Powder Technology 294 (2016) 338–347

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Synthesis and characterization of new zeolite materials obtained from fly ash for heavy metals removal in advanced wastewater treatment

Maria Visa

Transilvania University of Brasov, Research Center: Renewable Energy Systems and Recycling, Eroilor 29, 500036, Brasov, Romania

ARTICLE INFO

Article history:
Received 23 August 2015
Received in revised form 7 February 2016
Accepted 10 February 2016
Available online 13 February 2016

Keywords:
Zeolite
Fly ashes
Heavy metals
Wastewater

ABSTRACT

Waste management and water quality are two of the main problems that humanity faces nowadays. Increased urbanization and industrialization lead to excessive release of wastes into the environment, including fly ash resulted from coal combustion. Fly ash reuse in developing low cost, efficient adsorbents of zeolite-type could support wastewater treatment according to the concept *wastes for waste treatment*. The ashes converted in zeolite materials were collected from two Combined Heat and Power Plants (CET Brasov and DEVA) from Romania. The zeolite materials were characterized by AFM, XRD, FT-IR, SEM, BET and surface energy measurements to outline the crystalline and morphology modifications. The zeolite-type substrates were obtained by using the fly ashes modified through hydrothermal processes using a low concentration of NaOH, and were further used for heavy metals removal (Cd^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}) from synthetic solutions with mono-, bi-, and five-cations. In order to obtain maximum efficiency during the heavy metals removal of the adsorption conditions (contact time, optimum amount of substrate and initial concentration) were optimized. These parameters were further used in the thermodynamic and kinetic modelling of the adsorption processes. Correlated with the surface structure, composition and morphology, the kinetic adsorption mechanisms and the substrate capacities are further discussed.

1. Introduction

Pollution was identified as one of the major threats to humanity; therefore investigations are dedicated to implementing the concept of waste removal using wastes. Water is one of the most affected environmental factors, loaded daily with heavy metals from various industries.

Heavy metals are persistent pollutants, non-biodegradable, easily accumulated in living organisms even at low concentrations, causing serious illnesses [1]. The largest amounts of heavy metals are directly discharged into rivers, with high toxicity risks as hydrated ions are more toxic than metal atoms, because they are absorbed faster and disturb the enzymatic processes. The main sources of heavy metals in wastewater and surface water are [2]: electroplating and metal surface treatment, metal and plastic coating, metallurgy of easily fusible alloys, rechargeable batteries manufacturing (Ni-Cd), electronic industry, petroleum refineries, paint and pigment for leather industry, mining and the glass production [3].

According to the initial concentration and the composition of the pollutant systems, alternative methods developed for heavy metals removal are: chemical precipitation by adding reagents in order to form low-soluble heavy metal compounds (hydroxides, sulphides and carbonates), coagulation and flocculation adding gelling reagents. However, the remnant concentration value usually exceeds water quality standards, thus advanced wastewater treatment processes are compulsory [4].

Adsorption can represent a viable solution, being employed as ion exchange, biosorption [5], adsorption on natural substrates as bentonite [6] or on highly effective substrates as zeolites [7,8]; the major advantage of adsorption is the possibility of large scale processing, being less energy intensive compared to other advanced processes as: electrochemical reduction, micro-filtration, ultra-filtration, nano-filtration [9], electrodialysis [10], or reverse osmosis [11].

The new concept *wastes for waste treatment* is now largely applied for wastewater treatment using solid wastes resulted as by-products from coal combustion, among which fly ash represents more than 65%. An economic and efficient process is the conversion of fly ash into zeolites [12–14] like zeolite-X [15], zeolite-A [7], zeolite-P [16], Na-P1 [17], K-chabazite and k-phillipsite [18], synthesized using various methods.

Zeolites have wide applications used as adsorbents, molecular sieves, ion exchange (waste water treatment), air purification and many more.

Many studies are reporting on fly ash, raw, modified or on dispersed TiO_2-fly ash, tested as adsorbents for heavy metals removal from wastewater [19,20–22]. The adsorption performance of zeolites is much

E-mail address: maria.visa@unitbv.ro.

http://dx.doi.org/10.1016/j.powtec.2016.02.019
0032-5910/

Table 1
Fly ashes composition.

Major oxides [Wt.%]											
CHP	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	MnO	LOI*	% ** SiAlFe
FACET	53.32	22.05	8.97	5.24	2.44	2.66	0.63	1.07	0.08	1.58	86.34
FADEVA	46.05	20.08	9.93	6.07	2.35	2.28	0.83	0.06	0.09	4.45	76.06

LOI* loss of ignition. %** Sum of %Si Al and Fe.
The SiO_2: Al_2O_3 ratio above 2.40 (FACET) and 2.29 (FADEVA) shows that fly ashes represent a possible precursor for zeolites materials.

better than of fly ash, thus the development of performant zeolite adsorbents using fly ash became a route more recently investigated, including single or two heavy metals' removal [23,24].

Due to the fact that wastewater is loaded with more heavy metals and organic pollutants, the present paper presents a comparative study between two types of zeolite materials prepared through hydrothermal method, using two fly ashes as raw materials. These are investigated as adsorbents for the simultaneous removal of heavy metals (Cd^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Pb^{2+}) from solutions containing up to five cations.

2. Materials and methods

The raw fly ash (FA) used in the experiments was obtained from lignite coal burned in the CPH plant CET Brasov (FACET) and from S.E. Deva – Mintia (FADEVA), Romania. According to the ASTM standards [25] the fly ashes collected from the electro-filters of the two plants are of F type because the sum of the major compounds (SiO_2, Al_2O_3 and Fe_2O_3) is over 70%, and CaO < 6.5%, Table 1. These fly ashes do not aggregate with water.

2.1. Zeolite materials synthesis and characterization

Preliminary experimental tests proved that the raw or washed FA has very low adsorption efficiency, less than 10%, mainly as result of their low specific surface (6.14 g/m^2 and 10.13 g/m^2) and the heterogeneity charge on the surface.

The raw fly ashes were washed with ultra-pure water, under mechanical stirring (100 rpm, Nahita GJ-1 stirrer), at room temperature (22 ± 1 °C), for 48 h, in order to remove the soluble compounds K_2O, Na_2O, MgO, CaO. The ratio between raw fly ash and ultra-pure water ratio was 1:10 [g/mL]. Afterwards the suspension was filtered and dried at 105-115 °C. The washed and dried fly ashes were mechanically sieved (Analysette 3 Spartan) and the 40 μm fraction was selected. This fraction represents 38.5% for washed FACET Brasov (FAwCET) and 60.8% for washed FADeva (FAwDeva); the rest could be further used for obtaining geo-polymers, in concrete manufacturing, for bricks and ceramic tiles, or as filler in plastics, etc.

During the hydrothermal process the washed fly ash was treated with sodium hydroxide 2 N solution. The zeolite materials were obtained under stirring in autoclave, at 150 °C and 5 atm. After the reactions were completed, the suspended matter was washed with ultra-pure water until constant pH was obtained, afterwards it was filtered and dried at 105-115 °C over night. The zeolite materials obtained were denoted ZCET40 and ZDs40.

The crystalline structure of raw fly ashes, ZCET40 and ZDs40 was evaluated by XRD (Advanced D8 Discover Bruker diffractometer, $Cu_{K\alpha1}$ = 1.5406 Å, 40 kW, 20 mA, 2θ range 10°…70°, scanning step 0.02°, scan speed 2 s/step). Complementary data were obtained by FTIR spectroscopy (Spectrum BX Perkin Elmer BX II 75548, λ = 400–4000 nm). Surface characterization included micro-porosity and BET specific surface measurements (Autosorb-IQ-MP, Quantachrome Instruments), roughness and macro-pores size distribution using AFM (Ntegra Spectra, NT-MDT model BL222RNTE, in semi-contact mode with Golden silicon cantilever, NCSG10, at constant force 0.15 N/m, with a 10 nm tip radius) and morphology using scanning electron microscopy before and after adsorption (SEM, S-3400 N-Hitachi, accelerating voltage of 20 KV). The surface elemental composition was evaluated using energy dispersive X-ray spectroscopy (EDS Thermo Scientific Ultra Dry).

2.2. Removal the heavy metals by adsorption: experiments

The pollutant systems were synthetically prepared using ultra-pure water. Experimental tests were done on mono-, bi- and five-component

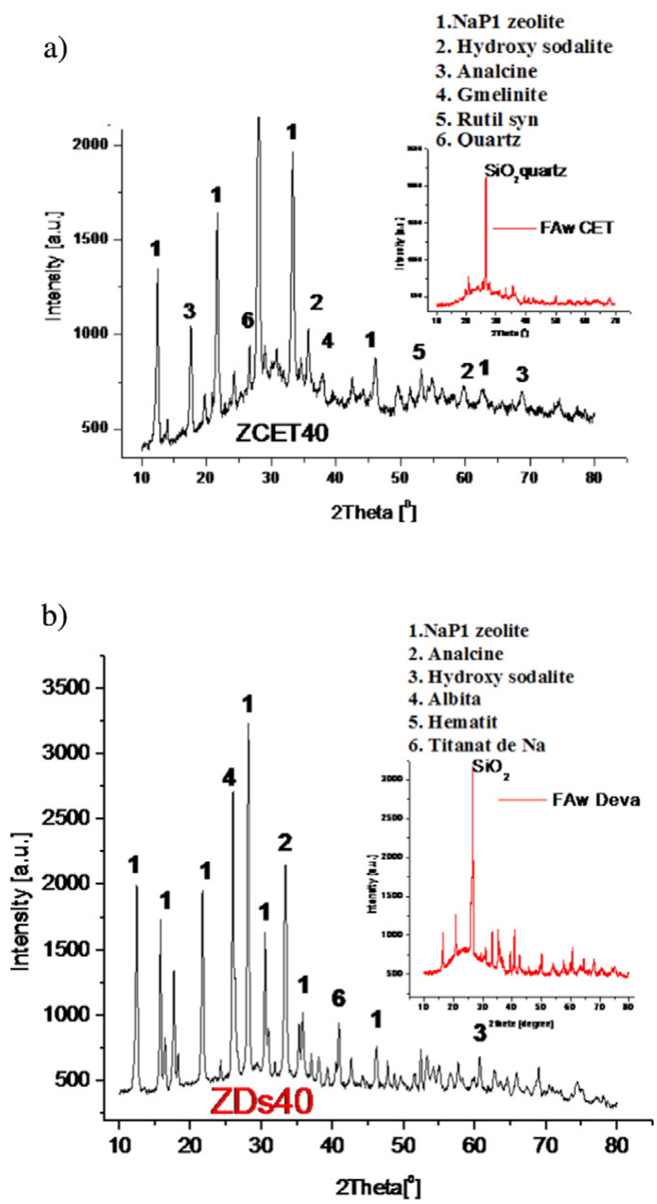

Fig. 1. (a) XRD data of ZCET40 and FAw CET; (b) XRD data of Z Ds40 and FAw DEVA.