

**Degradation Reactive Black 5 dye from aqueous solutions using ozonation with pumices and pumices modified by nanoscale zero valent iron (nZVI)**

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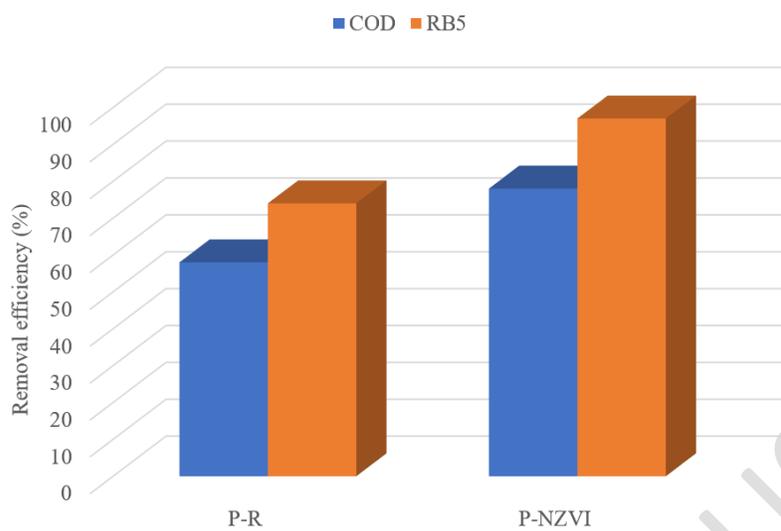
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## Graphical abstract

Removal efficiency of COD and RB5 by ozonation with raw pumice and pumice-nZVI



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**ABSTRACT:** Reactive Black 5 (RB5) dyes are a dye widely used in textile industries. The nanocatalytic ozonation of RB5 solution in the presence of pumice modified with nanoscale zero valent iron (nZVI) catalysts and pumice raw investigated in a laboratory scale batch reactor. The effects of solution pH (3-11), reaction time, pumice dosage (10, 15 and 20 g/L) and COD removal were evaluated. Natural mineral raw pumice and pumice-nZVI was used directly in nanocatalytic ozonation of dye of RB5 solution. Compared with raw pumice, pumice-nZVI into the ozonation reactor greatly accelerated the rate of RB5 degradation. The results indicate that with increasing (pH, and pumice dosage) increased rate RB5 degradation. Molecular ozone direct oxidation mechanism was proved in nanocatalytic ozonation with pumice, and hydroxyl radical mechanism was demonstrated to play a main role in nanocatalytic ozonation with nZVI.

**Keywords:** zonation, pumice, RB5, degradation, nanoscale zero valent iron (nZVI)

## 1. Introduction

Organic dyes are among the most important groups of wastewater contaminant, introduced into it through various industries including textile industry (Li *et al.*, 2004, Aguedach *et al.*, 2005). Today, around 100,000 types of dye (Ehrampoosh *et al.*, 2011), with over  $7 \times 10^5$  tons are produced for different uses including in textile, paper and leather production (Robinson *et al.*, 2001, Pearce *et al.*, 2003, Mahmoodi *et al.*, 2006). Over 280,000 tons of the total global production of dyes annually enters directly into a wastewater (Maas and Chaudhari 2005, Somasiri *et al.*, 2008, Rahmani *et al.*, 2010). Among the dyes, reactive dyes have more applications because of bright dyes, excellent dyefastness and ease of application (Elwakeel 2009). Various physical, chemical and biological processes have been studied in the removal of dyes from wastewater (Hassaan *et al.*, 2020, Khashij *et al.*, 2020, Munagapati *et al.*, 2020, Parsaeian *et al.*, 2020). Advanced oxidation processes (AOPs) are alternative methods for the elimination of types of refractory compounds, principally due to the formation of hydroxyl radicals (HO•). During advanced oxidation processes (AOPs), additional reactions occur in the presence of light that produce hydroxyl radicals or increase the production rate of hydroxyl radicals that are capable of rapidly oxidizing organic contaminants and converting them into harmless end-products, such as H<sub>2</sub>O and CO<sub>2</sub>, and inorganic ions from atoms, which have been successfully used for the treatment of wastewaters from petrochemical, textile, and pharmaceutical industries (Dimoglo *et al.*, 2004, Tekin *et al.*, 2006, Chakinala *et al.*, 2009, Nachiappan and Muthukumar 2010, Oller *et al.*, 2011, Farzadkia *et al.*, 2014, Wang *et al.*, 2014, Gholami *et al.*, 2016). Previous studies have documented the removal/degradation of benzotriazole with advanced techniques in recent years (e.g., ferrate (VI) oxidation, ultrasonic,

adsorption, photochemical degradation)(Hem *et al.*, 2003, Xu *et al.*, 2010, Zúñiga-Benítez *et al.*, 2014, Bahnmüller *et al.*, 2015, Yazdanbakhsh *et al.*, 2016).

Pumice is a volcanic rock that has a porous structure and large surface area (Yavuz *et al.*, 2008). The pumice crystal structure creates open channels that make it easy for water and ions to pass through (Catalfamo *et al.*, 2006). The easy processability of pumice as well as its use as a suitable and cost-effective adsorbent is of interest (Moraci and Calabrò 2010).

Nanocatalytic ozonation is a promising technology for the effective removal of water and wastewater contaminants that are refractory to conventional oxidation treatments. The main advantages of the catalytic processes with respect to traditional non-catalytic ozonation are better ozone utilization, increased contaminant removal efficiency and greater degree of organic matter mineralization (Legube and Leitner 1999).

Among the various types of nanoparticles, Nanoscale zero-valent iron (nZVI) with small size, large surface area and high reactivity, is a good choice for use in processes to remove contaminants in water and wastewater (Fazlzadeh *et al.*, 2016). The use of pumice, bentonite and zeolites along with iron nanoparticles increases its dispersibility (Liu *et al.*, 2015).

The Nanocatalytic ozonation is an advanced oxidation process (AOP) that underlines generation of highly reactive hydroxyl radicals ( $\cdot\text{OH}$ ) from a mixture of  $\text{Fe}^{2+}$  (ferrous ions) and  $\text{O}_3$ . In Nanocatalytic ozonation (based using nano zero valent iron) and process (nZVI/  $\text{O}_3$ ), ferrous and then ferric are formed. During a regular cycle, these ions increase the efficiency of the process (Weng *et al.*, 2013, Yazdanbakhsh *et al.*, 2016).

This study presents experimental results on RB5 degradation by Nanocatalytic ozonation using raw and modified pumice. This is a natural mineral catalyst; Pumice has supplied an economical and feasible choice for nanocatalytic ozonation of RB5 in water.

## 2. Materials and methods

### 2.1. Materials

Chemicals used in the synthesis of nZVI, pumice, chloridric acid, sodium hydroxide, RB5 dye, ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ), sodium borohydrate ( $\text{NaBH}_4$ ), ethanol, and starch were prepared from CMC (Germany). All laboratory preparations of the study were carried out according to the regulations set in the Standard Methods. Spectrophotometer was read using a method based on the determination of the absorption of each of these concentrations of Reactive Black 5 dye in the optimum wavelength (599nm) Fig 1.

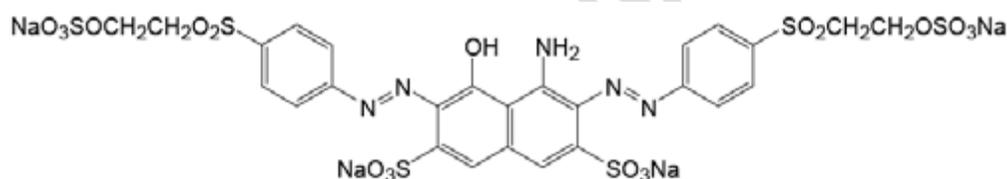
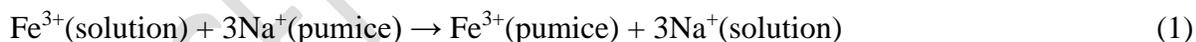


Figure 1. The chemical structure of the RB5

All other chemicals required in the experiments were analytical grade reagents that were used without further purification (Merck). A stock solution of RB5 (1 g/L) was prepared in distilled water and in this study, a concentration of 50 mg / L was used for the experiments. Ozone was generated from pure oxygen by an ARDA ozone generator (Model AEGCOG-5S), and was fed continuously to the ozonation reactor at 0.61 mg/ L min. The mass of ozone produced was measured by iodometric titration methods. The aqueous ozone concentration was determined by spectrophotometry using the indigo method (Clesceri *et al.*, 1996). The COD was measured by Open reflex methods(Gholami *et al.*, 2016).

## 2.2. Preparation and characterization of catalyst

The pumice used in this investigation was a natural pumice that was obtained from the Miane region (North West of Iran). Chemical composition of the pumice determined by an Oxford (ED2000) XRF equipments. The surface morphology and shape of samples were taken by a scanning electron microscope (SEM) system (model: XL-30, Philips). Pumice-supported nanoscale zero-valent iron was prepared using conventional liquid-phase methods via the reduction of ferric ion ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ ) by borohydride ( $\text{NaBH}_4$ ) and pumice was used as a support material (Shi *et al.*, 2011). For preparation of surface-tailored pumice with  $\text{Fe}_2(\text{SO}_4)_3$ , 50 g pumice was added into a 1000 ml of 0.075 M ferric sulfate solution. The mixtures were intermittently agitated with a shaker at 200 RPM. After 48 h the pumices were washed several times using demineralized water to decrease the electrical conductivity. Finally, the modified pumice was dried in the ambient air for 48 h (Ahmadi *et al.*, 2017). After converting the pumice to its cationic form with a Sodium Chloride solution and adding the cationic pumice into the metal salt solution, the  $\text{Na}^+$  bound in the structure of the pumice was exchanged with  $\text{Fe}^{3+}$  from aqueous solution Eq. 1:



1 g of the pumice with 30 mL of  $\text{Fe}_2(\text{SO}_4)_3$  solution (1M) in the presence of nitrogen gas were mixed for 3 hours. Then this solution was diluted in 5-fold with ethanol and water solution (1: 1). In the next step, 100 mL of  $\text{NaBH}_4$  was added to this mixture in the 25 °C and placed on the magnetic stirrer for 30 minutes. After this time period, according to the Eq. 2 pumice was coated. The nZVI was separated and then washed three times with acetone at 65 °C using injecting

nitrogen gas stored in a desiccator(Ahmadi *et al.*, 2017). The synthesized materials were separated from the liquid solution via the magnet and dried at 65 °C overnight.



For determining  $\text{pH}_{\text{ZPC}}$  pumice raw and modified, the 0.01 molar solution of Sodium Chloride as an electrolyte and Sodium hydroxide and Hydrochloric Acid with the purity of 0.1 molars were used as a controlling factor of pH. Pore 30 ml of the electrolyte solution in 6 erlene of 50ml and adjusts its pH to a range of 2 to 12 using acids and alkaline. Then add 0.5 g pumice to each airline. Erlene was put on the shakers in a speed of 120 rounds per minute for 48 h and their final pH level was read using pH-meter after infiltration. The  $\text{pH}_{\text{ZPC}}$  point of pumice was determined using the graph of the primary levels of pH. In this graph, drawing a line with a 45-degrees angle with the graph, those points with the same primary and final values of pH were taken as the  $\text{pH}_{\text{ZPC}}$  (Dastgheib *et al.*, 2004).

### 3. Results and discussion

#### 3.1. Structural Analysis

The crystal structure of the pumice, X- ray fluorescence method (XRF) was used. The obtained results from chemical analysis of the sample are shown in Table 1. The results of the structural characterization tests showed that this mineral sample was mostly composed of pumice (over 65%) and some impurities such as clays, feldspar and quartz. The SEM image of the raw pumice and pumice modified with nanoscale zero valent iron (nZVI) sample is illustrated in Figure 2.

Table 1. XRF results of chemical compositions for pumice

LOI	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Total
8.01	1.87	0.866	14.5	66.219	0.14	0.037	2.7	2.5	0.42	2.61	99.952

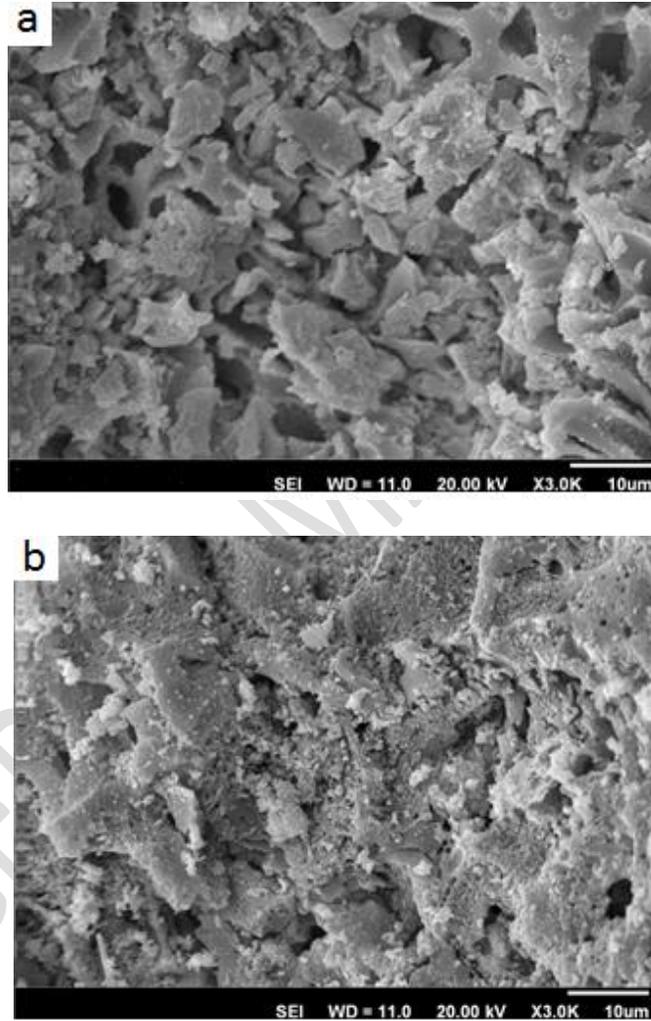


Figure 2. SEM of raw pumice (a) and pumice-nZVI (b)

### 3.2. Effect of the solution pH

The results of the impact of pH (3- 11) on the ozonation processes with raw pumice and pumice-nZVI have been given in Fig 3. To determine the effect of pH, specify the optimal pH, and understand the effect of RHS in removal efficiency, in this study RB5 dye solution with a concentration of 50 mg/L was prepared and the removal efficiency was investigated. As seen in the figure, in the process of ozonation, with minutes of ozonation. The results of this step indicate that in the process of nanocatalytic ozonation using raw pumice, with a rise in pH, the performance rate of RB5 degradation has increased from 37.1 percent to 82 percent (pH 2 to pH 9). On the other hand, in the process of nanocatalytic ozonation using modified pumice after 60 minutes of ozonation, the performance rate of RB5 degradation has increased from 51.2 percent to 99.8 percent (pH 2 to pH 9). As results indicate, in all pHs, the process of nanocatalytic ozonation has performed better compared to conventional processes of ozonation and with a rise in pH, the process of dye degradation increase.

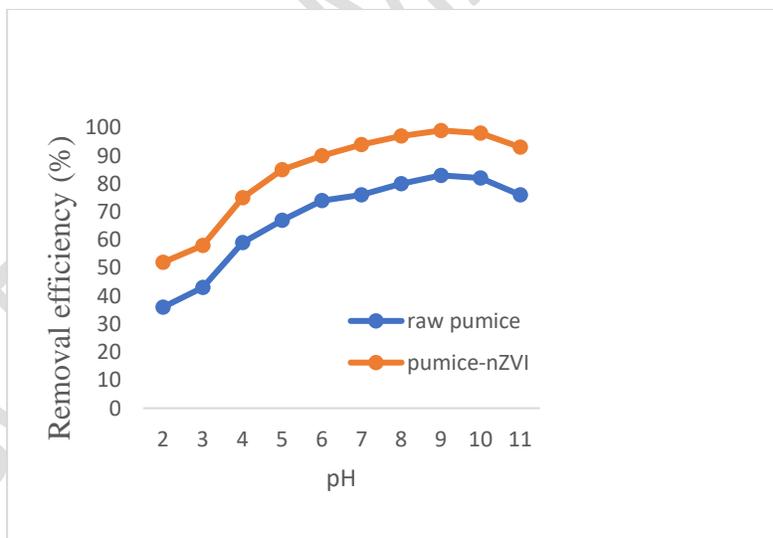


Figure 3. Effect of pH on removal efficiency of RB5 for ozonation raw pumice and pumice-nZVI

On the other hand, it was qualified to the dye structure as well as pumice structure and its  $pH_{ZPC}$ . As noted, before,  $pH_{ZPC}$  of unprocessed and that of modified pumice will equal 7.3 and 7.11

respectively. Analyses indicate that in pHs upper than  $pH_{ZPC}$ , active groups decay in the pumice surface and thus increase in the nucleophilic character of these groups. Under this condition, the organic groups decomposed in the pumice surface increase the quickness of ozone reaction. Electron donating in these acidic acting groups transfers electrons to ozone and increase the progress in the speed of reaction and radicalization of ozone in the pumice surface. Finally, this electron transferring makes ozonized anions and contributes to radical cycle (Valdés *et al.*, 2009). On the other hand, increase in pH triggers an increase in  $OH^-$  ions. This ion is among the factors, which with an increase in pH; act as initiators of the ozone decomposition reaction and precipitating the decomposition process. Chain reactions occurring in the ozone decomposition processes have been suggested as follows (Kasprzyk-Hordern *et al.*, 2003). However, with the reduction of pH of the solution the number of sites with positive charge on the surface of nanoparticles and the adsorbent surface increases and an electrostatic attraction develops between the site with a positive charge on the surface of nanoparticles and the adsorbent and the molecules of reactive red 198 dye with a negative charge. With further absorption of dye molecules, nanocatalytic removal in turn increases (Alijani *et al.*, 2013). Some works of literature attribute the dye degradation in the acidic conditions of the active non-hydroxyl radical in the catalyzer surface (Mortazavi *et al.*, 2010). It seems that as the pH increases (9 to 11) the removal efficiency is reduced, that due to ionization of functional groups such as hydroxyl that it can reduce the amount of hydrogen radicals, negative charge is developed across the surface of nanoparticles whereby an electrostatic repulsion is developed between the surface of the nanoparticles with negative charge and the molecules of RB5 dye with a negative charge (Ahmadi *et al.*, 2017).

### 3.3. The effect of dose of the materials

One of the most important issues that should be taken into consideration in studying removal using catalysts is determining the suitable dose, which was another parameter that was investigated. Fig. 4 indicates the effect of the initial dose of the materials on the removal efficiency of RB5 dye under pH=8, contact time of 60 min with dye's initial concentration of 50 mg/L. As indicated in the figure, in the contact time of 60 minutes with an increase in the catalyzer dose from 10 to 20 g, the performance rate of RB5 dye degradation will increase. For example, with RB5 dye, an increase from 10 to 20 g of raw pumice, the performance rate of degradation increased from 68 percent to 76 percent. Also, with an increase in processed pumice-nZVI dose from 10 to 20 g, the performance rate of RB5 degradation increased from 94 percent to 98.

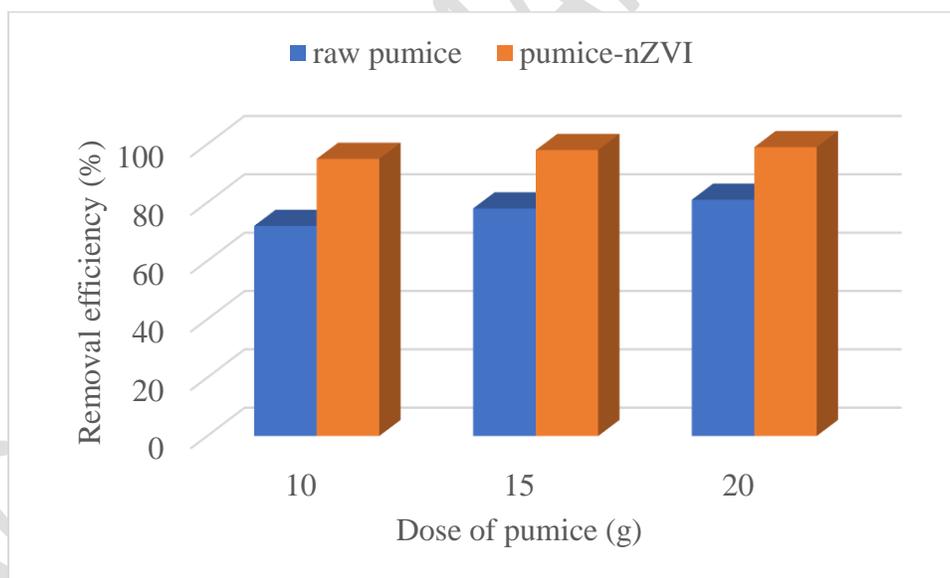


Fig 4: effect of dose of the materials on removal efficiency RB5 for ozonation raw pumice and pumice-nZVI

This increase in dye decomposition in the nanocatalytic ozonation process has occurred as the result of an increase in the ozone decomposition in the pumice surface, which adds to the concentration of the radicals in the surface and in the liquid volume. Adding the catalyzer dose will increase the surface area and active sites of ozone absorption in the surface. Increased contact area between the deposited adsorbent and the contaminant, enumeration of active sites, and production of free electrons in the conductive band are among the reasons of elevation of removal efficiency with the increase in the dose of the materials (Samarghandi *et al.*, 2011). In this regard, Ghaneian *et al.* along with Samarghandi *et al.* have reported an increase in the removal efficiency with the growth of a dose of the materials (Samarghandi *et al.*, 2011). This increase also adds to the surface reactions and radical production in the nanocatalytic ozonation process. Many writers have reported the increase in performance rate of ozonation using catalysis with metal bases (Valdés *et al.*, 2009). On the other hand, In catalyst coating nZVI behavior of ferrous ion is more important at low ferrous ion concentration and becomes less important as the concentration of ferrous ion increases with a ratio to oxidant concentration, because not all ferrous ions can be converted into ferryl ions and adequate ferrous ions will be available for the activation of oxidants at high ferrous ion concentration. The effect of initial nZVI concentration is also important for the performance of the system. (Ahmadi *et al.*, 2017).

#### *3.4. Effect of the nanocatalytic ozonation on the degradation of COD*

Results show the amount of the COD degradation of RB5 in nanocatalytic ozonation with pumice-nZVI and raw pumice are that 81 and 54 percent, respectively. As indicated by the results in Fig 5, nanocatalytic ozonation with modified pumice-nZVI will decompose the dye

further and will make it more mineralized, whereas ozonation with raw pumice will have less effect on COD degradation.

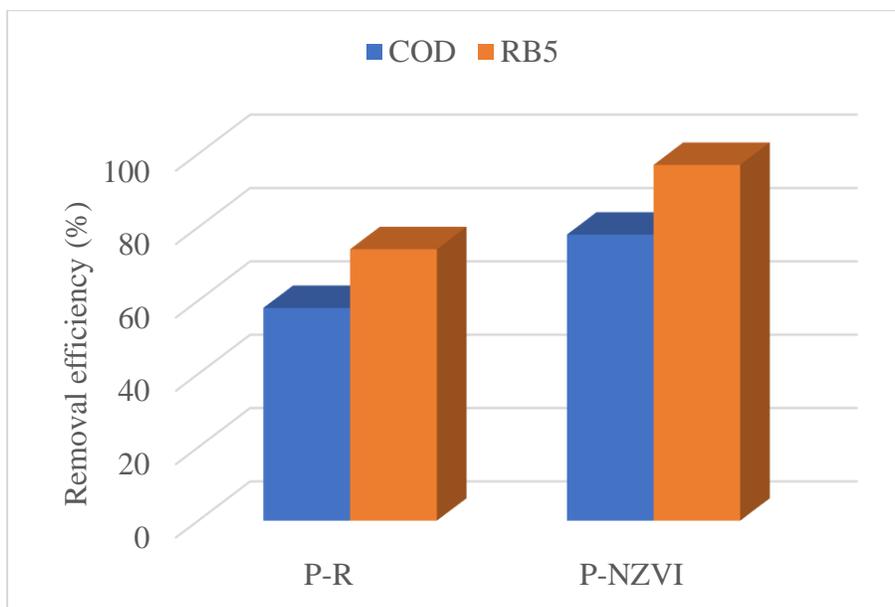


Fig 5. Removal efficiency of COD and RB5 by ozonation with raw pumice and pumice-nZVI

According to the results, it can be said that the effect of the presence of nano catalyst with ozonation results in a more complete analysis of the organic components than the method raw pumice. As COD is an indicator of decomposition of organic components, the catalytic ozonation will act to complete decomposition of a larger part of the dye than partial decomposition, while common oxidizers such as ozone will act to partial decomposition and in some cases, to add COD. The mechanism through which the  $O_3/nZVI$  system produces oxidants involves the two-electron oxidation of nZVI followed by the Fenton-like reaction. Initially, nano zero valent iron is oxidized through a two-electron transfer from the particle surface to  $O_3$  (Khataee *et al.*, 2010). Qu and Zheng examined the heterogeneous nanocatalytic ozonation with active carbon chains in phenol degradation from the wastewater. They reported that use of a level of 2 g active carbon chains solved in 250 ml of water containing 100 mg. phenols, the

nanocatalytic process can delete 99 percent of phenol content and 95 percent of chemical oxygen demand (COD) in the course of 30 minutes(Qu *et al.*, 2007).

#### **4. Conclusions**

The results indicate that with increasing (pH, and pumice dosage) increased rate RB5 degradation. Molecular ozone direct oxidation mechanism was proved in nanocatalytic ozonation with pumice, and hydroxyl radical mechanism was demonstrated to play a main role in nanocatalytic ozonation with nZVI. As a natural mineral catalyst, pumice has supplied an economical and feasible choice for catalytic ozonation of RB5 in industrial wastewater.

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