Removal of Basic Red 9 (BR9) in Aqueous Solution by Using Silica with Nano-Magnetite by Enzymatic with Fenton Process

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ABSTRACT: Magnetite ($FeO.Fe_2O_3$) nanoparticles immobilized on silica and modified by treatment apolaccase were used to decolorize the industrial wastewater from basic red 9 (BR9 by way of Fenton and Fenton-like processes. The surface changes to the silica were determined by scanning electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction and energy-dispersive X-ray spectroscopy. The decolorization system's optimum parameters, $3 \leq pH \leq 9$; $20°C \leq Temp. \leq 80°C$; initial BR9 concentration (0-50 ppm), and adsorbent concentrations (0-0.2 g/50 mL) were studied to understand their effects on BR9 removal. The optimal parameters values were: pH: 6.0, temperature, 40-60°C; contact time, 30 min; initial BR9 concentration, 50 ppm; and adsorbent concentration: 0.1 g. Under these conditions immobilized magnetite nanoparticles and their apolaccase modified counterparts showed decolorization efficiencies of 81.01% and 88.6%, respectively, for the removal of BR9 from industrial waste water by way of Fenton and Fenton-like processes. These experiments also showed the adsorbent to be re-useable, cheap, biocompatible, easy to prepare, nontoxic (nanomagnetite particles, H_2O_2 and silica fume) and capable of generating Fenton reaction conditions with or without additional treatment with apolaccase. The adsorbent was shown to be useful in the decolorization of toxic dyes from industrial wastewater.

Key word: Nano, Fenton, Apolaccase, Basic red 9 (BR9), Decolorization, Wastewater, Nano magnetite, Silica, Immobilization

INTRODUCTION

Basic red 9 monohydrochloride (BR9) is a component of magenta dye (C.I. 42510). Basic red 9 monohydrochloride is used as a biological dye and as a dye for textiles (silks and acrylics), leather, fur, paper, carbon paper, plas-tics, glass, waxes, polishes, soaps, cosmetics, drugs, toilet sanitary preparations, automobile antifreeze solutions, anodized aluminum, high-speed photoduplicating inks, photo-imaging systems, and ink-jet computer printers (Martins *et al.,* 2006).

Waste dyes were very dangerous for ecology, health and environmental to be caused cancer. Todays, the decolorization of dyes from waste water is most important and attractive because they can be hazardous effects (Robinson *et al.,* 2001a; Robinson *et al.,* 2001b; Ventura-Camargo and Marin-Morales 2013). In the textile industry the process of dyeing results in the production of large amounts of wastewater exhibiting intense coloration that has to be eliminated before release into natural water streams. Aspecial problem is encountered in the application of synthetic dyes which have a complex aromatic molecular structure and are designed to be resistant to physical, chemical and microbial fading (Correia *et al.,* 1994; Wesenberg *et al.,* 2003). Synthetic dyes are not uniformly susceptible to biodegradation in conventional biological waste water treatment resistance to microbial azo dyes,

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which are used extensively in many industries, are the largest class with a wide variety of colors and structures. The common wastewater treatment using physical and chemical methods used for removal of dyes, that is, adsorption, chemical transformation, incineration, photocatalys is or ozonation are effective but rather costly (De Moraes *et al.,* 2000). Therefore, much attention has been paid to the development of water treatment techniques that lead to complete destruction of the dye molecules. Because of the high oxidative power of the hydroxyl radical numerous processes based on the group of these types, have been categorized under the name of progressive oxidation processes (AOPs). AOPs have been engaged for the reduction of harmless/refractory organic, as well as inorganic, contaminants found in water or wastewater. The most often used AOPs contain heterogeneous photo catalytic oxidation(Arslan and Balcioglu 2001; Hoffman *et al.,* 1995; Ollis 1970; Perez *et al.,* 1997; Lizama *et al.,* 2001; So *et al.,* 2002), ozonation joint with hydrogen peroxide (H_2O_2), ultraviolet (UV) light, or both H_2O_2/UV, Fenton and photo-Fenton reagents(Alaton *et al.,* 2002; Arslan and Balcioglu 2001; Neamtu *et al.,* 2002; Solmaz *et al.,* 2006).
Fenton technology is extensively studied and described as a remarkable other for the management of industrial wastewater having non-biodegradable organic contaminants (Deng *et al.,* 2008).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^* + OH^*$$

Heterogeneous Fenton and Fenton like processes have just received abundant consideration. In heterogeneous Fenton reaction, iron salts, were adsorbed on the surface of supported catalysts, and in an appropriate aqueous intermediate; the reduction-oxidation reactions between Fe(II)/Fe(III) take place in presence of hydrogen peroxide which promote the formation of reactive components such as (•OH) and hydroperoxyl (•OOH) radicals. The radicals produced by the breakdown of hydrogen peroxide can oxidize organic compounds. The area of active iron ions present at both the reagent area and in the loose liquid stage. Consequently, the Fe (III)/Fe(II) complex made on the area of support can reply with H_2O_2 thus permitting iron ions to join in the Fenton catalytic cycle (Gurtekin and Sekerdag 2008; Neyes and Baeyens 2003; Sum *et al.,* 2004; Sun *et al.,* 2006).
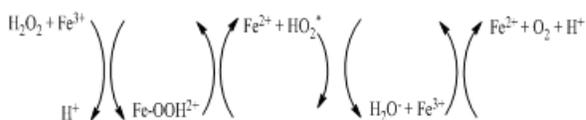
The Fenton reaction, which is the decomposition of hydrogen peroxide catalyzed by a ferrous ion and leads to oxidation of Fe^{2+} to Fe^{3+}, produces an OH radical in acidic medium. Then, the photo-reduction of Fe^{3+} by light also produces an OH radical, which enables to continue the photo-Fenton catalytic cycle process, in which iron is cycled between the +2 and +3 oxidation states. Iron catalyzes the formation of OH radicals in the photo-Fenton process. Therefore, the photo-Fenton oxidation process is controlled by the amounts of iron and hydrogen peroxide in the solution (Tokumura *et al.,* 2013).

Laccase (benzenediol: oxygen oxidoreductase, EC 1.10.3.2) is a fragment of wide group of enzymes called polyphenol oxidases having copper atoms in the catalytic area and are regularly named multicopper oxidases (Alcalde 2007). Laccase refereed catalysis arises with reduction of oxygen to water accompanied by the oxidation of substrates such as polyphenols, methoxy-substituted phenols, aromatic diamines and a variety of other compounds. When the Cu ions were removed from active center of laccase enzyme, it was converted to apolaccase. It was thought that the apolaccase could be connected to nano Fe (II/III) ions and apolaccase was regained it's activity.

There is a need to develop alternative and cost-effective treatment processes for colorness effluents. The present study was an attempt to develop a cost effective method for dye decolourisation using fenton and fenton like reaction.In this work, the decolorization of the BR9 by heterogeneous Fenton and Fenton like process using immobilized Nano-magnetite on silica and modified with apolaccase catalyst were researched. The effects of different initial immobilized Nano magnetite concentration, initial pH, initial contact time, initial temperature and initial BR9 on the decolorization efficiency of the process were discussed.

MATERIALS & METHODS
EAE-sephadex, ammonium sulphate, ABTS [2,2'azino-bis (3-ethylbenzylthiazoline-sulphanic acid)], Na_2HPO_4, CH_3COONa, dipiclonic acid, BR 9 (Table 1), magnetic nano particles Fe_3O_4 (Iron I, II oxide) (Castro *et al.,* 2001), silica and hydrogen peroxide (30%, w/w) were purchased from Sigma-Aldrich. All of the chemicals used were analytical grade without any further purification.

To obtain immobilized Nano particle, 0.03 M Fe_3O_4 in the form of magnetic nanoparticles, was dispersed in 100 mL deionized water. Then 25 gr silica was added into the reaction mixture (Table 1). The resultant mixture was mixed 24 h using a stirrer (500 rpm, 25 °C). The mixture was centrifuged at

Table 1.General characteristics of magnetic nanoparticles Fe_3O_4, silica and BR 9 (Gessner and Mayer 2002)

Chemical formula	Molar mass	Surfence Area	Particle Size
Fe_3O_4	231.53g/mol	$>60 \, m^2/g$	50-100 nm
SiO_2	60.08 g/mol	$175 - 225 \, m^2/g$	-
Chemical formula	**Molar mass**	**Color index number**	λ_{max}
$C_{19}H_{18}ClN_3$	323.82g/mol	42500	545nm

5.000 x *g* for 20 min. The pellet was washed three times with distilled water to remove the residual Fe_3O_4. The resultant wet paste was dried in an oven at 40 ºC for 72 h. The immobilized surface was grinned before use in experiments.

Lactarius volemus was picked in April-May near the city of Hasankale in Turkey's eastern province of Erzurum. It was recognized by a botanist and reserved at -40 ºC to avoid spoilage.

Lactarius volemus (25 g) was powdered in liquid N_2, then mixed uniformly with 50 mL of 1 M KCl in a blender and centrifuged at $5000 \times g$ for 60 min. The enzyme, present in the supernatant, followed the methods of Nadaroglu and Tasgin (2013), which included ammonium sulfate precipitation from 0% to 100% range of $(NH_4)_2SO_4$ concentrations, anion exchange chromatography and gel filtration chromatography).

The ABTS reagent was used as a substrate in the spectrophotometric determination of laccase activity. One activity unit (EU) represented the amount of enzyme that oxidized 1 μmol of ABTS min^{-1} and enzyme activity was expressed in U l^{-1} (He *et al.* 2003; Niku-Paavola *et al.* 1990).

Laccase (100 mg) was dissolved in 5 mL of 0,2 M phosphate buffer (pH: 7,0) containing 0,075 M dipicolinic acid. The solution, which was places into a dialysis sack, and dialyzed in 1 L of the same buffer for 5 hours. Subsequently, it was dialyzed for 18 hours against deionized water, including 5-6 changes. Following these, the solution was dialyzed for 5 h against 0.01 M acetate buffer (pH 5.0), which also served in activity measurement. At this point almost 100% pure apoenzyme was obtained (Demir *et al.,* 1993).

The chemical and mineralogical compositions of Fe_3O_4 immobilized silica samples were determined by scanning electron microscopy and various spectral analyses. A scanning electron microscope (SEM; Metek, Apollo prime, Active area 10 mm^2, Microscope inspect S50, SE detector R580) was used to examine the surface of native adsorbent and metal-loaded adsorbent, at a 5000-fold magnification.

Before SEM examinations, sample surfaces were coated with a thin layer (20 nm) of gold to obtain a conductive surface and to avoid electrostatic charging during examination. The same procedure was also used for the energy dispersive X-ray (EDX) spectra analysis in order to determine the elemental composition of the powdered Fe_3O_4 immobilized silica.

In addition, the Fourier Transform Infrared Spectroscopy (FTIR) analyses were carried out to identify functional groups and molecular structure in the Fe_3O_4 immobilized silica and enzyme-modified Fe_3O_4 immobilized silica. FTIR spectra were recorded on the Mattson 1000 FTIR spectrometer. The spectrum of the adsorbent was measured within the range of 4000-400 cm^{-1} wave numbers.

XRD pattern of the adsorbent determined by XRD (Rigaku D-Max 2000) and was analyzed with CuKα ($\lambda= 0.154$ nm) radiation with 2θ, 5º-100º (with a step size of 0.1).

All decolorization experiments were made in a 100 mL – stoppered Erlenmeyer flasks continingBR9 (50 mg/L) and 1 g Fe_3O_4 immobilized silica in 50 mL distilled water. The pH was adjusted to the desired value using either 0.1 M NaOH or 0.1 M HCl which was followed by addition of processes. The reactions were initiated by adding 3% (w/w) H_2O_2 solution to the flasks. Then, the flasks were placed in a shaker (200 rpm) at the room temperature. The samples were taken out from the flasks periodically by using a micropipette and the reaction mixture samples were centrifuged at 5000 x g for 10 min. The supernatant was filtered through using 0.45 nm filters. The concentration of BR 9 was measured spectrometrically at 545 nm.

In the all the studies runs, as described above, other parameters were kept stable and samples were taken at regular time for the analysis.

The decolorization efficiency of BR9 was defined as follows:

$$DE(\%) = \frac{[BR9]_0 - [BR9]_t}{[BR9]_0} \times 100$$

The effect of the quantity of magnetite nanoparticles immobilized on silica fume was studied by varying the surface material concentration between 0.0125 and 0.2 mg/50 mL. Also, the activity of the catalyst to decolorize Basic Red 9was tested underdifferent reaction parameters: $3 \leq pH \leq 9$, $20°C \leq T° \leq 80°C$, and initial concentration of Basic Red 9from 3.25 to 50 ppm.

The relationship between the amounts of dye removal and contact time was analyzed. It is observed that BR9 removal increases in the first 30 min of contact time. Basically, the removal of copper is fast at the beginning while it gradually decreases with time until it reaches equilibrium. This indicates that the concentration of BR9 in the solution decreased rapidly within 15 min and the removal was virtually completed within 30 min of contact time.

All of the tests were conducted in triplicate. Data were expressed as mean ± standard error. Statistical analyses were performed with SPSS version 10.0 software (SPSS Inc., Chicago, IL., USA), and the important treatment differences were determined with a 95% confidence interval ($P \leq 0.05$) using Tukey's test.

RESULTS & DISCUSSIONS

The laccaseenzyme was purified using a method of Nadaroglu and Tasgin (2013) for this determination, the collapse of $(NH_4)_2SO_4$, anion exchange chromatography and gel filtration chromatography were used. For each purification steps, protein amount and enzyme activity were calculated. The purification fold was found to be 149.53 fold from obtained results (Table 2).

The effect of Nano-Fe_3O_4 immobilized on silica was studied by varying surface material concentration (0.0125-0.2 mg/50 mL). Also, the activity of this catalyst to decolorize BR 9 was tested by different parameters such as pH in the range 3-9, optimum temperature in the range of 20-80 °C initial concentration of basic red 9 from (3.25-50 ppm).

From Fig. 1, it was observed that BR9 removal increases in the first 30 min of reaction time. Basically, the removal of BR9 was fast at the beginning while it gradually decreases with time until it reached equilibrium. These results were indicated that the concentration of BR9 in the solution decreased rapidly within 15 min and the removal was virtually completed within 30 min of contact time.
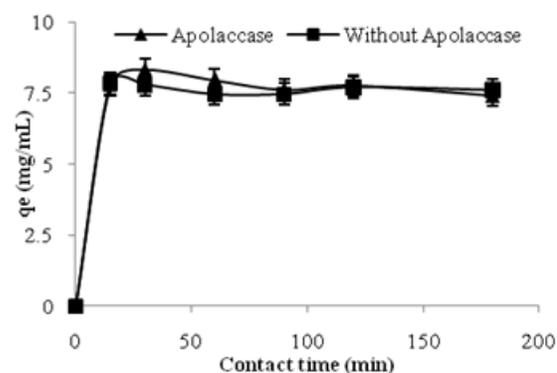
Fig. 1. Effect of contact time on the removal of BR9 by Fe_3O_4 immobilized and apolaccase modified silica

pH level of the aqueous solution was an important operational parameter in the fenton process as it was effected solubility of the dye, concentration of counter ions on the functional groups of adsorbent and degree of ionization of adsorbate during reaction (Fig. 2A) (Amuda *et al.* 2007).

In other words, the uptake and percentage removal of dyes from the aqueous solution were strongly affected by the pH of the solution (Benhammou *et al.* 2005; Ghazy and Ragab 2007; Onundi *et al.* 2010). Normally, Fenton reaction was resistant in lower pH (Lin and Lo 1997; Meric *et al.* 2004; Modirshahla *et al.* 2007) but our research was shown to be upper pH 6 for best dye removing. The upper pH stability of Fenton reaction was raised by immobilized nano-

Table 2.The purification process of laccase from Russulaceae (*Lactarius volemus*)

Enzyme Fraction	Volum mL	Activity EU/mL	Total Activity EU	%	Protein (mg/ml)	Specific EU/mg	Purificatio Fold
Crude extract	50	156.3±0.11	7.82×10^3	100	187.5±0.44	0.83	-
$(NH_4)_2SO_4$	40	86.9±0.24	3.5×10^3	44.8	41.1±0.05	2.11	2.54
DEAE-Sephadex	25	78.6±1.36	1.97×10^3	24.8	5.6±1.8	14.04	16.92
Sephacryl S 200	25	69.5±1.5	1.74×10^3	22.3	0.56±0.23	124.11	149.53
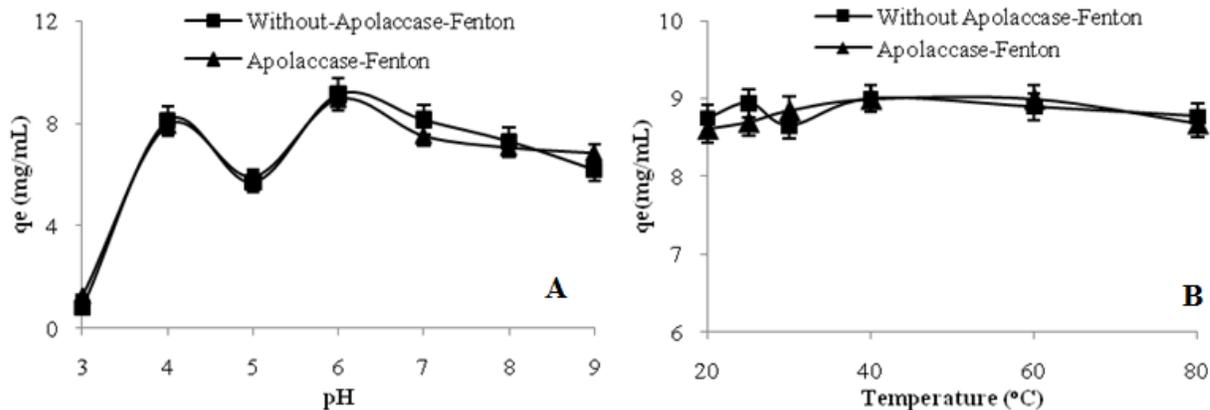
Fig. 2. Effect of pH (A) and temperature (B) on the removal of BR9 by Fe₃O₄ immobilized and apolaccase modified silica

magnetite and modified apo-laccase. This dye removing process could be used near of neutral pH, than the harmful effect was decreased and the data were illustrated in Fig. 2A (Nadaroglu *et al.* 2014).

It was affected the adsorption rate by altering molecular interactions and solubility of adsorbate, BR9, enzyme and Nano-magnetite (Nadaroglu *et al.* 2014). In Fig. 2B, it was showed the effect of temperature on the decolorization effect of Fenton reaction with Nano-magnetite immobilized with/ without apo-laccase modified. It was observed that the degree of decolorization increased in parallel with the increasing temperature. Maximum decolorization of BR9 were obtained at 40-60 °C for two processes. Effectiveness of fenton processes at upper temperature was advantage for industrial discharge. Because industrial discharges had upper temperature. In Fig. 3, it was shown the decolorization effects of the Fenton process without or with apolaccase. Using Fenton process are achieved to removal of BR9 without apolaccase 81% and modified with apolaccase 87%. Firstly the rate of decolorization of BR9 highly increases with an increase the concentration of both adsorbent. Decolorization was reached equilibrium after 0.1 g adsorbent concentration (Fig. 3). This optimization of the process condition had ensured the low cost and removal of dyes efficiency. So it was calculated optimum time, pH, temperature, dosages reagents. Chemical and mineralogical compositions of immobilized Fe₃O₄ with silica samples were determined using EDX, SEM, FTIR.

The SEM is useful for determining the particle shape, porosity and appropriate size distribution of the adsorbent (Kocaer and Alkan 2002). The SEM images of nano-magnetite-silica, BR9 adsorbed nano-
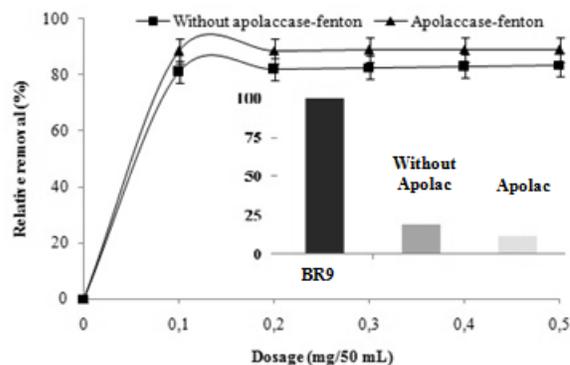
Fig. 3. Effect of adsorbent dosage on the removal of BR9 by Fe₃O₄ immobilized and apolaccase modified silica

magnetite-silica and nano-magnetite-silica-apolaccase are shown in Fig. 4 (a,b,c). SEM spectra was shown some differences at surface after fenton and enzymatic fenton reactions It is clear that, nano-magnetite-silica-apolaccase has considerable numbers of pores where, there is a good possibility for dyes to be trapped and adsorbed into these pores. Based on analysis of the images taken by SEM before and after the dye fenton process, highly heterogeneous pores within Silica-nano magnetite apolaccase particles were observed. After BR9 dye treatment, the pores were packed with dyes.

The same machine was also used for the EDX and SEM spectra analysis in order to determine the elemental composition of the powdered Fe₃O₄ immobilized silica, Silica-nano magnetite-BR9 and Silica-nano magnetite-BR9 apolaccase. The elemental composition changes were shown after fenton and enzymatic fenton reactions. The increased amount ofcarbon and iron was shown that enzyme and nanomagnetite was binded to the surface ofsilica

Silica-nano magnetite **Silica-nano magnetite-BR9** **Silica-nano magnetite-BR9-apolaccase**
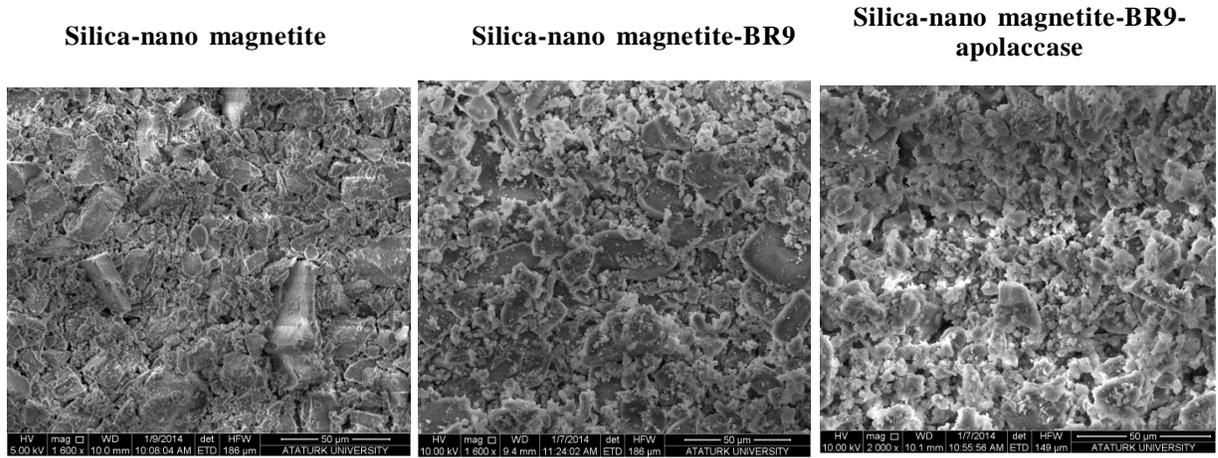
Fig.4. SEM Images of adsorbents

Element	Wt% At%		EDX of silica-nano magnetite
CK	02.71 05.98		
OK	14.30 23.66		
FeL	02.53 01.20		
SiK	72.19 68.05		
AuM	08.27 01.11		
Matrix Correction ZAF			

Element	Wt% At%		EDX of silica-nano magnetite-BR9
OK	35.57 53.54		
FeL	20.60 08.88		
SiK	43.82 37.57		
Matrix Correction ZAF			

Element	Wt% At%		EDX of silica-nano magnetite-BR9-apolaccase
OK	30.40 49.14		
SiK	40.71 37.49		
FeK	28.89 13.38		
Matrix Correction ZAF			
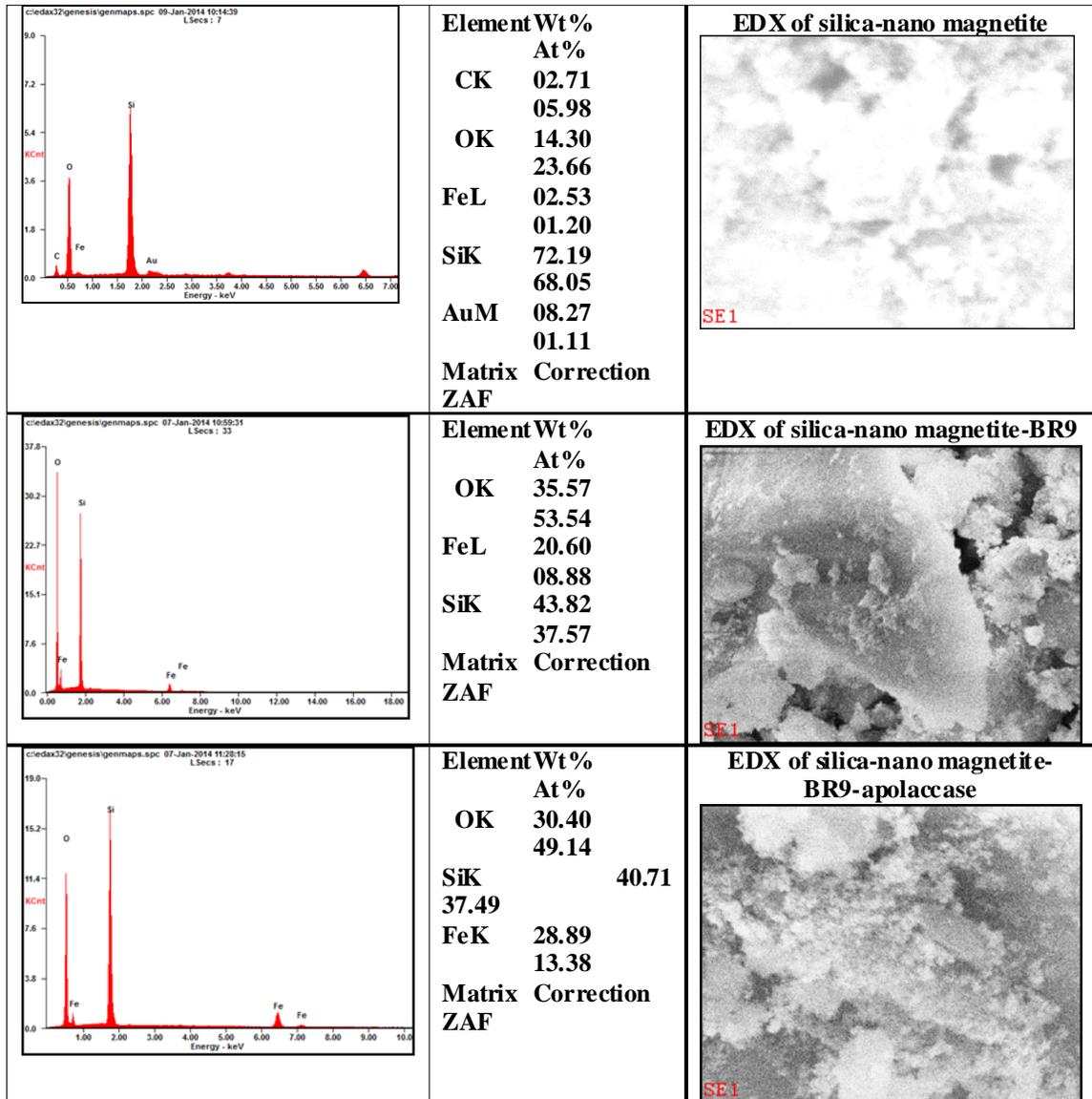
Fig. 5. EDX images of adsorbents
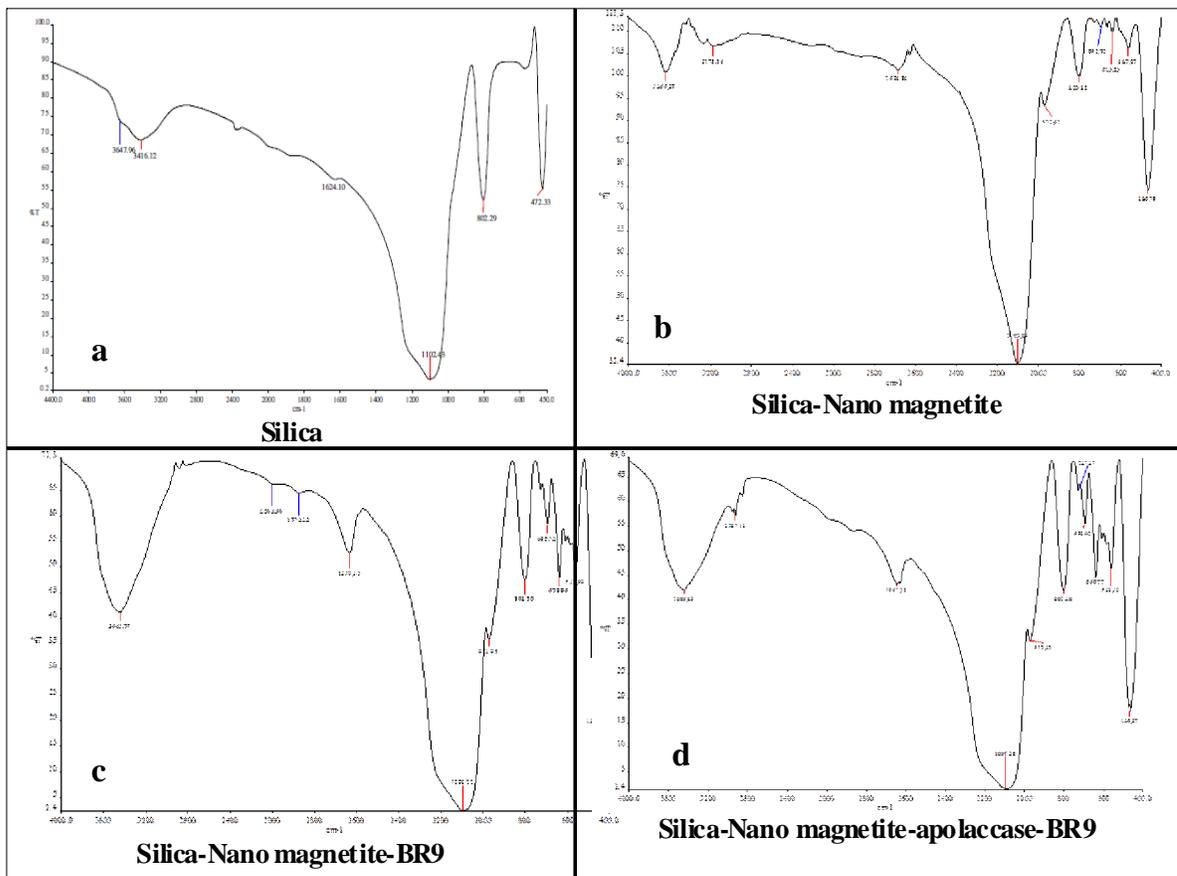
Fig. 6. FTIR Images of adsorbents (a: Silika, b: Silica-Nano magnetite, c: Silica-Nano magnetite-BR9, d: Silica-Nano magnetite-apolaccase-BR9)
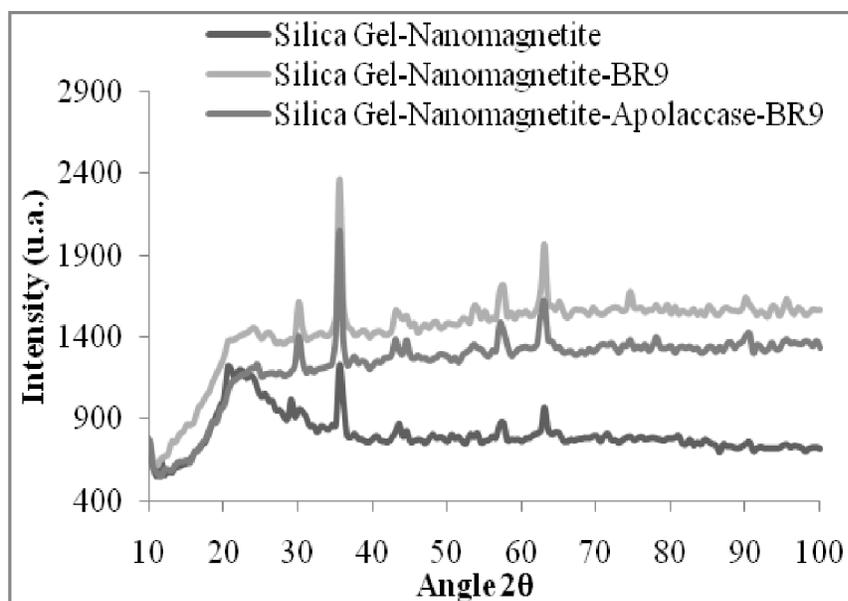
Fig. 7. XRD Images of adsorbents

matrix (Fig.5). In addition, the FTIR analyses were carried out to identify functional groups and molecular structure. Silica-magnetite, Silica-magnetite-BR9 and Silica-magnetite-apolaccase-BR9 surface structure are shown in Fig 6.

The structure of silica was compared with nano magnetite-immobilized silica and enzyme modified nano magnetite immobilized silica (Fig. 6a-d).Silica bonds and the bonds of the structure of the vibrational bands; Si-O (472 cm^{-1}), silanol-OH bend (802 cm^{-1}), the asymmetric Si-O-Si stretching, tetrahedral form SiO$_4$ (1102.43 cm^{-1}), molecular water bending- OH (1624.1 cm^{-1}) and adsorbed water and OH stretch(3000-3800 cm^{-1}), respectively; were observed. Especially after doing fenton reaction completely change the structure of the fingerprint region of Silica-magnetite nano-apolaccaseBR9 structure. It is indicated that this reaction was occurred (Swann and Patwardhan 2011).

As a result of XRD analysis, it was determined that 20^o(111) peak is belong to the structure in the siloxane (Si-O-Si) (Fig. 8). The diffraction peaks corresponding to (220), (311), (400), (511), (440) are quite identical to characteristic peaks of the Fe$_3$O$_4$ crystal with the cubic spinal structure (Fu *et al.,* 2004; Ghandoor *et al.,* 2012) (Fig.7).

XRD shows the decrease of the peak intensity of Si phase in case of coloured silica-magnetite indicates that the removal process is mainly accompanied by a fenton reaction which occurred between the dye molecules and the dissolved portion of the silica-magnetite-apolaccase (Saraya and Aboul-Fetouh 2012).

CONCLUSIONS

The laccase enzyme could be a commercial enzyme which was widely used for the removal of toxic dyes in different areas including the textile industry. In this work, the apo-enzyme was immobilized to silica which was reactived with nano Fe (II/III) ions for enhancing the Fenton reaction activity, to remove the BR9 dye. Fenton reaction was occurred using this enzyme and it was observed that the yield of the Fenton reaction was increased. Using Fenton process was achieved to removal of toxic dye BR9 without apolaccase 81% and modified with apolaccase 87%. The results presented in this paper offer new opportunities for the environmentally friendly use of silica-magnetite-apolaccase matrix and fenton was provided a facile method for the effective degradation of azo-dyes.

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