

Synthesis and characterization of silver doped magnetic-nanoclay montmorillonite/iron oxide/silver nanocomposite for environmental applications through effective dye degradation

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Abstract

Magnetic-nanoclay montmorillonite/iron oxide (MMT/Fe₃O₄) nanocomposite was prepared by coprecipitation method and montmorillonite/iron oxide/silver (MMT/Fe₃O₄/Ag) nanocomposite was synthesized, called as chemical reduction method, by reduction of silver nitrate (AgNO₃) salt with sodium borohydride (NaBH₄) as reducing agent. These nanocomposites were characterized by Brunauer-Emmett-Teller Surface Area and Porosity Dimension (BET), X-Ray Diffractometer (XRD), Fourier Transform Infrared Spectrum (FTIR), Scanning Electron Microscope (SEM) and Vibrating Sample Magnetometer (VSM). Subsequently, MMT/Fe₃O₄/Ag was used in degradation of Rhodamine B (RhB) in the presence of NaBH₄ to evaluate catalytic activity of its and consequences were monitored using UV-Visible Spectrofotometer (UV-Vis). Moreover, various parameters including pH, catalyst dosage, initial dye concentration and amount of NaBH₄ were investigated for optimum reaction conditions. The reduction reactions followed pseudo-first order kinetics and complete degradation of RhB were achieved in 8 minutes using MMT/Fe₃O₄/Ag as catalysts while degradation of 46% of RhB were achieved in 60 minutes using MMT/Fe₃O₄.

Introduction

In recent years, synthetic dyes have been largely used in several industries such as plastic, cosmetic, leather, paper, textile, food and pharmaceutical as dyestuff. It is guessed that about 700,000 tons of dyes are commercially produced per a year and 15-20% of water containing these dyes are emitted into water bodies and soil during dyeing and finishing process. Dye wastes also have posed a serious danger to the environment in addition of aquatic living being and human being because of their hazardous and toxic impact (Nandhini et al. 2019; Naseem et al. 2019). Wastewater contaminated with dye disrupts the balance of water uncontaminated with dye and diffuses deep into clean water and thus influences water ecosystem. Aquatic organisms are exposed to these dyes due to the presence of synthetic dyes in water. When people feed on creatures like fish living in these waters, they may face many ailments such as cramps, mental disorder, hypertension, etc. Many studies on benzidine-based dyes have been shown as a carcinogenic substance that causes a serious toxic effect on the human bladder and skin. In a research by Javaid and Qazi (2019) was presented several dye used in textile industry and their detrimental impact (Javaid and Qazi 2019). RhB is a cationic dye that has been used in food and textile as colorant agent (Glossman-Mitnik 2013; Rafique et al. 2020) and applied in industries, analytical chemistry and biological studies over the years (Oplatowska and Elliott 2011). It is one of the most commonly used basic red dye of xanthene class. In this study, RhB, which causes many adverse effects on humans and animals such as respiratory tract, eye and skin irritation, neurotoxicity, carcinogenicity and reproductive toxicity, was used as a source of contaminant (Lou et al. 2020). RhB molecule can exist in three forms including cationic or protonated form, the zwitterionic form and colorless lactone form (Sagoo and Jockusch 2011; Catone et al. 2018) (Fig. 1). There is an equilibrium between these three forms of RhB in many solvents. Elimination of RhB from wastewater is a significant phenomenon because of its carcinogenicity, reproductive and developmental toxicity, neurotoxicity and chronic toxicity towards humans and

especially aquatic living being (Jain et al. 2007; Veisi et al. 2019). Thus, wastewater contaminated with RhB have to be treated before drain into the environment.

Among the many nanoparticle types, magnetic nanoparticles (MNP) have attracted great attention for research in the last 10 years due to their use in many fields such as magnetic fluids, catalysis, biotechnology and biomedicine, magnetic resonance imaging, data storage and environmental remediation (Lu et al. 2007; Pegu et al. 2014). Researchers are particularly showing great interest iron oxide MNP on account of their unique properties such as fast magnetic recovery, facile detection, and ease of recyclability with an external magnetic field (Sharma et al. 2019). In this context, iron oxide MNP coated with metals such as Ag (Xing et al. 2019), Au (Azad et al. 2011; Chen et al. 2019) and Cu (Ghafuri et al. 2019) to improve its catalytic properties have been used for dye degradation in recent years. The catalytic activity of Ag nanoparticles (AgNPs) synthesized with the aim of a more successful dye degradation have been proved by many studies. Using AgNPs for dye degradation experiment have evaluated more efficient, simple and useful as a suitable catalyst. Besides, AgNPs exhibit electrical, optical, biological, non-toxic, chemical, catalytic, antibacterial etc. properties (Shahriary et al. 2018; Veisi et al. 2019). Mostly, AgNPs can be synthesized by means of silver ions reduction in solution through a reducing agents (citric acid, NaBH_4 or other organic compounds) or in gaseous environments in high temperature (Cheng et al. 2013).

Clays are accepted as the materials of 21st century due to their plentiful, cheap and environmentally friendly. Clays are used over 100 industrial application such as agricultural, engineering and construction, environmental remediation and geology (Maisanaba et al. 2015). MMT clay that used for nanocomposites as supports is a 2:1 type of phyllosilicates clay. The molecular formula of MMT clay is $\text{M}_x(\text{Al}_{2-x}\text{Mg}_x)(\text{Si}_4)\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ (where $\text{M}=\text{Al}^{3+}$, Mg^{2+} , Fe^{2+} or Fe^{3+}). It is a member of the smectite family and its structure arise from aluminosilicate layers where one Al^{3+} octahedral sheet positioned between two Si^{4+} tetrahedral sheets. The margin between two layers is known as interlayer distance. In the layer of aluminosilicate, partial isomorphous replacement of Si^{4+} and Al^{3+} cations leads to a lack of charge. Hydrated alkali and alkaline earth metal cations occupy the interlayer space of MMT so as to stabilize lack of charge. These cations that largely modifiable able to harbor various guest molecules (metal complexes, metal nanoparticles and organocatalysts) for MMT clay (Sharma et al. 2010; Chen et al. 2011; Kumar et al. 2014). Thus, with modification on MMT with acids, organic materials or transition metal nanoparticles, the surface area and porosity of MMT will be significantly developed (Zeynizadeh et al. 2020). Many researcher synthesized nanocomposite with metals such as MnO_2 (He et al. 2018), Ag and AgCl (Sohrabnezhad et al. 2014), ZnO (K\iran\csan et al. 2015), TiO_2 (Khataee et al. 2015), La-Fe (Fida et al. 2017), Cu (Mekewi et al. 2016; Zeynizadeh et al. 2020), Fe_3O_4 (Zeynizadeh et al. 2020) on MMT for dye degradation.

In this study, MMT/ Fe_3O_4 and MMT/ Fe_3O_4 /Ag nanocomposites were synthesized by co-precipitation and chemical reduction method, respectively. They were characterized by various technique to demonstrate their pore structure, crystalline structure and magnetic properties. Catalytic activities of prepared these

nanocomposites were evaluated on degradation of RhB in the presence of NaBH_4 . The effects of various parameters such as pH, initial concentration etc. on degradation of RhB were also investigated. The results were monitored in UV-Vis.

Materials And Methods

Chemicals

Montmorillonite K 10 (MMT, Sigma-Aldrich), sodium borohydride (NaBH_4 , Sigma-Aldrich), silver nitrate (AgNO_3 , Sigma-Aldrich), sodium hydroxide (NaOH , Sigma-Aldrich), Rhodamine B (RhB, Sigma-Aldrich), ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Merck), ferrous chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, Merck), ammonia solution %25 (NH_3 , Merck), sodium chloride (NaCl , Merck), nitric acid %65 (HNO_3 , Honeywell) were used without further purification. All the other chemicals were of analytical grade and used as received. Distilled water is used throughout all the experiments.

Characterization techniques

Surface area

The surface area of each sample were determined by N_2 adsorption/desorption at 77 K using QuadraSorb Station 1 Quantachrome porosimeter according to the Branuer-Emmet-Teller Surface Area and Porosity Dimension (BET) method and were degassed at 300 °C, for 3 hours before measurement.

Surface functional groups

Fourier transform infrared spectroscopy (FTIR, Brucker Vertex 70) was used to determine surface functional groups of particles in the 4000-400 cm^{-1} region.

Monitoring of degradation experiments

The degradation experiments of RhB were monitored using UV-Vis (Shimadzu UV-1700 UV-Vis).

Morphology characterization

The morphology of MMT, MMT/ Fe_3O_4 and MMT/ Fe_3O_4 /Ag materials were observed by scanning electron microscopy (SEM, Hitachi-SU 1510)

Crystalline structure X-Ray diffraction

Crystallinity patterns of MMT, MMT/ Fe_3O_4 and MMT/ Fe_3O_4 /Ag materials were studied using X-Ray diffraction (XRD, GNR-APD 2000 Pro) in the range of $2\theta = 2-80^\circ$.

Magnetization

The magnetization measurement of MMT/Fe₃O₄/Ag nanocomposite was performed using Vibrating Sample Magnetometer (VSM, Cryogenic Limited PPMS) at room temperature.

Determination of point of zero charge (pH_{pzc})

The point of zero charge (pH_{pzc}) of the MMT/Fe₃O₄/Ag nanocomposite was determined by batch equilibration technique (Stoia et al. 2017). 25 mL of 0.01 mol/L NaCl solutions were prepared in six different beakers and the pH values of the solutions were adjusted to 2, 4, 6, 8, 10 and 12 using solutions of HNO₃ and NaOH. The initial pH of the solution (pH_{in}) was recorded with a pH meter. 50 mg of MMT/Fe₃O₄/Ag was added into each of the beakers. The suspensions were shaken (150 rpm) for 24 hours at 25°C and then the MMT/Fe₃O₄/Ag was magnetically separated from the aqueous phase. The final pH of the solution (pH_{fin}) was measured and the difference between initial and final pH – the so-called ΔpH – was plotted against the initial pH values. The pH_{pzc} values were calculated from ΔpH versus pH_{in} plots, at the pH where pH = 0. The pH_{pzc} value of MMT/Fe₃O₄/Ag was found to be 5.62 (Fig. A1).

Synthesis

Synthesis of magnetic-nanoclay MMT/Fe₃O₄ nanocomposite

Magnetic MMT/Fe₃O₄ was synthesized by chemical co-precipitation of chloride salts of Fe³⁺ and Fe²⁺ (Chen et al. 2017). For the synthesis of MMT/Fe₃O₄, MMT (2.0 g) was added into deionized water (200 mL) and the suspension was ultrasonicated for 30 min. On the other hand, a solution of FeCl₃.6H₂O (1.67 g) and FeCl₂.4H₂O (0.43 g) in deionized water (100 mL) was prepared. Then prepared this solution was mixed with pre-prepared MMT suspension. While final solution (300 mL) was stirred by a mechanical mixer (400 rpm) at 65 °C, it was adjusted pH to 10.2 using ammonia (by adding drop-by-drop) to take place precipitation of Fe₃O₄. After final solution was stirred for 1 hour at 65 °C, deep brown precipitate was formed bottom of beaker and filtered by filter paper. Obtained this precipitate was washed by deionized water for several times and then was dried under vacuum condition for 24 hours at 65 °C (Fig. 2).

Synthesis of MMT/Fe₃O₄/Ag nanocomposite

The synthesis procedure of MMT/Fe₃O₄/Ag was partly modified from literature (Shahriary et al. 2018). Magnetic-nanoclay MMT/Fe₃O₄ (0.5 g) was dispersed in deionized water (200 mL) by ultrasonic bath for 30 min. Meanwhile, a solution of AgNO₃ (30 mg) in deionized water (20 mL) was prepared and added into the solution of MMT/Fe₃O₄. Obtained mixture was vigorously stirred for 2 hours at room temperature. 0.1 g of NaBH₄ was quickly added so as to reduce Ag(I) ions in the AgNO₃ solution during mixing. Then, mixture was filtered by filter paper and after precipitate was washed by deionized water for several times, it was dried under vacuum for 24 hours at 65 °C (Fig. 2).

Degradation of RhB

In order to evaluate the catalytic activities of MMT/Fe₃O₄ and MMT/Fe₃O₄/Ag, solution of RhB (12 mg/L, 100 mL) and solution of NaBH₄ (0.01 mol/L, 25 mL) were prepared. All the catalytic experiments were carried out in a 3.5 mL of UV-cuvette at room temperature. Firstly, 3 mL of RhB and 0.3 mL of NaBH₄ were added to UV-cuvette. And then, 7.5 mg of MMT/Fe₃O₄ and MMT/Fe₃O₄/Ag were used separately to reduce and decolourize RhB dye solution. In addition to this, various parameters such as catalyst dosage (0.45 – 2.12 g/L), amount of NaBH₄ (0.0375 – 0.45 mL) and pH (3.1-10.3) were investigated. All experiments of reduction were monitored with UV-Vis. Particles were separated using a magnet after the degradation of RhB was finished. Separated particles were reused by washing and drying for the next cycle.

Results And Discussion

Characterization

XRD analysis

Fig. 3 (a) and (b) show the XRD powder pattern of MMT, MMT/Fe₃O₄ and MMT/Fe₃O₄/Ag. Characteristic peaks of MMT have been shown at $2\theta = 17.7^\circ, 19.8^\circ, 29.8^\circ, 35^\circ, 55^\circ$ and 62° relevant to the hexagonal structure. The reflections at $30^\circ, 35.06^\circ, 39.5^\circ, 56.4^\circ$ and 68° are accounted for cubic structure of Fe₃O₄. XRD patterns of MMT and MMT/Fe₃O₄ do not observe perceptibly differential due to similarity of characteristic peaks of MMT and Fe₃O₄ (Hosseini Nasab and Safari 2019). The XRD peaks of MMT/Fe₃O₄/Ag at $2\theta = 38.1^\circ, 44.3^\circ, 64.7^\circ$, and 77° are related to silver crystals diffraction of (111), (200), (220) and (311) (Shameli et al. 2011). The results from XRD show that AgNPs were successfully immobilized on the MMT surface coated with magnetic particles. The average crystallite size of the MMT/Fe₃O₄/Ag nanocomposite was calculated by following Debye-Scherrer's formula given by Eq. (1)

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where, D is crystallite size and K is Debye-Scherrer's constant, λ stands for X-ray wavelength, β indicates the full width at half maximum intensity of the XRD peaks and θ is the diffraction angle (Isa et al. 2020; Sankaran and Kumaraguru 2020; Shaheen and Ahmad 2020). The average crystal size of MMT/Fe₃O₄/Ag calculated using the Debye-Scherrer formula was found to be 15 nm.

BET analysis

The specific surface area and pore volume of the MMT, MMT/Fe₃O₄ and MMT/Fe₃O₄/Ag are given in Table 1. As seen from the Table 1, there is a gradual decrease in the surface area and pore volume of the MMT after loading Fe₃O₄ and AgNPs on the MMT surface. It shows that the specific surface area of

MMT reduced from 210.037 m^2/g to 179.412 m^2/g and MMT surface was loaded with Fe_3O_4 as a result of the decrease in the pore volume. Likewise, it is seen that the specific surface area of the MMT/ Fe_3O_4 particle decreases to 164.997 m^2/g after loading with AgNPs and the pore volume decreases. This phenomenon probably shows that some pore mouths are blocked by Fe_3O_4 and AgNPs (Dashtian and Zare-Dorabei 2017; Zeynizadeh et al. 2020).

VSM analysis

The magnetic property of the MMT/ Fe_3O_4 /Ag nanocomposite was characterized by VSM system at room temperature with the field sweeping from -10000 to +10000 Oe. Fig. 3 (c) shows the magnetic hysteresis (M-H) loop of the MMT/ Fe_3O_4 /Ag nanocomposite and the magnetic saturation (M_s) value of the MMT/ Fe_3O_4 /Ag nanocomposite is calculated 4.8 $emu.g^{-1}$. This value proves the magnetic behavior of the nanocomposite, which indicates that it can be easily separated from the suspension with using a external magnet after the reaction

(Liu et al. 2018) (Fig.5(b)). However, this value is relatively lower than the magnetic saturation value of magnetic nanoparticles synthesized by the co-precipitation method, which is 30-50 $emu.g^{-1}$ (Lu et al. 2007). The lower M_s value of MMT/ Fe_3O_4 /Ag may be attributed to non-magnetic AgNPs surrounding the magnetite nanoparticles (Kurtan et al. 2015).

FTIR analysis

The FTIR spectra of MMT, MMT/ Fe_3O_4 and MMT/ Fe_3O_4 /Ag are shown in Fig. 3 (d). The absorption peaks at 3622 cm^{-1} and 795 cm^{-1} seen in the MMT spectrum are related to stretching vibrations of Al-OH and Si-O groups, respectively. The strong absorption peak at 1032 cm^{-1} is caused by Si-O-Si stretching vibrations. Absorption peaks seen at 919 cm^{-1} , 831 cm^{-1} and 518 cm^{-1} are peaks attributed to vibrations of Al-Al-OH, Al-Mg-OH and Si-O-Al, respectively. The

Table 1 The surface characteristic of MMT, MMT/ Fe_3O_4 and MMT/ Fe_3O_4 /Ag

Sample	Specific surface area (m^2/g)	Pore volume (cc/g)	Micropore volume (cc/g)	Micropore area (m^2/g)
MMT	210.037	0.374	0.122	125.64
MMT/ Fe_3O_4	179.412	0.340	0.097	106.86
MMT/ Fe_3O_4 /Ag	164.997	0.334	0.088	91.49

broad peak in 3409 cm^{-1} shows the OH stretching in the structure and the peak at 1628 cm^{-1} shows the water molecule in the structure of MMT. The absorption peaks at 459 cm^{-1} and 1445 cm^{-1} in the MMT/ Fe_3O_4 magnetic nanoclay is assigned to the Fe-O vibration and N-H vibration that prove the

presence of Fe in the structure of MMT/Fe₃O₄ (Hosseini Nasab and Safari 2019). The FTIR spectra of AgNPs formed by reduction of Ag⁺ ions in MMT/Fe₃O₄/Ag structure is shown in 1738 cm⁻¹ (C = O stretching), 1368 cm⁻¹ (C-H group) and 1022 cm⁻¹ (ether linkages) (Sohrabnezhad et al. 2016).

SEM analysis

MMT, MMT/Fe₃O₄ and MMT/Fe₃O₄/Ag were analyzed by SEM-EDX characterization method. SEM images of these, EDX spectrum and weight percentages of elements and element mapping are given in Fig. 4. The SEM images show that Fe₃O₄ and AgNPs are uniformly distributed on the MMT surface. EDX analysis was performed to verify the surface composition of the MMT/Fe₃O₄/Ag nanocomposite and results show the presence of Fe and Ag elements in the MMT/Fe₃O₄/Ag. Moreover, the presence of Fe and Ag was approved using the elemental mapping images. According to these results, it could be deduced that MMT/Fe₃O₄/Ag nanocomposite was successfully synthesized by both co-precipitation and chemical reduction methods.

Evaluation Of Catalytic Performances Of MMT/Fe₃O₄ And MMT/Fe₃O₄/Ag Nanocomposites On Degradation Of RhB

Experiments on degradation of RhB were carried out using MMT/Fe₃O₄ and MMT/Fe₃O₄/Ag nanocomposites in the presence of NaBH₄ as reducing agent at room temperature. To investigate catalytic activity of Ag, MMT/Fe₃O₄ and MMT/Fe₃O₄/Ag nanocomposites were used separately. Catalytic reduction of RhB was monitored using UV-Vis by recording the time-dependent UV-Vis absorption spectrum at wavelengths in the range of 200-700 nm. RhB has two characteristic absorption peaks originating from aromatic content of RhB at 259 nm and transition C=O and C=N groups at 554 nm. To monitor the degradation of RhB by UV-Vis, peak density at 554 nm, which indicates the reddish violet color and absorption of the RhB solution, is taken into account. Fig. 5 (a) shows the catalytic reduction of RhB with MMT/Fe₃O₄ in UV-Vis. When the reduction reaction is started, the peak density at 554 nm slightly decreases depending on the time. However, the degradation rate of RhB was only 46% within 60 minutes and no peak at 400 nm was observed. When MMT/Fe₃O₄/Ag nanocomposite was added into solution of RhB (12 mg/L) to degrade RhB, a significant decrease in degradation rate of RhB occurred under the same conditions and 100% of degradation rate occurred within 8 minutes (Fig. 8 (b)). As seen in Fig. 5 (b), RhB was discolorized in the presence of NaBH₄ and the peak density at 554 nm was zeroized. After complete degradation of RhB, a new peak showed up at 400 nm because of Ag in the MMT/Fe₃O₄/Ag nanocomposite (Khan et al. 2017). The MMT/Fe₃O₄/Ag nanocomposite was easily separated from the suspension by external magnet.

Fig. 5 (c) shows plots of ln C/C₀ versus reaction time showing that the degradation follows pseudo first order kinetic rate law. Because concentration of NaBH₄ was higher than concentration of RhB, rate constant for degradation of RhB could be calculated by the pseudo first order kinetic rate law Eq.2 (Sahoo et al. 2016; Khan et al. 2017; Ucar et al. 2017):

$$k \cdot t = \ln C_0 - \ln C = \ln A_0 - \ln A \quad (2)$$

here, k is the rate constant. C_0 and C are the concentration of RhB at time $t = 0$ and $t = t$ where as A_0 and A are the absorbance of RhB ($\lambda_{\max}(\text{RhB}) = 554 \text{ nm}$) at time $t = 0$ and $t = t$, respectively. The ratio of C to C_0 (C/C_0) was calculated from the ratio of the absorbance's (A_t/A_0) at 554 nm for RhB. k constant value was calculated as 0.3454 min^{-1} for degradation of RhB.

The k constants for Ag containing nanoparticles obtained from different studies are given in Table 2.

k constant value was calculated as 0.3454 min^{-1} for degradation of RhB. k constant values obtained from different studies are given in Table 2. According to the Table 2, MMT/Fe₃O₄/Ag nanocomposite have shown better catalytic efficiency when compared to other metal nanocatalyst including Fe or Ag metals.

pH Effect

One of the most important factors affecting the degradation time of RhB is the solution pH. This is due to metal ions and functional groups in nanoparticles. In the graph given in Fig. 6 (a), four different pH values (3.1, 5.2, 7.1 and 10.3) were examined for the degradation of RhB and pH adjustments were done with 0.1 mol/L NaOH and 0.1 mol/L HNO₃. The results shows that 100% degradation of RhB was recorded as 25, 8, 21 and 15.5 minutes at pH 3.1, pH 5.2, pH 7.1 and pH 10.3, respectively. The rate constant values obtained from these pH values were calculated as 0.1986, 0.3454, 0.2676 and 0.2690 min^{-1} for pH 3.1, pH 5.2, pH 7.1 and pH 10.3, respectively, and are given in Fig. A2. In strong acidic and basic mediums, degradation rate of RhB was quite low compared to pH 5.2 and the minimum time required to completely decompose the RhB was obtained at this pH. There can be two reason for this; (i) surface charge of nanocomposite i.e value of pH_{pzc} and (ii) forms of RhB at different pH values. RhB has different chemical forms in water and these chemical forms are affected by the solution pH. RhB has positively charged cationic form when $\text{pH} < 4$ and RhB has chargeless zwitterionic (both negatively and positively charged neutral molecule) form when $\text{pH} > 4$ (Fig. 1). The pH_{pzc} value of the MMT/Fe₃O₄/Ag nanocomposite was found as 5.62 (Fig.A.1) and the particle surface is positively charged below this pH value ($\text{pH} < \text{pH}_{\text{pzc}}$) and negatively charged above it ($\text{pH} > \text{pH}_{\text{pzc}}$) (Üner et al. 2017). When $\text{pH} > \text{pH}_{\text{pzc}}$, cationic species are degraded, anionic species are degraded while $\text{pH} < \text{pH}_{\text{pzc}}$ (Tripathi et al. 2013). Therefore, the particle surface is positively charged at pH values less than 5.62, and RhB molecules are also positively charged below pH 4. This will cause an electrostatic repulsion between nanoparticle and dye molecules. However, due to the presence of carboxylic (COO⁻) anions in the structure of RhB when the pH value is 5.2, RhB molecules interact electrostatically with the positively charged MMT/Fe₃O₄/Ag nanocomposite surface, thereby observing the lowest degradation time. With the increase of pH (7.1 and 10.3) value of RhB solution, the positive charge on the particle surface reduced and the surface negatively charged. So, the degradation time increased as a result of the electrostatic repulsion with the COO⁻ anions in the zwitterionic form of RhB (Fig. A3). In parallel with these results, optimum pH value for this study was determined as 5.2.

Catalyst Dosage

The degradation of RhB was studied by varying MMT/Fe₃O₄/Ag nanocomposite dosage ranging from 0.45 to 2.12 g/L (Fig. 6 (b)). A significant reduction in RhB degradation reaction time was observed when using catalyst dosage of 0.45 to 1.51 g/L, while an increase in reaction time was observed when catalyst dosage of 2.12 g/L was used. As more catalytic active sites and reactive surface for RhB occur with increasing catalyst dosage, transfer of electrons and hydrogens to RhB molecules is accelerated (Li et al. 2019).

However, the catalyst dosage of 2.12 g/L had a slowing effect on degradation of RhB due to agglomeration of particles as a result of the decrease in surface area with the catalyst dosage exceeding 1.51 g/L. Basavegowda et al. (2017) observed similar results for RhB in their study

Table 2 Comparison of calculated k constants in different studies for RhB

Dye	Catalyst	Rate constant, <i>k</i> (min ⁻¹)	References
RhB	Ag-loaded Fe ₃ O ₄ @C nanospheres (Ag-Fe ₃ O ₄ @C)	0.220	(Li et al. 2015)
	FeAgPt alloy nanoparticles	0.256	(Basavegowda et al. 2017)
	Silver nanoparticle starch (AgNP-starch)	0.1794	(Joseph and Mathew 2015)
	PVDF/PDA/Ag Membrane	0.1271	(Ma et al. 2018)
	MMT/Fe ₃ O ₄ /Ag nanocomposite	0.3454	This work

(Basavegowda et al. 2017). Therefore, the appropriate dosage of MMT/Fe₃O₄/Ag nanocomposite was determined as 1.51 g/L.

Initial Dye Concentration

Fig. 6 (c) shows the effect of initial dye concentration on the degradation of RhB. For this purpose, the initial concentration values ranging from 4.80-20 mg/L and the reaction times required for the degradation of the RhB dye were examined. As shown in the Figure 12, degradation efficiency for RhB decreased with increasing the initial concentration of RhB. 20 mg/L of RhB was degraded at the rate of %100 within 34 minutes while 4.80, 8, 12 and 16 mg/L of RhB were degraded within 5, 8, 9 and 15 minutes, respectively.

NaBH₄ concentration and amount were constant during catalytic reactions. Since the degradation times of 12 mg/L of RhB and 8 mg/L of RhB were close to each other, determined optimum RhB concentration for this study was chosen as 12 mg/L.

Amount Of NaBH₄

Fig. 6 (d) shows the effect of amount of NaBH₄ on the degradation of RhB. As clearly seen from the graph, the degradation efficiency increased with the increase in the amount of NaBH₄. Although the catalytic reaction continued for 50 minutes, it came true only 45% when amount of 0.0375 and 0.075 mL of NaBH₄ were used. However, when amount of 0.15, 0.30 and 0.45 mL of NaBH₄ was used in order to degrade RhB at the rate of %100, the catalytic reaction times recorded as 14, 8 and 3.5 minutes, respectively. Because, increase in the amount of NaBH₄ led to produce more hydrogen and thus attach over the MMT/Fe₃O₄/Ag nanocomposite. This mechanism, called electron transfer process, is explained by BH₄⁻ ions generated from ionization of NaBH₄. Namely, BH₄⁻ ions diffuse into the MMT/Fe₃O₄/Ag nanocomposite together with RhB molecules. Diffused BH₄⁻ ions produce hydrogen bonded on the MMT/Fe₃O₄/Ag surface. RhB molecules reach the MMT/Fe₃O₄/Ag surface and are rapidly attached here because of electrostatic interactions (positive charge over the MMT/Fe₃O₄/Ag nanocomposite and negatively charged RhB molecules due to COO⁻ anions in the structure of RhB at pH=5.2). Hydrogen interacts with the RhB molecules through the MMT/Fe₃O₄/Ag nanocomposite, which acts as an electron conveyor, and the RhB molecules are degraded. In addition, while BH₄⁻ ions are nucleophilic, RhB molecules are electrophilic compared to metal nanoparticles. During the catalytic degradation reaction, RhB molecules capture electrons from BH₄⁻ ions through metal nanoparticles. Hereby, metal nanoparticles play a role as an electron relay center in the degradation of RhB in the presence of NaBH₄ (Fig. A4) (Naseem et al. 2019). Determined optimum amount of NaBH₄ was chosen 0.30 mL.

Recycling Of MMT/Fe₃O₄/Ag Nanocomposite

Reusability of MMT/Fe₃O₄/Ag was evaluated in degradation of RhB in the presence of NaBH₄ for optimized reaction conditions. The MMT/Fe₃O₄/Ag was separated from the suspension medium by external magnet to reuse after the completion of the first catalytic reaction to degrade RhB and then washed with ethyl alcohol and distilled water and dried in the oven at 65 °C for 2 hours for next cycle. This process was repeated each cycle. Fig. 7 shows the recyclability of the MMT/Fe₃O₄/Ag in five successive reactions for RhB. According to the Fig. 7, the MMT/Fe₃O₄/Ag nanocomposite can be successfully reused without the significant loss of its catalytic activity.

Conclusion

In this study, firstly MMT/Fe₃O₄ magnetic-nanoclay was synthesized by co-precipitation method and then Ag was doped to the MMT/Fe₃O₄ by chemical reduction method in order to obtain MMT/Fe₃O₄/Ag

nanocomposite. Presence of Ag and Fe ions in the MMT/Fe₃O₄/Ag nanocomposite were confirmed via using various methods like FTIR, SEM and XRD. Thus, we have demonstrated that the MMT/Fe₃O₄/Ag nanocomposite was synthesized successfully. Synthesized nanocomposite was found as an efficient catalyst for degradation of RhB in the presence of NaBH₄ as reducing agent. In addition, various parameters including pH, catalyst dosage, initial dye concentration and amount of NaBH₄ were investigated to determine optimum reaction conditions. The optimum values of pH, catalyst dosage, initial dye concentration and amount of NaBH₄ were found to be as 5.2, 1.51 g/L, 12 mg/L and 0.30 mL, respectively. While MMT/Fe₃O₄ was degraded RhB only at the rate of %46 within 60 minutes, MMT/Fe₃O₄/Ag was degraded RhB completely within 8 minutes. Thus, we have demonstrated catalytic activity of Ag on degradation of RhB. And, we believe that the easy separation of this nanocomposite from the reaction medium with a external magnet makes it a promising nanomaterial for the treatment of contaminated water with RhB.

Declarations

Authors' contributions All authors contributed to the study conception and design. Material preparation, data collection, and analysis were performed by Musa Kazim Acar and Turkan Altun. The first draft of the manuscript was written by Ilkay Hilal Gubbuk, and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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Compliance with ethical standards

Ethical approval and consent to participate Not applicable.

Consent to publish Not applicable.

Data availability The datasets used and/or analysed during the current study are available from the corresponding author on reasonable request.

Competing interests The authors declare that they have no competing interests.

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Figures

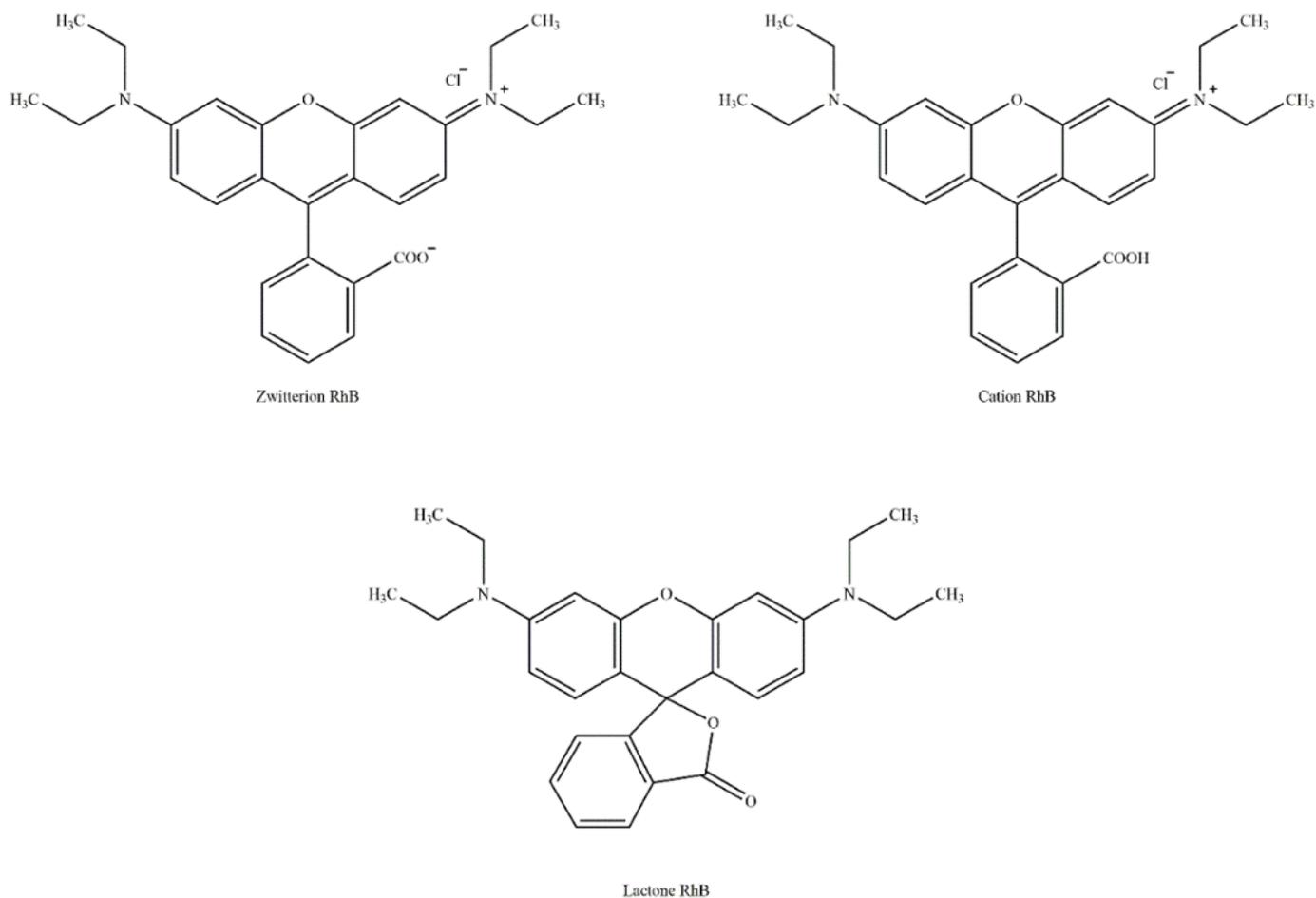


Figure 1

Cation, zwitterion and lactone forms of RhB

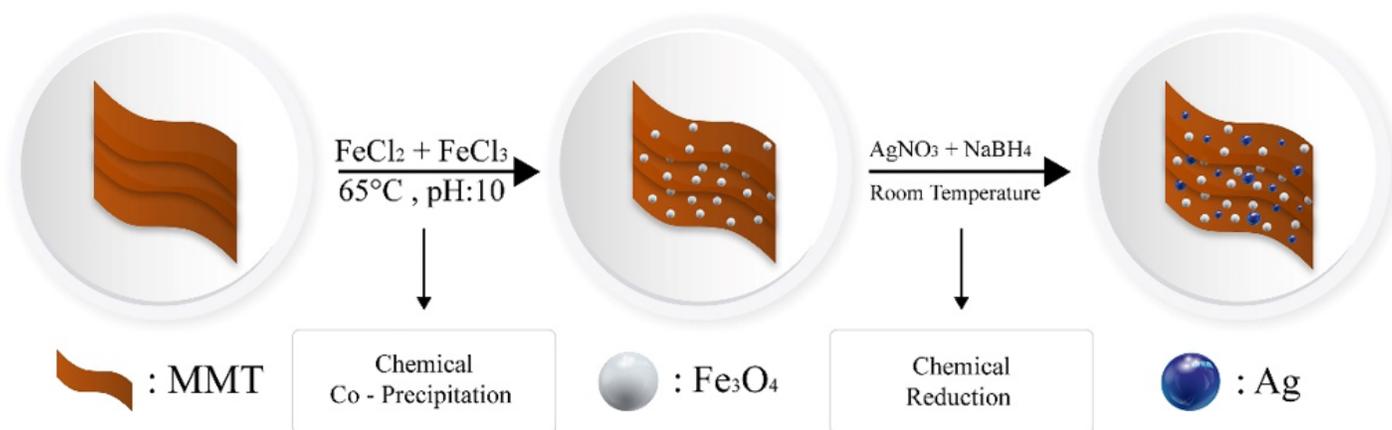


Figure 2

Schematic representation of the synthesis of MMT/ Fe_3O_4 and MMT/ Fe_3O_4 /Ag nanocomposites

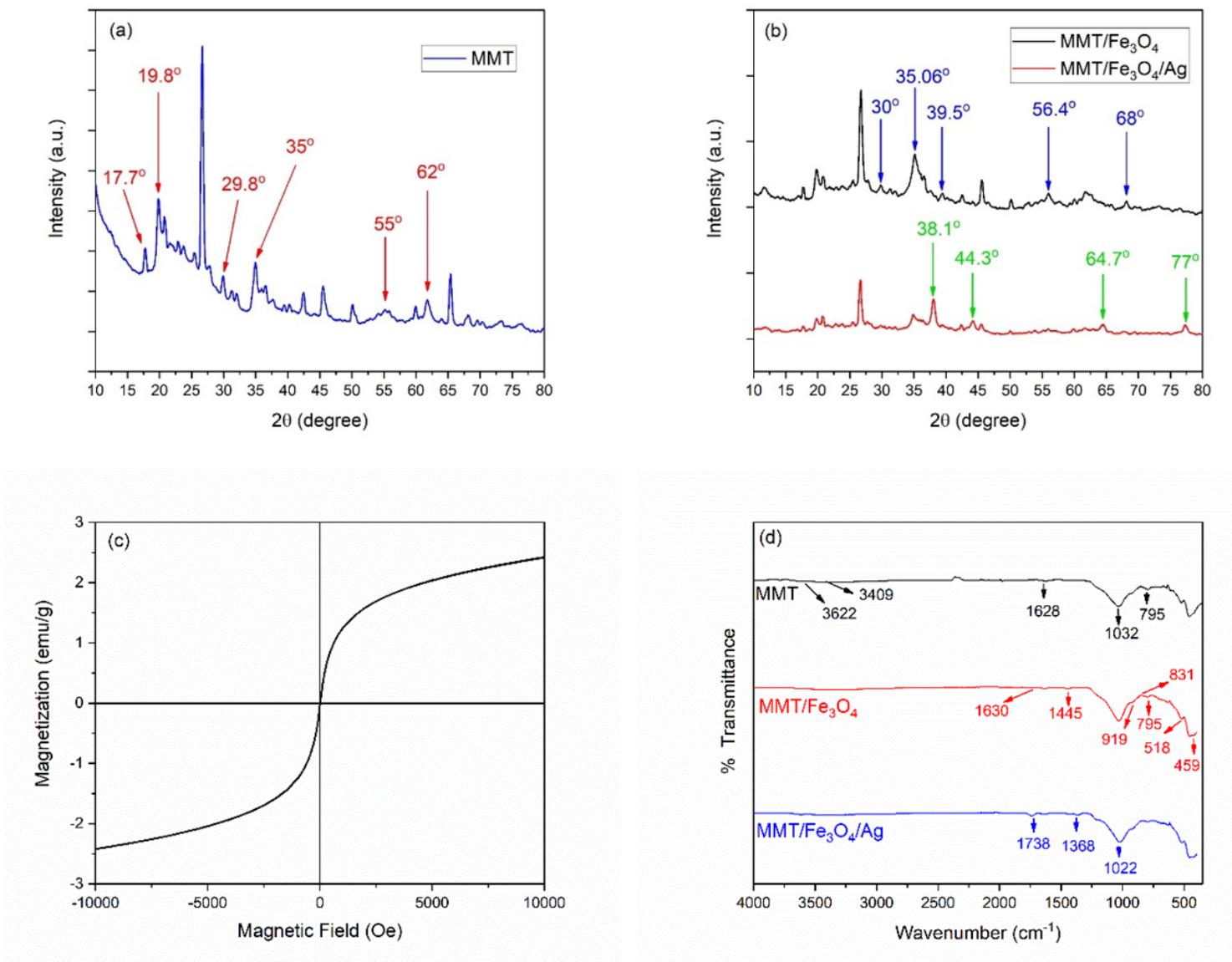


Figure 3

X-ray powder diffraction pattern of (a) MMT, (b) MMT/Fe₃O₄ and MMT/Fe₃O₄/Ag, (c) magnetization curve of MMT/Fe₃O₄/Ag and (d) FTIR analysis of MMT, MMT/Fe₃O₄ and MMT/Fe₃O₄/Ag

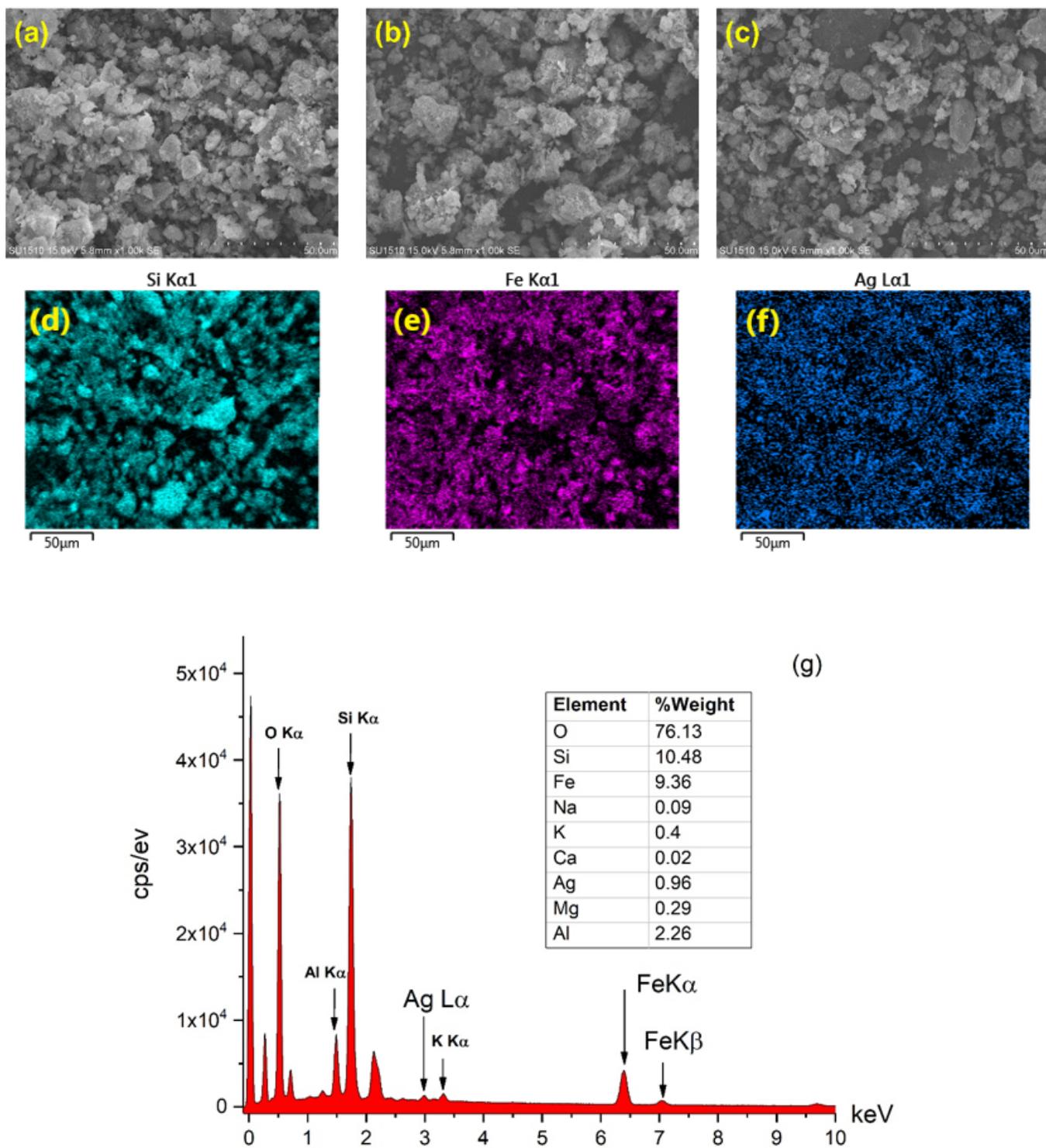


Figure 4

SEM images of (a) MMT, (b) MMT/Fe₃O₄ and (c) MMT/Fe₃O₄/Ag, elemental mapping image of (d) Si, (e) Fe and (f) Ag and (g) EDX spectrum of MMT/Fe₃O₄/Ag

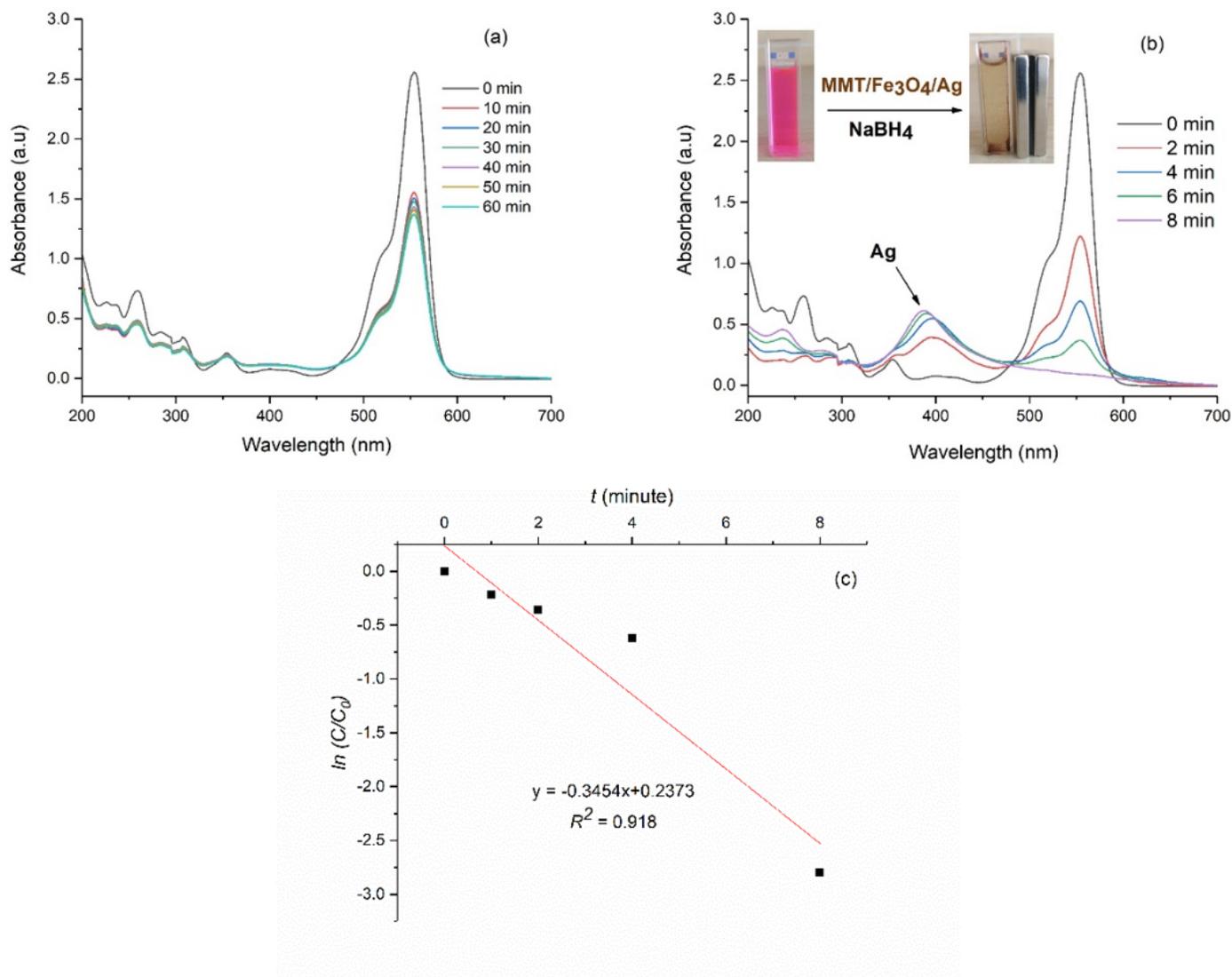


Figure 5

Time-dependent UV-Vis absorption spectra of RhB during catalytic reduction by (a) MMT/Fe₃O₄, (b) MMT/Fe₃O₄/Ag in the presence of NaBH₄ at room temperature [experiment conditions: pH=5.2, RhB=12 mg/L, catalyst dosage=1.51 g/L and NaBH₄=0.30 mL] and (c) Pseudo-first rate constant for the degradation of RhB by the MMT/Fe₃O₄/Ag nanocomposite in the presence of NaBH₄

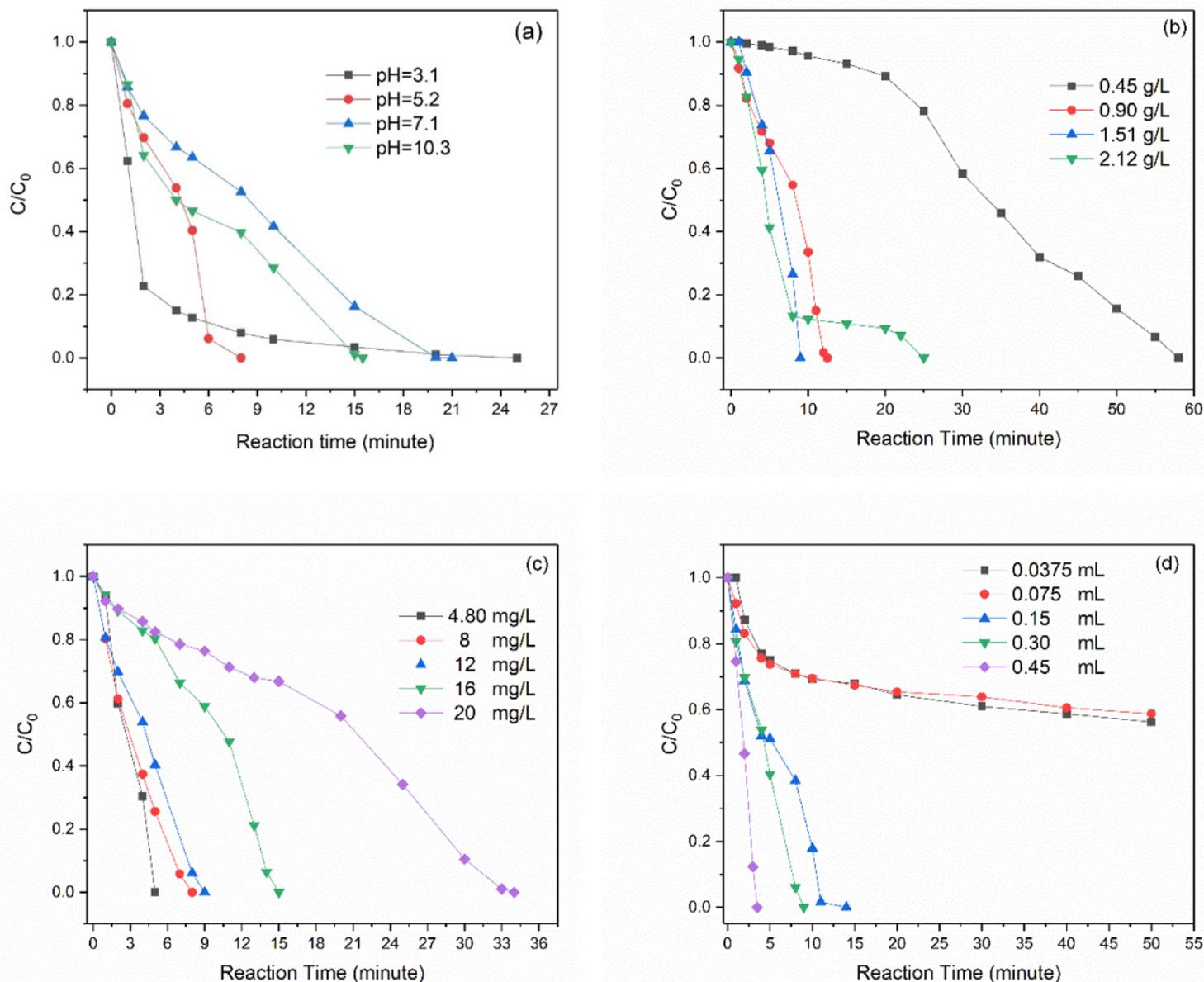


Figure 6

(a) Effect of pH on degradation of RhB using MMT/Fe₃O₄/Ag nanocomposite [experiment conditions: RhB=12 mg/L, catalyst dosage=1.51 g/L and NaBH₄=0.30 mL], (b) Effect of catalyst dosage on degradation of RhB using MMT/Fe₃O₄/Ag nanocomposite [experiment conditions: pH=5.2, RhB=12 mg/L and NaBH₄=0.30 mL], (c) Effect of initial concentration of RhB on degradation of RhB using MMT/Fe₃O₄/Ag nanocomposite [experiment conditions: pH=5.2, catalyst dosage= 1.51 g/L and NaBH₄=0.30 mL] and (d) Effect of amount of NaBH₄ on degradation of RhB using MMT/Fe₃O₄/Ag nanocomposite [experiment conditions: pH=5.2, catalyst dosage= 1.51 g/L and RhB= 12 mg/L]

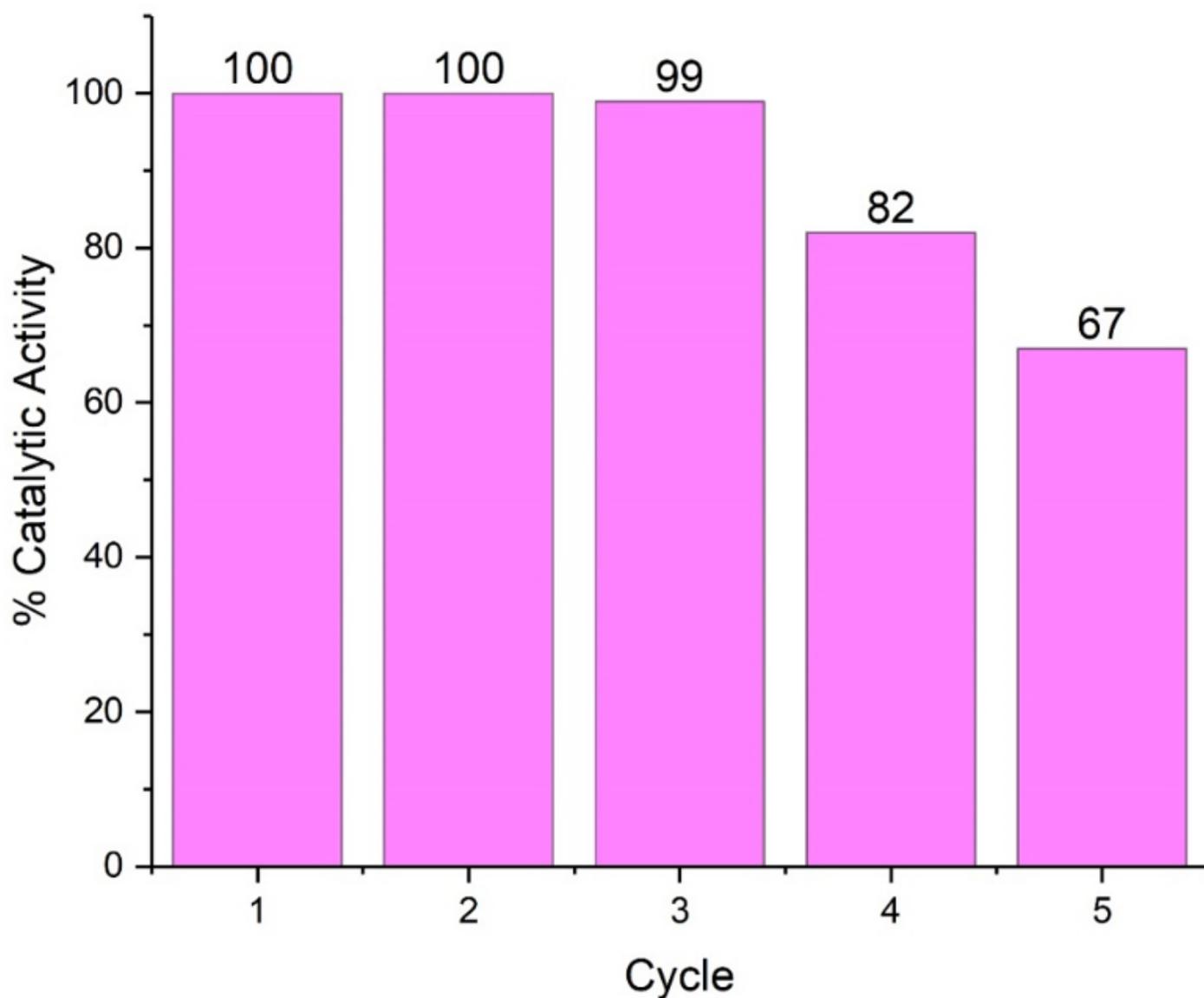


Figure 7

Reusability of MMT/Fe₃O₄/Ag nanocomposite

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