.[47] However, in the current study, the removal degree for heavy metals after 250 minutes is measured to be only 5-7 % (Fig. 7).

The pH of the water affects the adsorption properties of zeolites, and the removal of heavy

metals typically increased with increasing the pH.[40] Besides, the pH also affects the ionization degree of the sorbate (heavy metals) and the surface property of the sorbent (zeolite).[49] Heavy metal ions may form complexes with inorganic ligands such as OH^- depending on the pH, ionic composition and the particular type of the metal concerned. The character of metal complex that predominates at a particular pH, also affect the selectivity of zeolite.[50]

In order to investigate the influence of the water hardness on the sorption capacity of zeolites, two different samples were prepared, one containing cobalt and calcium and the other with cobalt only. As can be seen, a high selectivity towards removal of Co^{2+} is reached (82 %), while 57 % of Co^{2+} is removed from the sample containing Ca^{2+} as well (Fig. 8). These results can be explained with the smaller size of cobalt (0.209 nm) than calcium (0.242 nm), that facilitates the exchange of sodium for cobalt.

In summary, the high uptake for heavy metals removed from water is attributed to both ion exchange and adsorption processes. A direct replacement of monovalent sodium by divalent or trivalent heavy metals takes place during the first several minutes of treatment. The heavy metals exchanged with Na-EMT-type were essentially stoichiometric, and takes place in the microporous of the zeolite crystals. The use of nanosized EMT-type zeolite supported on luffa facilitates the diffusion through the pores and demonstrates improved sorption capacity by increasing the contact surface area. Besides, the hollow structures of the luffa fibers improve the sorption capacity of the composites. Both the zeolites and the luffa fibers are porous and have high stability (mechanical and hydrothermal) due to their crystalline and semi-crystalline structures, respectively. Therefore recycling of the zeolite/luffa composites will be possible.

4. Conclusions

The crystallization of nanosized EMT-type zeolite in natural luffa fibers yielding zeolite/luffa composite for water purification is reported. Four types of heavy metals (Cu^{2+} , Co^{2+} , Fe^{3+} , and Mn^{2+}) were removed from water samples by pure luffa fibers with an average removal degree of 5.5 %, while with pure EMT-type zeolite a removal degree between 61 and 82 % is achieved. Besides, the zeolite/luffa composite shows improved capacity toward the Cu^{2+} , Co^{2+} , Fe^{3+} , and Mn^{2+} cations, resulting in almost 85-95 % elimination from water within 250 minutes. The

following sequence of decreasing the heavy metals removal from the water samples by zeolite/luffa composite is established: $\text{Co}^{2+} > \text{Fe}^{3+} > \text{Cu}^{2+} > \text{Mn}^{2+}$. The composite has better performance in respect to pure luffa fibers and pure zeolite, which is explain with the high ion exchange capacity of the zeolite combine with highly accessible febrile structure of the luffa support. Moreover, the pure EMT-type zeolite and the zeolite/luffa composite possess enhance mechanical strength and long-term stability. The better performance of the zeolite/luffa composite than the pure zeolite is due to the more accessible porous structure due to the presence of macroporous luffa fibers and high crystalline microporous zeolite with inter-particle mesoporosity. In that case both the zeolites and the bulk luffa have better contact with the heavy metals resulting in high adsorption degree. Besides fast diffusion, high contact area and high sorption capacity of the zeolite nanoparticles embedded within the natural fibers is observed. Both materials, i.e., EMT-type zeolite and luffa fiber are yielding an environmentally friendly zeolite/luffa composite, which is particularly appropriate for waste water purification.

Acknowledgement:

The financial support from MEET, Materials for Energy Efficiency in Transport, INTERREG EC project is acknowledged.

5. References

- [1] S. Mintova, V. Valtchev, Deposition of *Zeolite A* on Vegetable Fibers, *Zeolites* 16 (1996) 31-34.
- [2] S. Mintova, V. Valtchev, Preparation of Zeolite-Covered Cellulose Fibers, 209th National Meeting Abstracts, American Chemical Society 1995.
- [3] K. Niu, A Study on the Preparation of Zeolite Y-Cellulose Composite Materials, M.S. Thesis, University of Nebraska- Lincol 2000.
- [4] H. Kim, N. J. Jeong, S. Ok Han. *App. Catal. B* 22 (2012) 116.
- [5] H. Wu, C. Wu, Q. He, X. Liao, B. Shi, Collagen fiber with surface-grafted polyphenol as a novel support for Pd(0) nanoparticles: Synthesis, characterization and catalytic application, *Mater. Sci. Eng. C*, 30 (2010) 770-776.
- [6] Z. N. Azwa, B. F. Yousif, A. C. Manalo, W. Karunasena, A Review on the Degradability of Polymeric Composites Based on Natural Fibres, *Mater. Design* 47 (2013) 424-442.
- [7] S. V. Joshi, L. T. Drzal, A. K. Mohanty, S. Arora, Are natural fiber composites environmentally superior to glass fiber reinforced composites? *Composites part A* 35 (2004) 371-376.

- [8] R. Kozłowski, M. Władysław-Przybylak, Flammability and Fire Resistance of Composites Reinforced by Natural Fibres *Polym. Adv. Technol.* 19 (2008) 446-453.
- [9] T. Nishino, N. Arimoto, All-cellulose composite prepared by selective dissolving of fiber surface, *Biomacromolecules* 8 (2007) 2712-2716.
- [10] Y. Lei, Q. Wu, F. Yao, Y. Xu, Preparation and Properties of Recycled HDPE/Natural Fiber Composites, *Composites Part A: Applied Science and Manufacturing* 38 (2007) 1664-1674.
- [11] M. Abdelmouleh, S. Boufi, M.N. Belgacem, A. Dufresne, Short natural-fibre reinforced polyethylene and natural rubber composites: Effect of silane coupling agents and fibres loading, *Compos. Sci. Technol.* 67 (2007) 1627.
- [12] E. Bozkurt, E. Kaya, M. Tanoğlu, Mechanical and thermal behavior of non-crimp glass fiber reinforced layered clay/epoxy nanocomposites, *Compos. Sci. Technol.* 67 (2007) 3394-3403.
- [13] G. Bogoeva-Gaceva, A. Dekanski, V. Panin, D. Poleti, A. Grozdanov, A. Buoždanov, M. Avella, G. Gentile, XLIV Meeting of the Serbian Chemical Society, Belgrade 2006, February 6.
- [14] N. S. M. El-Tayeb. Abrasive wear performance of untreated SCF reinforced polymer composite, *J. Mater. Process. Technol.* 206 (2008) 305-314.
- [15] F. Corrales, F. Vilaseca, M. Llop, J. Girones, J.A. Mendez, P. Mutj, Chemical modification of jute fibers for the production of green-composites, *J. Hazardous Mater.* 144 (2007) 730-735.
- [16] D. N. Saheb, J. P. Jog, Natural fiber polymer composites: A review, *Adv. Technol.* 18 (1999) 351-363.
- [17] J. Holbery, D. Houston, Natural-Fiber-Reinforced Polymer Composites in Automotive Applications, *JOM.* 11 (2006) 80-86.
- [18] A. K. Bledzki, O. Faruk, V. E. Sperber, Cars from Bio-Fibres, *Macromol. Mater. Eng.* 291 (2006) 449-457.
- [19] A. K. Mohanty, M. Misra, G. Hinrichsen, Biofiber, biodegradable polymers and biocomposites: an overview, *Macromol. Mater. Eng.* 276/277 (2000) 1-24.
- [20] V. F. Korchakov, O. F. Tatarenko, G. S. Bukhtjarov, N. M. Konyshchikov, A. G. Nosova, Method of Porous Material Producing, RU Pat. RU2118967 (C1), 109 (1998) 767.
- [21] K. Katsunao, Porous Mineral-Containing Formed Body and Its Production, JP Pat. 189 (2000) 793.
- [22] M. El-Roz, Z. Haidar, L. Lakiss, J. Toufaily, F. Thibault-Starzyk, Immobilization of TiO₂ nanoparticles on natural *Luffa cylindrica* fibers for photocatalytic applications, 3 (2013) 3438-3445.
- [23] Y. Toshio, M. Osamu, T. Yoji, JP Pat. 35 (1998) 886.
- [24] G.S. Lee, Y.-J. Lee, K. Ha, K.B. Yoon, Preparation of flexible zeolite-tethering vegetable fibers, *Adv. Mater.* 13 (2001) 1491-1495.

- [25] S. Sanga, Z. Liu, P. Tiana, Z. Liua, L. Qua, Y. Zhang, Synthesis of small crystals zeolite NaY, *Materials Letters, Mater. Lett.* 60 (2006) 1131-1131.
- [26] B. H. Wang, Y. Y. Xia, S. Y. Zhuang, Y. H. Zhang, T. T. Yan, *Imaging Sci. J* 25 (1998) 131-135.
- [27] S. Mintova, V. Valtchev, Synthesis of nanosized fau-type zeolite, *Stud. Surf. Sci. Catal.* 125 (1999) 141-148.
- [28] <http://www.iza-structure.org/databases/>.
- [29] K. S. Hui, C. Y. H. Chao, S. C. Kot, Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash, *J. Hazard. Mater.* 127 (2005) 89-101.
- [30] M. B. Hafez, A. F. Nazmy, F. Salem, M. Eldesoki, Fixation mechanism between zeolite and some radioactive elements, *J. Radioanal. Chem.* 47 (1978) 115-122.
- [31] S. K. Ouki, M. Kavannagh, Performance of natural zeolites for the treatment of mixed metal-contaminated effluents, *J. Waste Manage. Res.* 15 (1997) 383-394.
- [32] V. J. Inglezakis, M. A. Stylianou, D. Gkantzou, Removal of Pb(II) from aqueous solutions by clinoptilolite and bentonite as adsorbents, *Desalination* 210 (2007) 248-256.
- [33] C. P. Huang, F. B. Ostovic, Removal of cadmium (II) by activated carbon adsorption, *J. Environ. Eng.* 104 (1978) 863-878.
- [34] C.Y. Lin, D.H. Yang, Removal of pollutants from wastewater by coalbottom ash, *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* 37 (2002) 1509-1522.
- [35] E. I. Basaldella, P. G. Vazquez, F. Iucolano, D. Caputo, Chromium removal from water using LTA zeolites: effect of pH, *J. Colloid Interface Sci.* 313 (2007) 574-581.
- [36] I. M. Kolthoff, E. B. Sandell, E. J. Meehan, S. Brucjenstein (Eds.). *The Macmillan Company, London* 1969.
- [37] C. A. Rios, C. D. Williams, C. L. Roberts, Removal of heavy metals from acid mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites, *J. Hazard. Mater.* 156 (2008) 23-35.
- [38] J. C. Izidoro, D. A. Fungaro, J. E. Abbott, S. Wang, Synthesis of zeolites X and A from fly ashes for cadmium and zinc removal from aqueous solutions in single and binary ion systems, *SciVerse ScienceDirect* 103 (2013) 827-834.
- [39] E. Alvarez-Ayuso, A. Garcia-Sanchez, X. Querol, Purification of metal electroplating waste waters using zeolites, *Water Res.* 37 (2003) 4855-4862.
- [40] S. K. Ouki, M. Kavannagh, Performance of Natural Zeolites for the Treatment of Mixed Metal-Contaminated Effluents, *Waste Manage. Res.* 15 (1997) 383-394.
- [41] X. Zou, J. El Falla, J. M. Goupil, G. Zhu, V. Valtchev, S. Mintova, Green removal of aromatic organic pollutants from aqueous solutions with a zeolite –hemp composite, *RSC Adv.* 7 (2012) 3115-3122.
- [42] V. J. Inglezakis, M. D. Loizidou, H. P. Grigoropoulou, Ion exchange of Pb²⁺, Cu²⁺, Fe³⁺, and Cr³⁺ on natural clinoptilolite: selectivity determination and influence of acidity on metal uptake, *J. Colloid Interface Sci.* 261 (2003) 49-54.

- [43] C. Covarrubias, R. Arriagada, J. Yanez, R. Garcia, M. Angelica, S. D.Barros, P. Arroyo, E.F. Sousa-Aguiar, Removal of chromium(III) from tannery effluents, using a system of packed columns of zeolite and activated carbon, *J. Chem. Technol. Biotechnol. J. Chem. Technol. Biotechnol.* 80 (2005) 899-908.
- [44] V.J. Inglezakis, M.D. Loizidou, H.P. Grigoropoulou, Equilibrium and kinetic ion exchange studies of Pb^{2+} , Cr^{3+} , Fe^{3+} and Cu^{2+} on natural clinoptilolite, *Water Res.* 36 (2002) 2784-2792.
- [45] E. P. Ng, D.Chateigner, T. Bein, V. Valtchev, S. Mintova, Capturing ultrasmall EMT zeolite from template-free systems, *Science* 335 (2012) 70-73.
- [46] J. F. Rubinson, K. A. Rubinson. *Contemporary Chemical Analysis*, first ed., Prentice-Hall, Singapore 1998.
- [47] V. O. A. Tanobe, T. H. D. Sydenstricker, M. Munaro, S. C. Amico. A comprehensive characterization of chemically treated Brazilian sponge-gourds (*Luffa cylindrical*), *polymer testing* 24 (2005) 474-482.
- [48] Y. Marcus, Ionic Radii in Aqueous Solutions, *Chem. Rev.* 88 (1988) 1475-1498.
- [49] S. Kesraouiouki, C. R. Cheeseman, R. Perry, Natural zeolites utilisation in pollution control: A review of applications to metals effluents, *J. Chem. Technol. Biotechnol.* 59 (1994) 121-126.
- [50] B. Singh, B. J. Alloway, F. J. M. Bochereau. Cadmium sorption behavior of natural and synthetic zeolites, *Commun. Soil Sci. Plant Anal.* 31 (2000) 2775-2786.

Tables

Table 1. Composition of luffa fibers.

Component	Content (wt.%)
Ash	0.7 ± 0.2
Extractives	3.1 ± 0.5
Total lignin	15.2 ± 1.0
Cellulose	65.5 ± 0.5
Hemicellulose	17.5 ± 0.5

Table 2. Chemical composition of pure EMT-type zeolite and zeolite/luffa composite (ZLC).

Concentration (mg/l)	Na	Al	Si
EMT-type zeolite	69.50	81.80	102.70
Zeolite/luffa composite	79.42	72.69	93.35

Table 3. Results for pure EMT-type zeolite, pure luffa fibers and zeolite/luffa composite (ZLC) derived from nitrogen sorption measurements.

Samples	S_{BET}	S_{ext}	V_{micro}	V_{meso}	d_{meso}^a	V_{total}
EMT zeolite	560.00	240.00	0.16	0.89	16	1.05
Luffa fiber	0.16	0.00	0.00	0.00	0.00	0.00
ZLC	70.00	35.00	0.015	0.10	22	0.115

S_{BET} : surface area ($\text{m}^2 \text{g}^{-1}$), V_{micro} : micropore volume ($\text{cm}^3 \text{g}^{-1}$)
 S_{ext} : external surface area ($\text{m}^2 \text{g}^{-1}$), V_{meso} : mesopore volume ($\text{cm}^3 \text{g}^{-1}$)
 d_{meso} : average mesopore size (nm). ^a determined by BJH method.

Table 4. Removal degree of heavy metals from water samples by pure luffa fibers, pure EMT-type zeolite, and zeolite/fiber composite (ZLC).

Metal cations	Luffa fiber	EMT zeolite	ZFC
Cu^{2+}	5 %	65%	85%
Co^{2+}	5.5 %	82%	95%
Mn^{2+}	6%	61%	82%
Fe^{3+}	7%	70%	90%

Table 5. Properties of metal ions in water.

Ion type	Crystal ion size (diameter) (nm)	$d_{\text{ion-W}}^{\text{a}}$ (nm)	Counter ion
Na ⁺	0.240	0.235	Cl ⁻
Ca ²⁺	0.246	0.242	Cl ⁻
Co ²⁺	0.144	0.209	NO ₃ ⁻
Cu ²⁺	0.146	0.215	SO ₄ ⁻
Mn ²⁺	0.166	0.219	NO ₃ ⁻
Fe ³⁺	0.130	0.205	NO ₃ ⁻

^a $d_{\text{ion-W}}$: the distance between ion and water molecule center.[48]

Figure captions

Fig. 1 XRD patterns of (a) pure luffa fibers (b) ZLC, and (c) pure EMT-type zeolite.

Fig. 2 SEM micrographs of (a, b) pure luffa fibers, and (c, d) zeolite/luffa composite at different magnifications.

Fig. 3 TG curves of (a) pure luffa fibers, (b) zeolite/luffa composite, and (c) pure EMT-type zeolite.

Fig. 4 Nitrogen adsorption/desorption isotherms of (a) pure luffa fibers, (b) zeolite/luffa composite, and (c) pure EMT-type zeolite.

Fig. 5 UV-vis spectra recorded from water samples containing (a) Co, (b) Cu, (c) Mn and (d) Fe under treatment with pure EMT-type zeolite for 250 minutes.

Fig. 6 UV-vis spectra recorded from water samples containing (a) Co, (b) Cu, (c) Mn and (d) Fe under treatment with zeolite/luffa composite for 250 minutes.

Fig. 7 Removal of (a) Co, (b) Cu, (c) Mn and (d) Fe from water using (■) pure luffa fiber, (●) pure nanosized EMT-type zeolite, and (◆) zeolite/luffa composite (ZLC).

Fig. 8 Removal of Co from double distilled water containing ◇ (Ca²⁺ and Co²⁺), and ◆ (Co²⁺) with pure EMT-type zeolite.

Figures

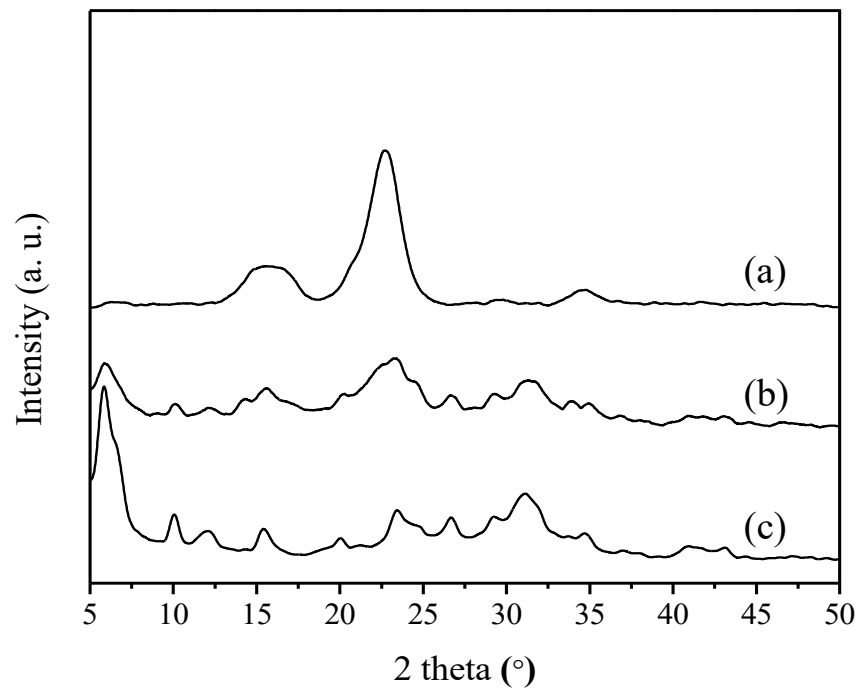


Fig. 1

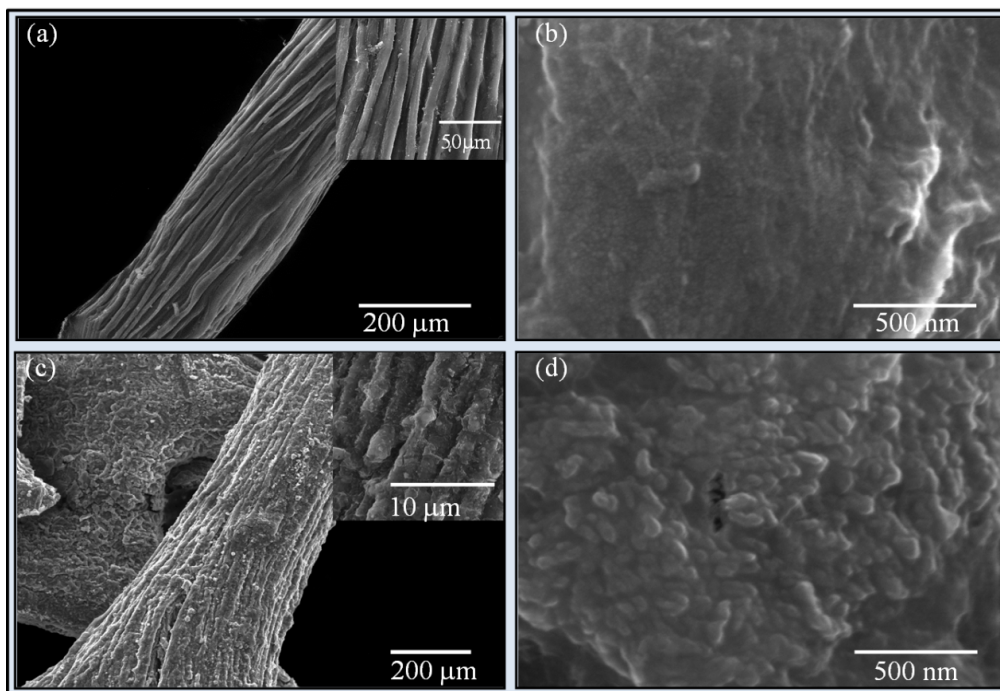


Fig. 2

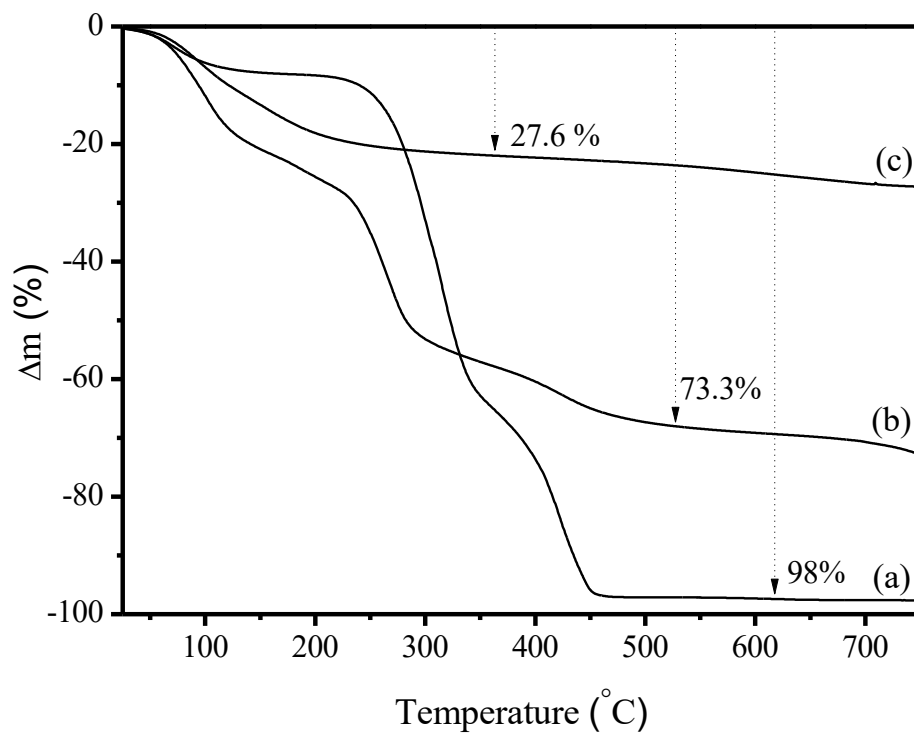


Fig. 3

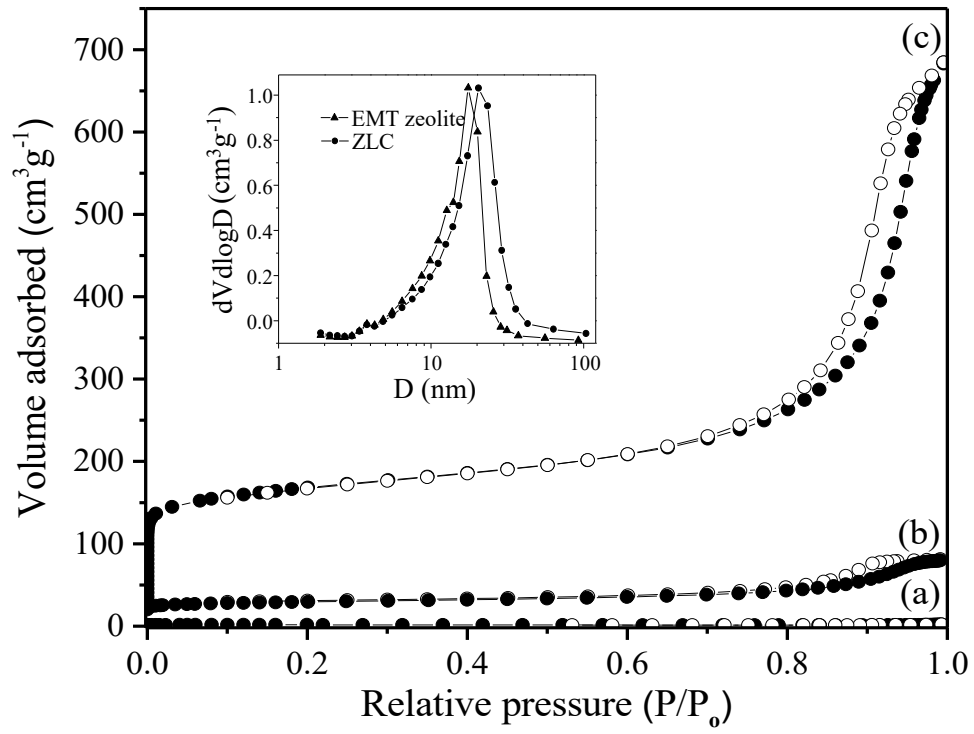


Fig. 4

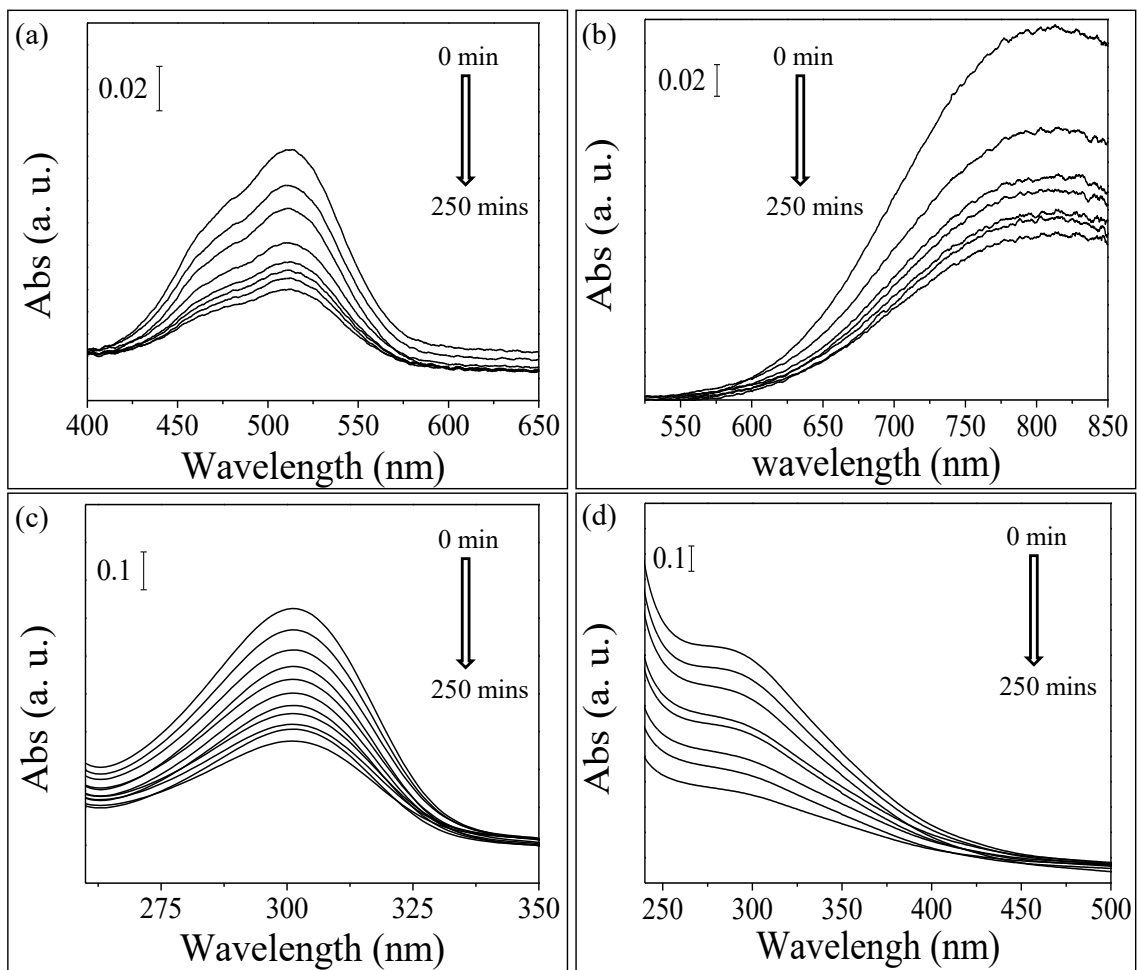


Fig. 5

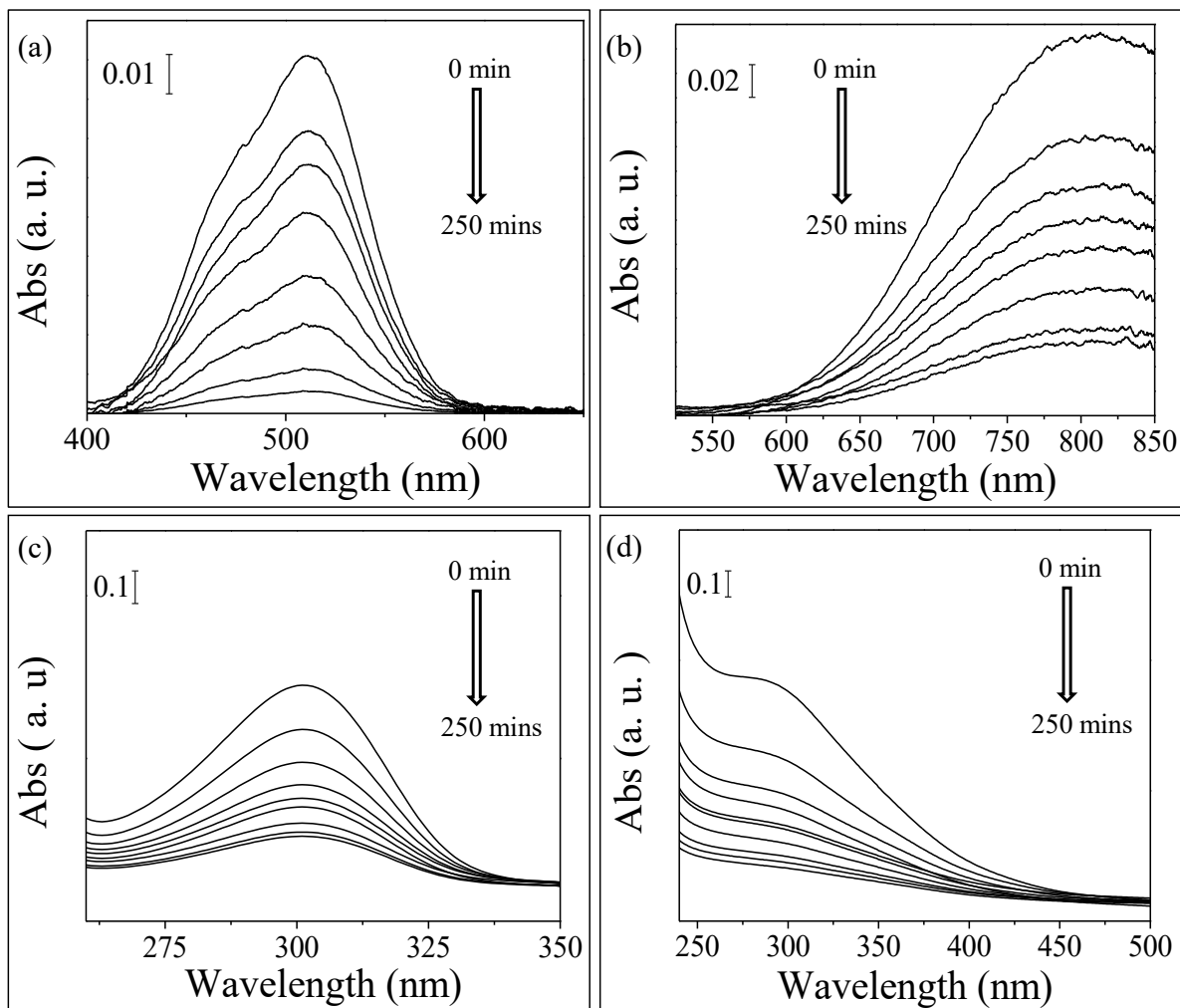


Fig. 6

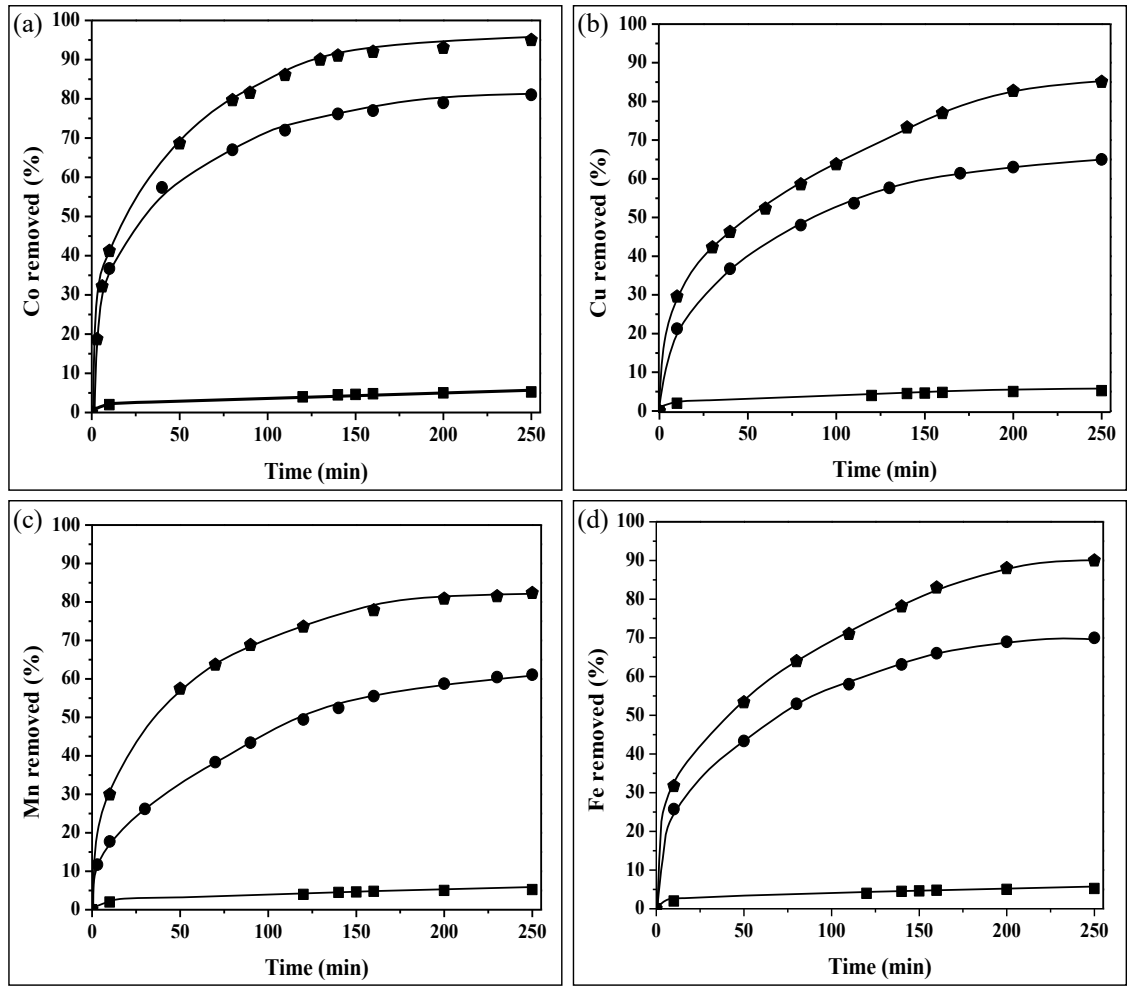


Fig. 7

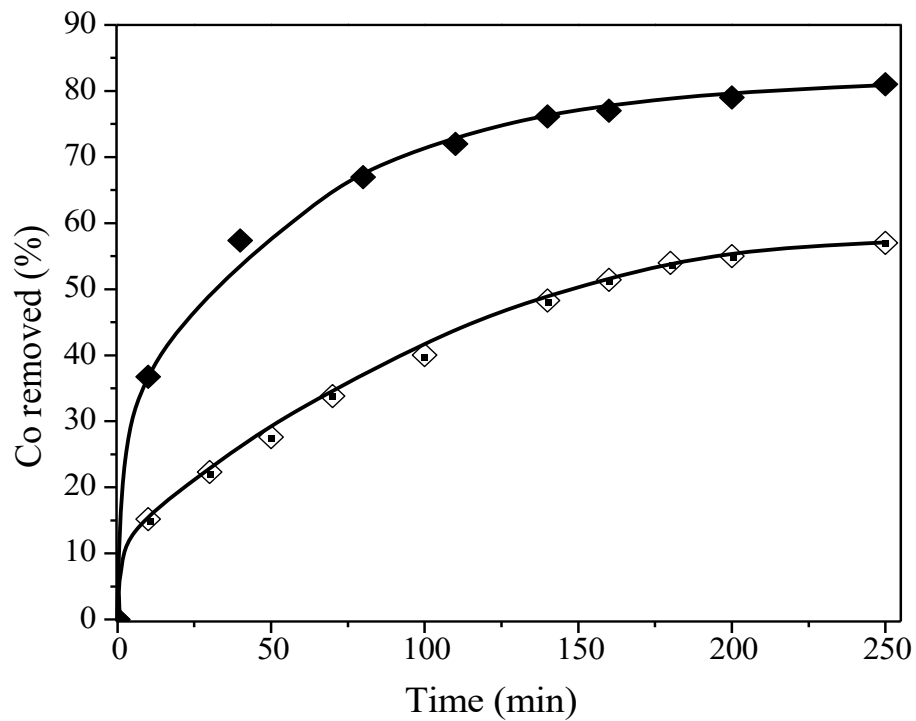


Fig. 8

Highlights

- Crystallization of EMT-type zeolite nanoparticles on luffa fibers.
- Zeolite/luffa composite is used for the removal of heavy metals (Cu^{2+} , Mn^{2+} , Co^{2+} and Fe^{3+}) from water.
- Above 95 % of the heavy metals are removed by zeolite/luffa composite.
- Both the zeolite and the luffa fibers are environmentally friendly.

