

DYE REMOVAL FROM WATER SOLUTION BY MEANS OF ZEOLITIZED WASTE ASHES AND SLAG FROM FOUR BULGARIAN THERMO-POWER-PLANTS

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Abstract: A simple and cost effective method was applied for the synthesis of composite products containing zeolite type FAU from waste materials (fly ashes and/or slag) of several Bulgarian coal burning TPP. The method consists in a prolonged alkaline treatment at room temperature of the respective wastes. The zeolitic composites thus obtained as well as the starting wastes were tested as absorbents of a textile dye (malachite green) from water solutions. It was demonstrated that in comparison with the starting wastes, the zeolitized products possess better absorption properties: they almost completely extracted the dye for much shorter times. This reveals possibilities for their prospective application for purifying polluted waters, e.g. from the textile industry.

ОТСТРАНЯВАНЕ НА БОЯ-ОЦВЕТТЕЛ ОТ ВОДЕН РАЗТВОР С ПОМОЩТА НА ЗЕОЛИТИЗИРАНИ ОТПАДНИ ПЕПЕЛИ И ШЛАКА ОТ ЧЕТИРИ БЪЛГАРСКИ ТОПЛОЦЕНТРАЛИ

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Резюме: Приложен е прост и икономически изгоден метод за синтез на композитни продукти, съдържащи зеолит тип FAU от отпадъци (пепели и шлаки) от няколко български ТЕЦ. Методът се основава на продължително третиране при стайна температура в алкални разтвори на съответните отпадъци. Получените зеолитни композити, както и изходните материали, са изследвани като абсорбенти на една текстилна боя (малахитово зелено) от водни разтвори. Установено е, че зеолитизираните продукти извличат боята почти напълно и за много по-кратки времена, отколкото изходните пепели и шлаки, което разкрива възможности за бъдещото им използване за пречистване на отпадни води, напр. от текстилната промишленост.

Introduction

Coal is an important raw material in the thermal power plants (TPP) either in Bulgaria or in the world. Global coal burning by-products, like fly ashes (FA) and slag (SL), are over 500 million tones per year [1]. Although the disposal and storage of such wastes is a large problem for the power generation industry, their degree of recycling is lower than 15-20% [2, 3]. At the same time, they have turned out to be useful secondary raw materials which could find many application fields [4 - 7]. What

concerns the annual producing of coal combustion waste products, it overcomes 34 million tones per year for the European Union, and it is over 6 million tones from the Bulgarian TPP [2, 5].

For the last decade, there has been an increased interest in the field of synthesis and application of the zeolites, and especially in recycling of FA and SL into zeolitic composites, using possibly simpler, faster and cheaper conversion methods [8 - 14]. The products of FA zeolitic conversion have found or can find many applications, e.g. for different ion exchange treatments, as molecular sieves, and adsorbents. Due to the specific zeolite structure, such composites are used in a wide range of environmental engineering processes, such as removal of heavy metals, ammonium ions or oil-derivative contaminants from polluted waters [1, 3, 15, 16].

As well known, effluents from different industries (textile, leather, paper, ceramic, food, paints and printing inks, hair coloring, etc.) are usually polluted by dyes. In many cases these dyes are dangerous, irritant and toxic for living organisms, and have to be removed in order to prevent environmental pollution. A recent study has been devoted on the absorption behavior of FA and zeolite-fly ash (ZFA) composites [17]. It has been established in all such investigations that not only FA but also zeolite-ash (ZFA) composites are especially suitable for the absorption of dyes from wastewater [7, 16 - 20].

Aim of the present study is to compare the possibilities for extraction of malachite green by several raw and zeolitized coal by-products (FA and/or SL) from Bulgarian TPP.

Materials, methods and experimental procedure

Samples of FA and/or SL were collected from several Bulgarian coal burning TPP, namely TPP "Varna" ("V"), "Republika" ("R"), "Rousse East" ("RE"), and "Svistov" ("S"). The "V" and "R" wastes consisted of FA, the "S" waste was milled SL, while the "RE" waste was a mixture of FA and SL. Detailed information about their content is available in our previous studies [5, 10, 11, 21].

Experiments for the synthesis of zeolitic composites were carried out, according to an idea of Derkowski et al. for chemical activation of FA at room temperature [13, 14], applied also in [2]. For this purpose samples of FA and/or SL from the mentioned TPPs were treated by 5M solution of NaOH for a period of one year. The products thus obtained were filtered, washed to neutral pH, dried and analyzed. Methods, such as Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray (EDX) analysis and X-Ray Diffraction (XRD), were used for characterization of the raw materials, as well as of the final products with respect to their morphology, elemental and mineral composition.

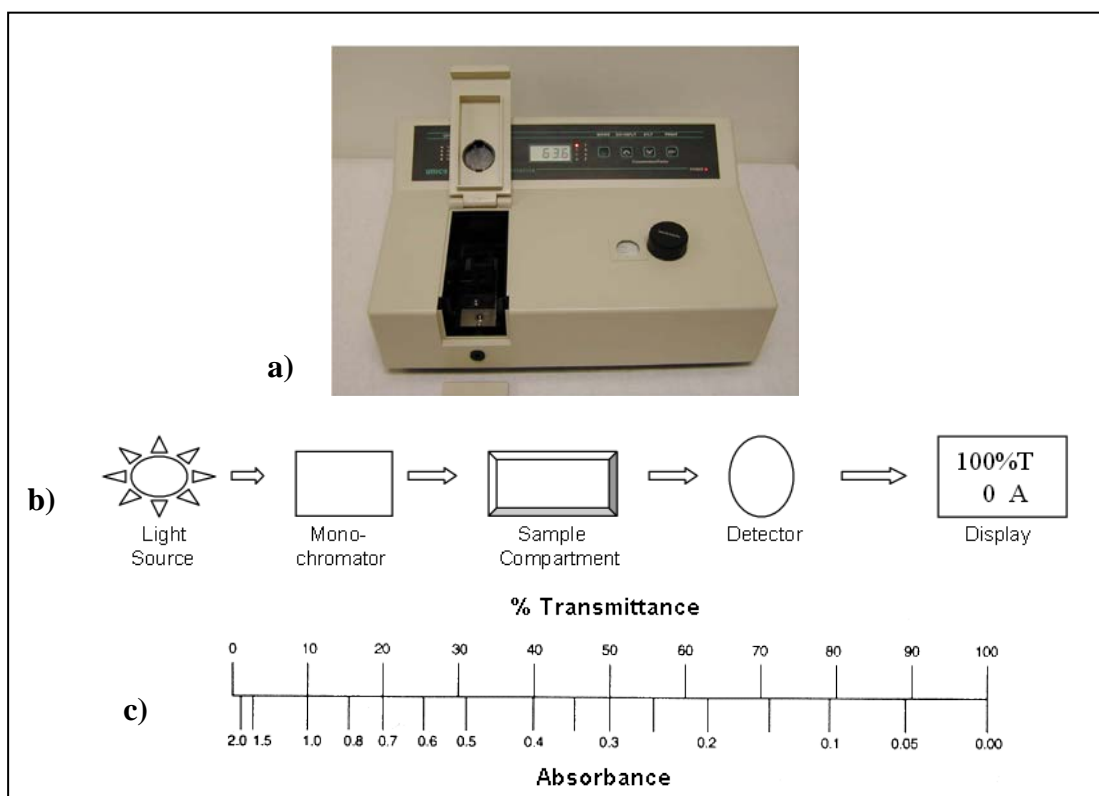


Fig. 1. Model 1200 Spectrophotometer (a), its block diagram (b), and scale of relation between absorbance and transmittance, according to eq.1

The dye used here - malachite green (MG), is an organic compound ($C_{23}H_{25}ClN_2$) that often appears as a pollutant in effluent waters, used for coloring of silk, leather, paper, etc. The initial concentration of MG in water solutions was 10 mg l^{-1} . The degree of its removal was determined by monitoring the absorbance changes at a wavelength of maximum of MG absorbance (617nm). All measurements of transmittance were carried out by using an UV spectrophotometer (1200 Series, Cole Parmer Instruments Company), Fig.1a, b. Full transmittance (100%T) was obtained using a test tube with a blank reference solution (distilled water). The relation between transmittance (%T) and absorbance (A) is visualized in Fig.1c, according to Eq.1:

$$(1) \quad A = 2 - \log(\%T)$$

This method of measurement needs a linear dependence between the absorbance (A) and the dye concentration (C) for construction of a calibration curve. The linearity was tested in the concentration interval of C from 10^{-3} to 10 mg l^{-1} . A calibration curve was drawn by measuring the transmittance of a set of samples with previously known dye concentration C (Fig.2a), and recalculating the respective absorbance (Fig.2b).

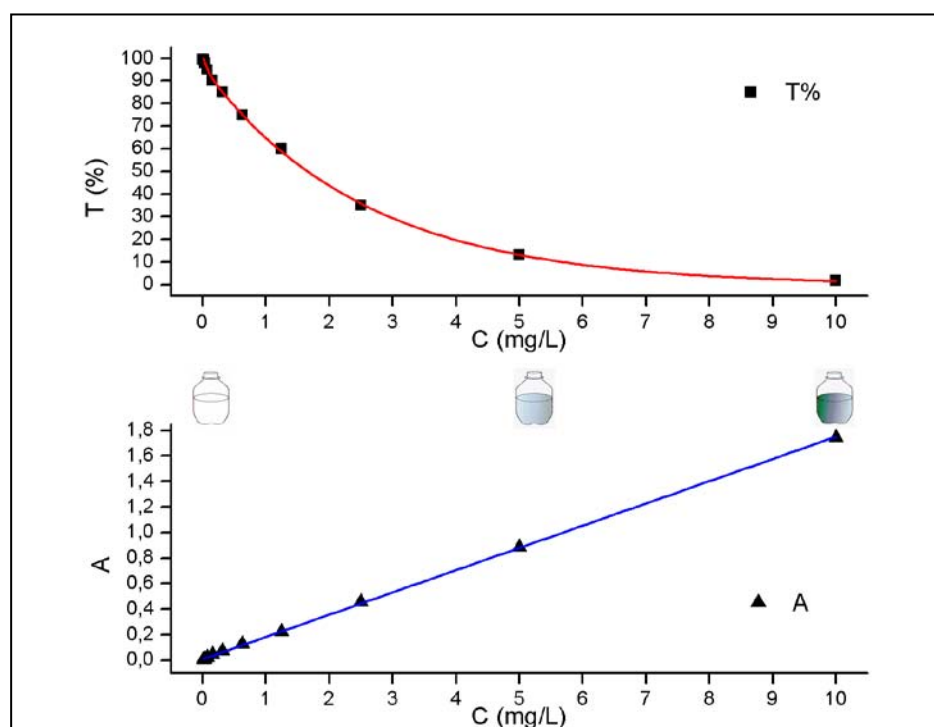


Fig. 2. Calibration curve, obtained using a set of samples with previously known concentration C

Results

The used starting materials (FA/SL) are very different with respect to their composition, size and shape of the particles [10, 11]. They contain significant amount of crystalline and amorphous aluminosilicates that could be utilized for zeolite production. Generally, the applied method of zeolitization is based on the alkali activated dissolution of aluminium and silicon containing phases in the FA/SL, and precipitation of zeolites from the respective gels. The main aluminium and/or silicon containing crystalline phases are found to be quartz (in "V" and "R" samples), that is the most difficult to be dissolved at room temperature, and mullite (in "V", "R" and "RE" samples). The most soluble and most reactive are those of the waste products which have a high content of amorphous aluminosilicates like the slag and to some extent the wastes which are mixtures from SL and FA ("RE").

Among the FA wastes, sample "V" has the smallest average particle size, and "RE" – the biggest one. More than half of all particles in each FA sample are of submicron size which enhances the dissolution of aluminium and silicon oxides needed for the zeolite synthesis. The specific surface of "R" sample is up to 2-3 times larger in comparison with the other waste samples. Accounting for the above mentioned differences, we can suppose that the waste products investigated should also possess different solubility in alkaline solutions.

The raw materials used are fine powder-like materials of complex composition. The particle morphology of these wastes is quite different as visible in Fig. 3.

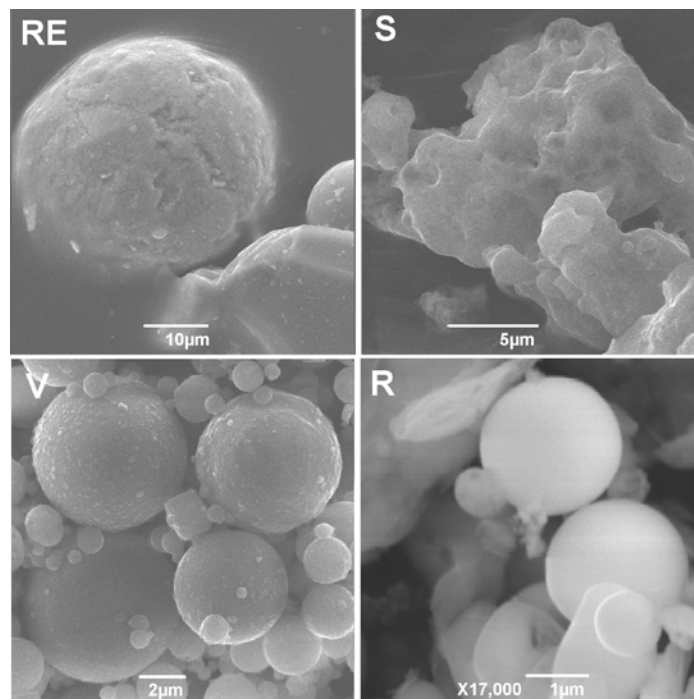


Fig. 3. SEM images of individual particles from four FA ("V", "R"), SL ("S") and FA+SL ("RE"). The white marker bar shows the sizes in micrometers

Using electron-microscopy we investigated also the morphology of the zeolite crystals grown on the surface of the FA and SL particles after one year of alkaline treatment at room temperature (Fig. 4). As seen, the zeolite crystals possess well developed octahedral shapes.

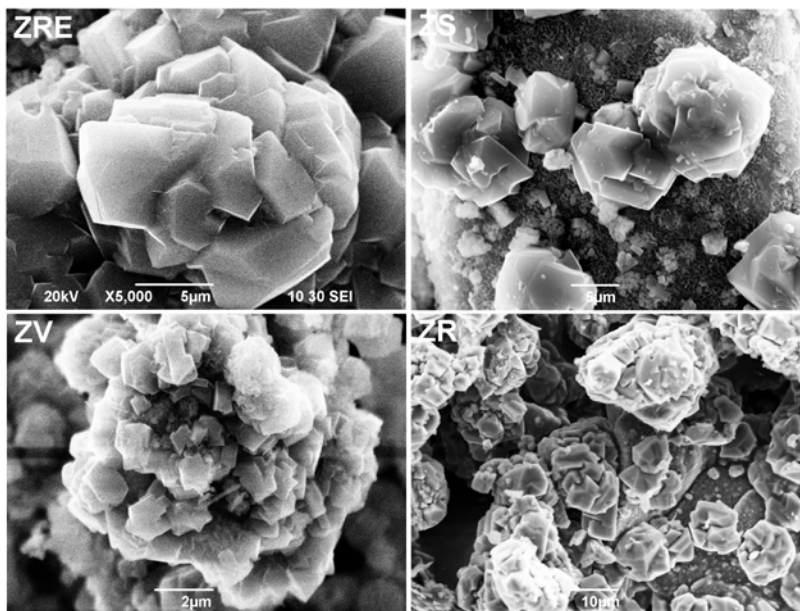


Fig. 4. Zeolite microcrystals grown on alkali activated particles of FA ("ZV", "ZR"), SL ("ZS") and FA+SL ("ZRE"). The white marker bar shows the sizes in micrometers

Our study showed that the most appropriate for the synthesis of zeolitic composites were the "RE" and "S" and to a certain extent the "R" wastes. The zeolite crystals formed after zeolitization of the first two wastes were characterized with almost perfectly grown faces and relatively big sizes as well as with a high degree of zeolitic conversion. For "RE" and "S" samples, both containing SL, this fact could be related to the better solubility in alkaline solutions due to the higher content of

amorphous phases in them. In contrast, smaller and not so well faceted zeolite crystals (“ZV”) were observed in respect to other FA sample (the “V” sample).

XRD investigations were used to determine the type of crystals, formed on the surface of initial FA or SL particles after alkaline activation. It was established that independently of the differences in the initial characteristics of FA and SL used, all newly grown crystals were of the group of faujasite (FAU), most probably zeolite X (see the Fig.5). Such type zeolite X was obtained at similar conditions of alkali activation of FA from another Bulgarian TPP [2]. As seen in Fig.5, the spectra of all zeolitized materials show a good enough coincidence in the peak positions with those of zeolite X. Moreover, since the diffractograms were recorded under the same conditions some conclusions could be made about the relative content of the zeolite X in the respective composites.

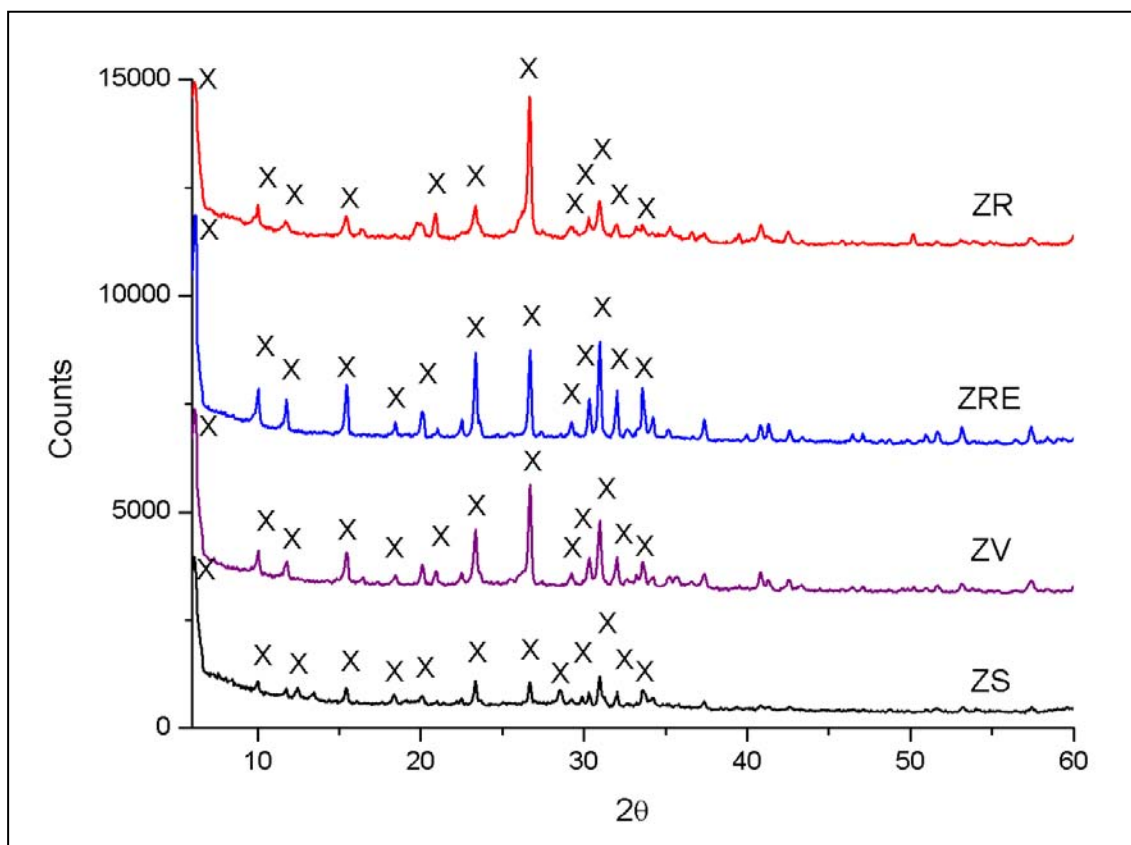


Fig. 5. X-ray diffraction (XRD) spectra of zeolitized FA/SL materials from TPP “V”, “R”, “RE” and “S” wastes evidencing the presence of zeolite FAU

As expected, due to the different mineral, chemical and morphological characteristics of the initial waste materials from TPP, the latter should exhibit different absorbance properties.

The absorption properties were investigated with respect to the initial “V”, “R”, “RE” and “S” wastes and to the zeolitized composites synthesized (“ZV”, “ZR”, “ZRE” and “ZS”). For this purpose, water solutions of the MG dye were used. All experiment lasted up to 48 hours. Fig.6 shows the transmittance (in %) of the water solutions of MG as a function of the time (in min) of absorption of the wastes and of the zeolitic composites investigated. The transmittance data were recalculated in terms of time dependent concentration C (mg l^{-1}) and were presented in Fig.7 for several times only, namely for 10 minutes, 1, 5 and 48 hours.

Among the initial untreated raw materials, the best results with respect to the kinetics and the degree of the MG removal was established for the FA sample “R”: The concentration of the MG solution was felt down to 0.9 mg l^{-1} after 48 h. The most unfavorable result was obtained for the SL sample “S” which reduced the MG concentration 3 times, only, i.e. down to 2.8 mg l^{-1} after 48 hours.

The studies shown in Figs.6 and 7 clearly demonstrate that the rate of MG removal by the raw FA/SL or their zeolitic composites is initially very high, but thereafter significantly decreases. This result could be explained by the fact that in the beginning all absorbent sites are vacant, and the solute concentration gradient is high, but afterwards they both decrease.

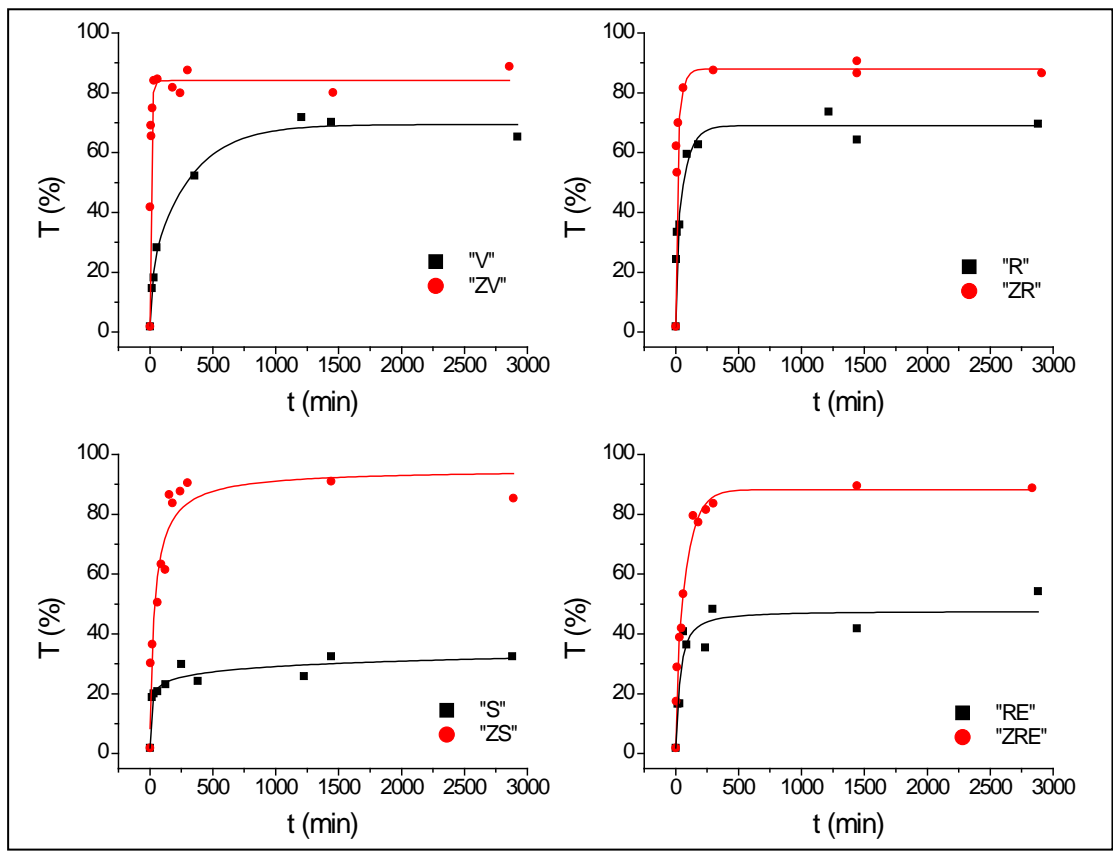


Fig. 6. Absorption kinetics of the initial wastes (black squares) and of the respective zeolitic composites (red circles) in water solutions of malachite green. Here, T (in %) and t (in minutes) are the transmittance of the solutions and time of the contact, respectively.

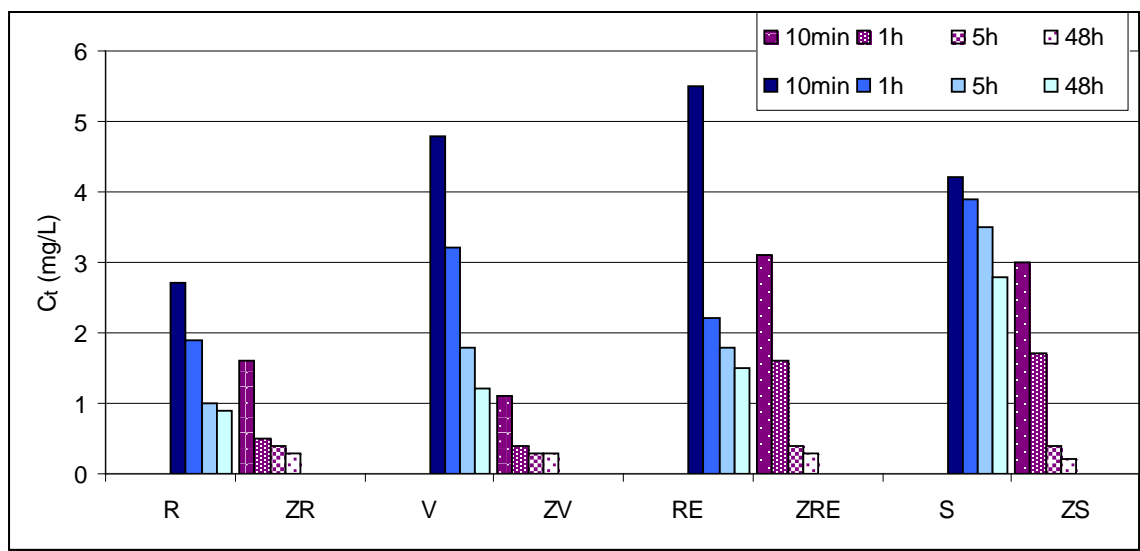


Fig. 7. The dye concentration C_t (mg l^{-1}) in water suspensions after time intervals t (from 10 min to 2 days) in contact with the raw materials ("R", "V", "RE", "S") - blue colored bars) or with the respective zeolitized products ("ZR", "ZV", "ZRE", "ZS") - purple colored bars)

The most probable reason for the similar absorption characteristics of all studied zeolitic composites is the presence of one and the same zeolite X (type FAU) grown on the surface of FA/SL particles, only. The dye concentration decreased with about 50% after the first 5-10 minutes of contact with the zeolitic composite, and 5 hours later it felt down to 95-98% for all samples studied. On the

bases of the results of the present study and of many other reviewed publications, it could be concluded that due to their unique properties, zeolites have a great potential as effective sorbent materials for a large number of water treatment applications, such as removal of different organic compounds and dyes.

Conclusion

A simple method was applied for the synthesis of zeolitized composites by using waste materials (fly ashes and/or slag) of several Bulgarian coal burning TPP, substantially different in their mineral, chemical and morphological characteristics. The method used is based on a low temperature alkaline treatment of the wastes. It turns out that independently from the wastes used the zeolitic composites synthesized contain one and the same zeolite, type FAU. The presence of this zeolite X is considered to be the main reason for the high and nearly equal absorption ability of the composite materials as demonstrated employing aqueous solutions of malachite green. These results convincingly evidences that the zeolitic composites synthesized by reprocessing of fly ashes and slag from thermal power plants, are not only extremely suitable for almost fully purifying of waters from some dyes, but also have a huge potential as a cost-effective and environmental-friendly solution that can improve the efficiency of waste water treatment.

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