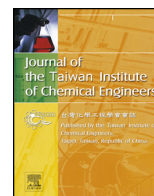




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## Three different clay-supported nanoscale zero-valent iron materials for industrial azo dye degradation: A comparative study

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### ABSTRACT

For evaluation of oxidative degradation of industrial azo dye Rosso Zetanyl B-NG (RZ B-NG), three clay supported nanoscale zero-valent iron materials were synthesized: bentonite, kaolin and native clay-supported nanoscale zero-valent iron (B-nZVI, K-nZVI and NC-nZVI). All clays used as a support material not only dispersed and stabilized nanoscale zero valent iron (nZVI) but also improved the adsorption and degradation of dye as they consequently improved heterogeneous Fenton oxidation. Under the optimal conditions, for the used nanomaterial concentrations of 112, 168 and 224 mg/L for B-nZVI, NC-nZVI and K-nZVI, the decolourization efficiencies achieved were 92.7, 92.1 and 91.6% and appropriate TOC removals were 57.8, 57.2 and 50.7% in the same order. The best catalytic performance was exhibited when B-nZVI was used. These results correlate with the specific surface area and mesoporous structure of the synthesized materials. They contributed to Fenton reaction enhancement by generating effective reaction sites for potential adsorption and subsequent oxidative degradation of the azo dye. Based on these results, all clay supported nanomaterials have proved to be superior heterogeneous Fenton-like catalysts for removing azo dyes from wastewater.

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## 1. Introduction

Dyes are important sources of water pollution and their degradation products may be carcinogens and toxic to mammals. It is estimated that about 15% of the total production of dyes are lost and discharged in the effluent during dye production and dying process. Azo dyes make up the majority (60–70%) of the dyes applied in textile processing and are considered to be recalcitrant, non-biodegradable and persistent [1,2]. Various treatment methods,

such as coagulation and flocculation, adsorption and ultrafiltration have been investigated to remove azo dyes from the wastewater. These high cost processes do not destroy dye molecules but only transfer them from one phase to another [3]. The second most extensively used way to treat dye wastewaters is biological. This method is a relatively inexpensive way to remove dyes and accounts for "green technology". The main disadvantage of the biological method is related to its long treatment period with a rather limited success as they cannot achieve "destructive" decolourization due to the fact that textile dyes are intentionally designed to resist biological, photolytic and chemical degradation [4,5]. Advanced oxidation processes (AOPs) are the most attractive technologies for dye wastewater treatment, able to oxidize quickly and non-selectively a broad range of pollutants [6–8]. However, possible by-product formation (mostly during ozonation and photocatalytic reactions) and sludge production are still a top priority concern as they represent a source of secondary pollution. A brief summary of AOPs and biological methods for treating azo dyes is presented in

**Abbreviations:** RZ B-NG, Rosso Zetanyl B-NG; B, bentonite; K, kaolin; NC, native clay; B-nZVI, bentonite-supported nanoscale zero-valent iron; NC, native clay-supported nanoscale zero-valent iron; K-nZVI, kaolin-supported nanoscale zero-valent iron; AFP, advanced Fenton process; TEM, transmission electron microscopy; SEM, scanning electron microscope.

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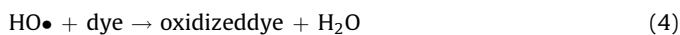
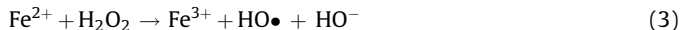
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Table A.1, highlighting the main advantages and disadvantages of each process [3,4,9–12].

Fenton process is particularly attractive and effective to degrade a wide range of azo dyes. It is also relatively cheap and easy to perform compared to other AOPs processes. On the other hand, classical Fenton process implies continuous loss of iron ions due to formation of solid sludge and also a heavy load of counter ions. This can be avoided by employing heterogeneous Fenton processes. Compared to homogeneous Fenton process, heterogeneous Fenton process has several advantages: pH range is wider, there is no sludge formation, catalyst loss is limited as active sites take place on surface of solid porous materials, and catalyst recycling is rather easy [12,13].

A great deal of interest has developed in the degradation of azo dyes by zero-valent iron (nZVI) particles, as they are inexpensive, environmentally friendly, easy to operate, and low iron concentration in effluent results in no further treatment demand [14,15]. In most studies the sole nZVI or supported nZVI was used for the effluent treatment, and the main mechanism was the reductive degradation of dye molecule (Eq. (1)). More recently nZVI is widely applied for wastewater treatment and organic compounds degradation in Fenton system [16]. In acidic conditions, the surface of the nZVI corrodes and generates in situ ferrous ions, which leads to Fenton reactions in the presence of hydrogen peroxide (Eqs. (2)–(4)). The nZVI surface can then reduce the ferric ions down to ferrous ions, and faster recycling of ferric iron at the iron surface occurs through Eq. (5) [1]. This process is named the advanced Fenton process (AFP) [17].

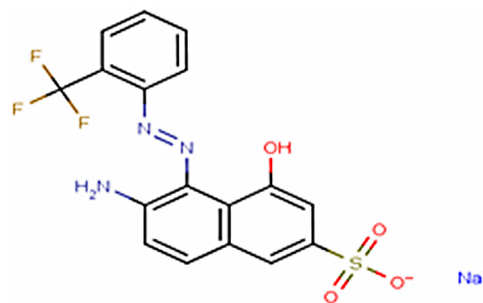


nZVI has the advantage that the small particle size results in a large specific surface area and great intrinsic reactivity of surface sites. However, nZVI nanoparticles tend to either react with surrounding media or agglomerate, resulting in significant loss of reactivity (Table A.1). To prevent particle aggregation, a wide variety of stabilizers have been proposed to modify nZVI particle surface characteristics [18–20]. More recently, kaolin-supported nZVI [21] and bentonite-supported nZVI [22] have been used to remove different dyes in aqueous solutions and to reduce the extent of nZVI aggregation. These indications suggest that implementing stabilized nZVI particles may represent an effective method for in situ remediation of industrial effluents.

In this study two commercial clays, kaolin and bentonite, as well as native clay, from the Potisje, Kanjiza locality (Vojvodina), were used for nZVI supporting and stabilization in order to treat wastewater containing azo dye RZ B-NG. This dye was chosen for the study as it is an extensively used dye in the textile industry in Serbia. Large amounts of textile wastewaters containing this dye are discharged into the environment without any kind of

**Table 1**  
Characteristic of Rosso Zetanyl B-NG.

Dye	Rosso Zetanyl B-NG
Formula	C <sub>17</sub> H <sub>11</sub> F <sub>3</sub> N <sub>3</sub> NaO <sub>4</sub> S
Class	Azo (-N=N-)
λ <sub>max</sub> (nm)	493.3
M <sub>w</sub> (g/mol)	433.34



**Fig. 1.** Chemical structure of Rosso Zetanyl B-NG.

treatment, so the investigation for the optimal treatment technique is necessary. In addition, literature data on RZ B-NG treatment are rather scarce [23].

The present study focuses on the following objectives: (1) characterization of synthesized materials (B-nZVI, NC-nZVI and K-nZVI,); (2) evaluation of two different mechanism of dye degradation with applied synthesized materials: reductive degradation and heterogeneous Fenton oxidation; (3) optimization of parameters in heterogeneous Fenton like process for RZ B-NG degradation; (4) correlation of dye degradation results and structural properties of synthesized materials.

## 2. Methods

### 2.1. Materials and chemicals

Industrial azo dye, Rosso Zetanyl B-NG, was obtained from textile factory Italtex-Intimo (Novo Milosevo, Vojvodina), and was used directly, without further purification. All solutions were prepared with deionized water. The characteristics and chemical structure of Rosso Zetanyl B-NG are shown in Table 1 and Fig. 1, respectively. All chemicals used were of analytical grade: FeCl<sub>3</sub> × 6H<sub>2</sub>O (Centrohem, Serbia, p.a.), NaBH<sub>4</sub> (Merck, >96%), CH<sub>3</sub>CH<sub>2</sub>OH (Sigma Aldrich, ≥99.8%), H<sub>2</sub>O<sub>2</sub> (NRK engineering, Serbia, 30%), H<sub>2</sub>SO<sub>4</sub> (J.T. Baker, >96%) and NaOH (POCH, >98.8%).

Kaolin and bentonite were obtained commercially. The bentonite was composed mainly of montmorillonite (more than 90%). Native clay was sampled from the clay pit in locality of Potisje, Kanjiza (Vojvodina) which represents loess-alluvial-swamp systems, and it belongs to brick clays. The chemical compositions of the used clays are presented in Table 2.

### 2.2. Preparation and characterization of clay supported nZVI particles

nZVI, B-nZVI, NC-nZVI and K-nZVI were prepared using conventional liquid-phase method by the reduction of ferric iron by borohydride. For clay-supported nanomaterials reduction was performed in the presence of kaolin, bentonite and native clay.

**Table 2**  
Chemical composition of clays used for supporting nZVI.

Compound	wt(%)		
	Kaolin	Bentonite	Native clay
SiO <sub>2</sub>	45.9	58.9	55.7
Al <sub>2</sub> O <sub>3</sub>	37.2	22.7	14.9
Fe <sub>2</sub> O <sub>3</sub>	3.34	4.83	5.78
MgO	1.40	1.40	2.86
CaO	0.250	1.85	5.90
K <sub>2</sub> O	0.140	0.240	0.830
Na <sub>2</sub> O	0.100	0.120	/
TiO <sub>2</sub>	/	/	0.800
Loss of ignition	11.7	9.96	14.03

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