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Synthesis of Zero-Valent Iron Nanoparticles on Polyester Non-Woven Fabric Using Green Chemistry Method for Wastewater Treatment in the Textile Dyeing Industry

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Abstract

Wastewater from the dyeing process is causing serious issues for the ecosystem and humans. Zero-valent iron nanoparticles have been proven as a promising material for environmental treatment through numerous previous studies. In this research, green-synthesized zero-valent iron nanoparticles were obtained from the leaf extract of the Cleistocalyx operculatus. These nanoparticles were then applied onto polyester non-woven fabric with alginate coating on the fabric surface. The polyester nonwoven fabric used in this study was (poly ethylene terephthalate) (PET) needle-punched non-woven fabric. The modified polyester non-woven fabric with alginate and zero-valent iron nanoparticles (PET/Alginate/nZVI), alginate-coated polyester non-woven fabric (PET/Alginate), and the original polyester non-woven fabric (PET) were evaluated for morphology and structure using scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). The capability of removing the organic dye Rhodamine B was assessed through UV-Vis spectroscopy. The influence of iron dosage, solution concentration, and solution pH on the dye removal capacity of the material was investigated. Results show that the material has been successfully synthesized for high-performance removal of Rhodamine B dye with an efficiency of 98% after 10 minutes of treatment, and it can be reused multiple times with an efficiency of over 70%.

Keywords: Alginate, green synthesis, polyester nonwoven fabric, zero-valent iron nanoparticles.

1. Introduction

The rapid development of Vietnam's textile industry entails factors that directly affect the environment. One of the serious sources of pollution from the textile industry is textile wastewater containing a large amount of dye residue, which greatly affects the water environment, aquatic species, and humans.

Zero-valent nano iron material is being focused on research and development in environmental treatment because of its outstanding properties such as low price, high on-site reactivity, and high treatment efficiency, it is also easy to manufacture and environmentally friendly [1,2]. Zero-valent nano iron has the ability to treat organic compounds through advanced oxidation by reacting with water to form hydroxyl radicals with strong oxidizing ability that directly reacts with dye molecules to produce intermediate compounds, finally CO_2 and H_2O and inorganic ions to achieve complete decomposition [3]. Synthesizing zero-valent nano iron with Cleistocalyx operculatus (CO) leaf extract is a green, friendly synthesis method and limits environmental oxidation [4]. There have been many studies on zero-valent nano iron for environmental treatment, but the problem of product recovery and reuse is still limited. Nano iron tends to agglomerate, reducing treatment efficiency.

Nonwoven geotextile (NG) fabrics are widely used in engineering industries such as irrigation, transportation and environment. NG fabrics consist of continuous short or long fibers randomly arranged and bonded together by thermal, chemical or mechanical means. NG fabrics have high durability, resistance to damage during construction, installation and use, the fabric has appropriate characteristics of back filtration and drainage and high durability when exposed to light. The polyester nonwoven fabric used in this study is a highly porous, permeable geotextile [5], capable of separating, filtering, protecting, reinforcing and draining water in all different directions, creating favorable conditions for the circulating exchange solution to enter the fabric structure, increasing waste water treatment efficiency. Alginate is purified from brown seaweed and has the ability to form gel when hydrated. Alginate is commonly used in the food, textile printing and pharmaceutical industries due to its

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compatible, biodegradable and non-toxic properties [6,7]. The abundance of carboxylic groups makes alginate capable of modifying fiber surfaces, which can provide additional sites for the binding of zero-valent iron nanoparticles (nZVIs) [7].

This research aims to manufacture polyester-poly (ethylene terephthalate) (PET) nonwoven fabric which was modified with alginate and zero-valent nano iron for wastewater treatment in the textile dyeing industry. In this process, zero-valent iron nanoparticles have a main and important role in removing color dyes. The structure of the dye molecules which are normally organic materials is broken to be simple intermediates and finally carbon dioxide, water, or other inorganic products through advanced oxidation process. While nonwoven fabric is used as a carrier, increasing the surface area, limiting the tendency of aggregation of zero-valent iron nanoparticles, increasing the catalytic area, processing capacity, and is convenient for recovering and reusing nZVIs. Alginate is used as a fiber surface modifier to improve the bonding efficiency between nZVIs and polyester fabric. PET/Alginate/nZVIs fabric was used to degrade Rhodamine B colorant according to adsorption and advanced oxidation mechanisms. In particular, nZVIs play a key role in the colorant treatment process as evaluated by UV-Vis ultraviolet absorption spectrum.

2. Experiment

2.1. Materials

The dispersed solution of zero-valent iron nanoparticles was prepared using a green chemistry method through the utilization of Cleistocalyx operculatus leaf extract as a reducing agent for Iron (III) chloride hexahydrate solution (FeCl3.6H2O; 99.0%; China). The dispersed solution of zero-valent iron nanoparticles with a concentration of 1000 ppm was used to modify nonwoven fabric coated with a layer of sodium alginate ($(C_6H_7O_6Na)_n$ 100.0%; China) through immersion and drying. To solidify the alginate layer after being coated with nano iron and alginate, the nonwoven PET fabric sample, which was modified, was immersed for 30 minutes in a 1% $CaCl_2$ solution ($CaCl_2$ - China, 98%). A Rhodamine B dye solution ($C_{28}H_{31}ClN_2O_3$; 99.5%; China) with concentrations of 2, 4, 5, 6, 8, and 10 mg/L was prepared to investigate the treatment ability of the PET/Alginate/nZVI fabric material. The Polyester nonwoven fabric weighs 150 g/m^2.

2.2. Synthesis of Materials

0.3 grams of PET nonwoven fabric was immersed in 0.1% sodium alginate solution for 10 minutes. After, the fabric was cured at 100 °C for 10 minutes, followed by rinsing with distilled water and drying at room temperature (PET/Alginate). The fabric sample was immersed in 4 mL of zero-valent iron nanoparticle solution with a concentration of 1000 mg/L, combined with ultrasonication for 5 minutes then cured at 100 °C for 15 minutes. Next, the functionalized fabric sample was dipped into 1% $CaCl_2$ solution, rinsed twice with distilled water after 30 minutes, and dried at room temperature. The PET/Alginate/nZVIs fabric was characterized to evaluate morphology, structure, and Rhodamine B dye treatment capability.

2.3. Evaluating the Structural Morphology of the Material

SEM was used to observe the surface morphology of samples: non-woven PET fabric before and after coating with alginate, and functionalized with zero-valent iron nanoparticles (nZVIs). The interaction between the materials was characterized using FTIR. The presence of nZVIs on the functionalized fabric samples and the iron nanoparticle content were assessed by atomic absorption spectrometric (AAS).

2.4. Evaluating the Ability to Treat Rhodamine B Dye

The treatment ability of Rhodamine B dye of the PET/Alginate/nZVIs material was evaluated using UV-Vis spectroscopy. The key factors influencing the RhB dye treatment efficiency were studied, including dosage of zero-valent iron nanoparticles coated on the fabric, namely 2, 3, 4, 5, 6, and 7 mL; RhB dye solution concentrations were changed to 2, 4, 5, 6, 8 and 10 mg/L; RhB solution pH values at 1, 3, 5, 7, 9; and RhB dye treating times of 5, 10, 15, 30, 60 minutes. After the treatment process, the RhB solutions before and after treatment were analyzed using UV-Vis spectroscopy, and the dye concentration was calculated at the characteristic wavelength of 554 nm.

Constructing a standard curve is a common method to evaluate the efficiency of dye treatment. Rhodamine B solutions with concentrations of 1, 2, 4, 6, 8, and 10 mg/L were prepared and measured using UV-Vis spectroscopy to construct the standard curve (the relationship between concentration and optical absorption).

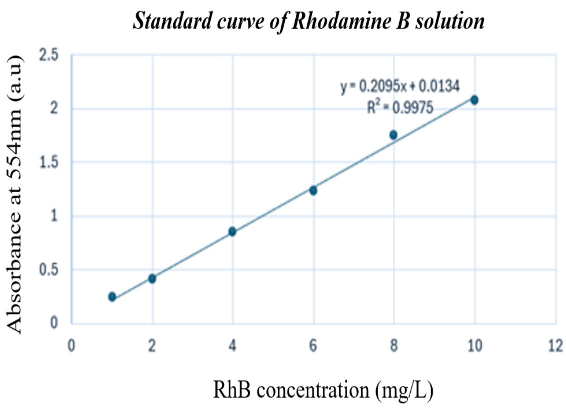

Fig. 1. Standard curve of Rhodamine B solution

3. Results and Discussion

3.1. The Synthesis Process of the Material, Its Morphology and Structure

Images of PET fabric before modification and after coating with iron and alginate are shown in Fig. 2. Observing the fabric samples reveals that the original PET fabric has a white color due to its chemical fiber origin, having been cleaned, treated, and commercialized. The PET fabric is quite porous with protruding fiber ends on the fabric surface, increasing the surface area available for nano iron coating. After coating PET fabric with nZVIs and alginate, the PET fabric has a black color of zero-valent nano iron, and the nano iron is evenly coated across the entire fabric surface.

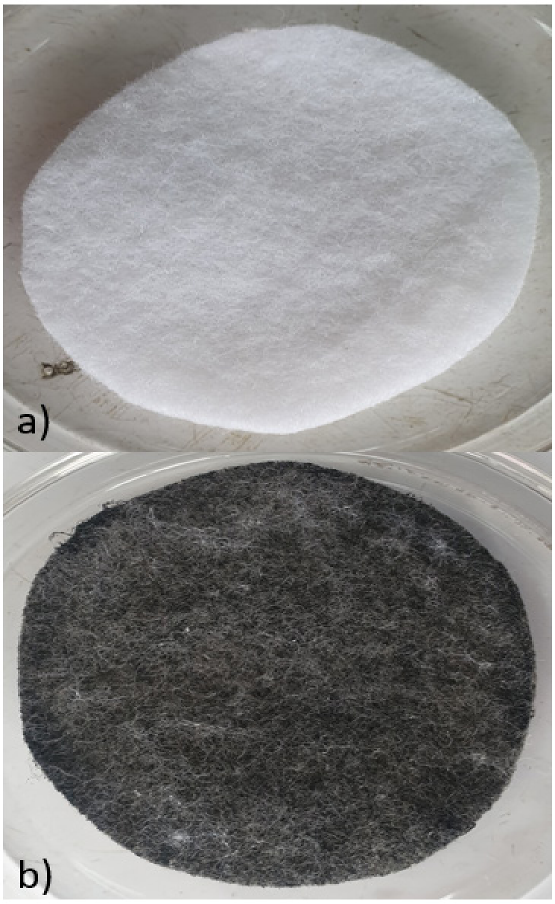

Fig. 2. PET fabric before (a) and after functionalized with alginate and nZVIs (b)

The morphology of PET fabric, PET/Alginate, and PET/Alginate/nZVIs fabric were observed by SEM (Fig. 3). PET non-woven fabric (Fig. 3a and 3b) consists of fibers with a cylindrical morphology, smooth and light reflection surface. After coating the fabric with a thin layer of alginate (Fig. 3c and Fig. 3d), there is a significant change in the fiber surface. The alginate coating fibers reduce light reflection compared to untreated PET fabric, and some alginate is embedded within the non-woven fabric matrix forming small clusters. Images of non-woven polyester fabric coated with nZVIs and alginate are shown in Fig. 3e and Fig. 3f. It is clearly visible that the surface of the fibers has changed significantly, zero-valent iron nanoparticles evenly coated on the fiber surface and also on the surface of alginate clusters within the non-woven fabric matrix.

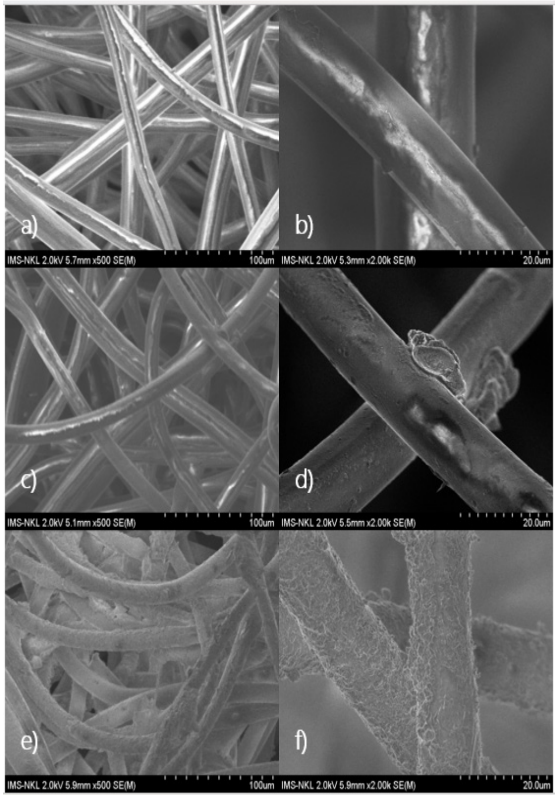

Fig. 3. SEM images of PET fabric (a, b); PET/Alginate (c, d) and PET/Alginate/nZVIs fabric (e, f)

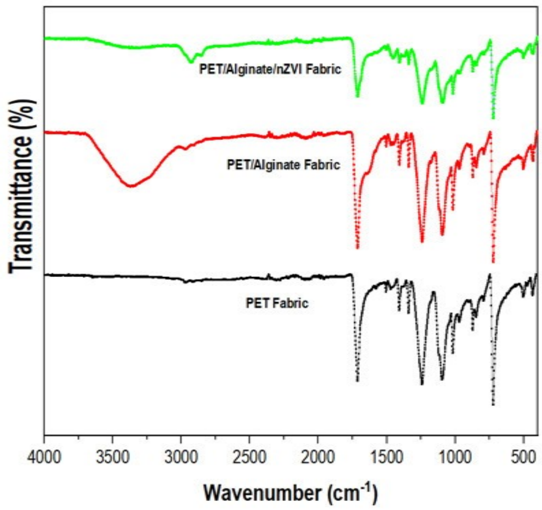

Fig. 4. FTIR spectrum of PET fabric; PET/Alginate and PET/Alginate/nZVIs fabric

FTIR spectroscopy was used to evaluate the bonding and chemical nature present in the materials.

The FTIR spectra of PET/Alginate/nZVI fabric were compared with those of PET fabric and PET/Alginate fabric (Fig. 4). The non-woven PET fabric exhibits several bands in the range of 1712 - 430 cm^{-1} associated with vibrations of C–H, C=O, C–O–C, and C=C bonds of the polyester non-woven fabric structure. At the wavenumber of 1504 cm^{-1}, and 722 cm^{-1}, characteristic peaks of aromatic C–H bonds are observed for all three fabric samples. The presence of C=O double bonds and C–O–C single bonds of esters results in peaks appearing at wavenumbers 1712 cm^{-1}, 1241 - 1094 cm^{-1}, respectively. Additionally, there are C=C double bonds at the wavenumber of 969 cm^{-1} for all samples.

The FTIR spectrum of PET fabric coated with alginate exhibits additional peaks at 3370 cm^{-1} corresponding to the O–H bond, 1597 cm^{-1} for the COO– bond, C–H bond at 1470 - 1452 cm^{-1}, and C–O–C bond at 1176 cm^{-1}, indicating the presence of alginate hydrogel on the surface of PET fibers. The FTIR spectrum of polyester fabric coated with zero-valent iron nanoparticles and alginate still shows characteristic peaks of both PET fibers and alginate. Additionally, a peak at 530 cm-1 appears, confirming the presence of Fe–O bond [6, 8-9].

The additional appearance of peaks corresponding to the O–H bond and the COO– bond in PET/Alginate fabric compared to the original PET fabric can demonstrate that the presence of alginate has enriched the carboxylic groups on the material's surface, providing additional sites for bonding with zero-valent nano iron particles. The Fe–O bond appearing in the FTIR spectrum of PET/Alginate/nZVIs fabric confirms the presence of nano iron on the fabric after modification.

To determine the actual presence and quantify the nZVIs coated on the surface of PET fibers, the functionalized fabric sample was immersed, extracted, and prepared for AAS analysis. The results indicated an iron concentration of 3.97 mg/L in the obtained solution. The nano iron concentration used to prepare the modified fabric sample was 4 mg/L. This demonstrates that the majority of the nano zero-valent iron used in the synthesis process has been coated onto the surface of polyester fibers during the modification process.

3.2. Rhodamine B Removal

To evaluate the efficiency of Rhodamine B dye removal, zero-valent iron nanoparticles were synthesized on PET fabric coated with alginate using the procedure outlined in the experimental section.

The influence of different amounts of zero-valent iron nanoparticles used in modifying 0.3 g of PET fabric from 0; 2; 3; 4; 5; 6; 7 mL on the efficiency of treating 50 mL of 5 mg/L Rhodamine B solution (Fig. 5). The efficiency removal of RhB dye of 0 mL nZVI sample reached only nearly 20% in the first use. While PET fabric was modified with Alginate and 2, 3, 4, 5, and 6 mL of nZVIs solution, the RhB dye removal efficiency reached over 98% in the first use and fluctuation between approximately 40% to 70% in the fifth reuse with the different amounts of the nZVIs solutions.

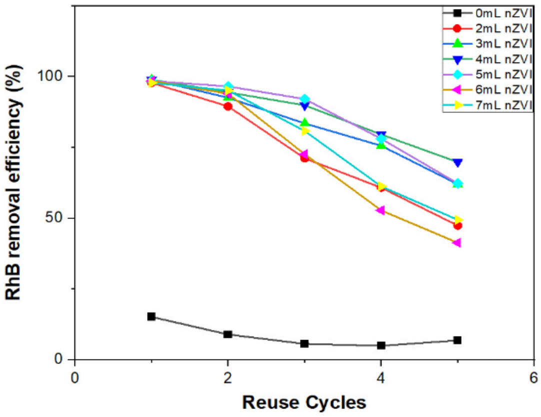

Fig. 5. Effect of zero-valent iron nanoparticles amount on RhB treatment efficiency of 5 mg/L through 5 reuses

The ratio between the adherent material - nZVIs and the substrate material - PET fibers is crucial as it relates to the thin, uniform coating of iron nanoparticles on the entire fabric, thereby providing a large working surface area and the best dye removal capability. With 4 mL of nZVIs solution (equivalent to 4 mg of iron presence), the RhB dye removal efficiency reached 98.99% in the first use and remained above 70% in the fifth reuse. The ratio of 4 mL of nano iron for modifying 0.3 g of non-woven PET fabric is the optimal ratio for Rhodamine B dye treatment.

The influence of processing time on the Rhodamine B (RhB) dye removal efficiency of PET/Alginate/nZVIs fabric was investigated with time intervals of 5; 10; 15; 30; 60 minutes. Additionally, the dye removal capabilities of PET fabric, PET fabric coated with Alginate, and PET fabric modified with nano iron were compared. The research results showed that the RhB dye removal efficiency of PET fabric was negligible. For PET fabric coated with alginate, the maximum removal efficiency was approximately 20%, while it reached 99.27% for the nZVIs functionalized fabric after 30 minutes. The results in Fig. 6 also indicated that after 10 minutes, the removal efficiency of the nano iron-modified fabric reached 98.32%, but it decreased to 96.6% at 15 minutes before increasing again and reaching 99.27% at 30 minutes.

Extending the processing time further showed almost no change in efficiency. This can be attributed to the adsorption and desorption mechanisms of alginate. Selecting 30 minutes as the optimal processing time for RhB dye treatment is ideal as most of the dye is processed by then, and the treatment efficiency reaches 99.27%. It can be confirmed that

PET fabric modified with nZVIs has good RhB dye removal capabilities, utilizing a combination of alginate's adsorption mechanism and nano iron's advanced oxidation mechanism. Specifically, the dye removal process of nano iron is the dominant process, five times more effective than the adsorption process of alginate [2, 4].

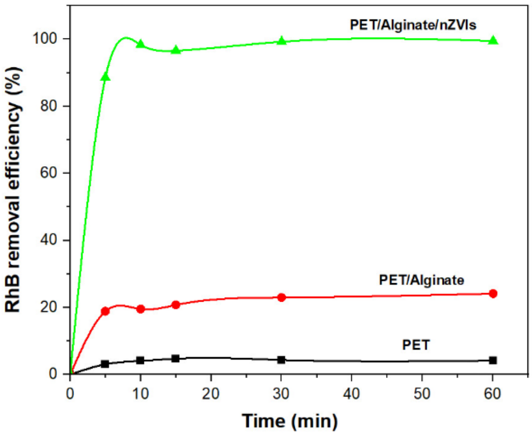

Fig. 6. Effect of treatment time of 5 mg/L RhB solution using PET Fabric-PET/Alginate Fabric-ET/Alginate/nZVIs Fabric

The influence of Rhodamine B (RhB) concentration on the treatment efficiency and reusability of nano iron-modified PET fabric was also evaluated by varying the RhB solution concentrations from 2 to 4, 5, 6, 8, 10 mg/L. The evaluation results in Fig. 7 showed that at a RhB solution concentration of 5 mg/L, the treatment efficiency in the first reuse exceeded 99%, and by the fifth reuse, the dye removal performance remained above 70%. The RhB solution with a concentration of 5 mg/L was chosen for further studies.

The pH of the solution is an important factor in wastewater treatment because for wastewater containing organic dyes, the color of the dye can change at different pH environments, leading to significant variations in treatment efficiency. The results in Fig. 8 show that at acidic and neutral pH environment (pH = 1; 3; 5; 7), the dye removal efficiency exceeded 95% in the first reuse and remained above 70% in the second reuse. When pH = 9, the treatment efficiency decreased to below 50% after the second reuse. Therefore, acidic and neutral environments are suitable for Rhodamine B (RhB) dye treatment using PET/Alginate/nZVIs fabric. The experimental results are consistent with previous studies on using nano iron for RhB dye treatment [10, 11]. At pH = 5, RhB dye was removed by over 90% after three reuses and over 75% after the fifth reuse. pH = 5 is the chosen environment for further studies and applications.

As mentioned above, the main objective of incorporating nZVIs onto non-woven polyester fabric is ease of recovery and reusability of the material after environmental treatment. Using PET fabric as the carrier material facilitates the removal of the material for reuse purposes, making it very convenient. Additionally, it can be used in the form of artificial aquatic mats, floating on treatment ponds to harness additional heat and sunlight resources.

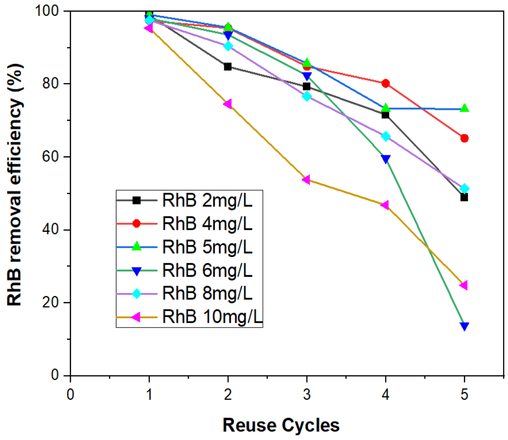

Fig. 7. Effect of RhB solution concentration on treatment efficiency

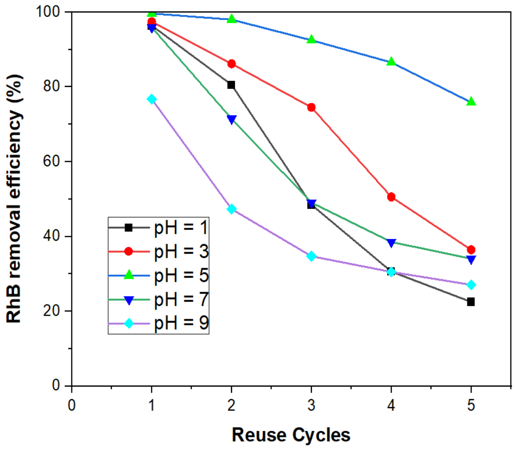

Fig. 8. Effect of pH of RhB solution on treatment efficiency

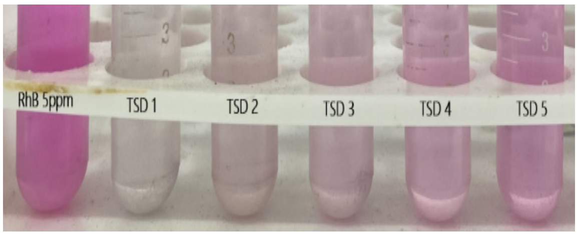

Fig. 9. 5 mg/L RhB solution after being treated with PET/Alginate/nZVI Fabric

Observing the images of Rhodamine B (RhB) dye solutions at 5 mg/L before and after treatment (Fig. 9) with different reuse cycles of the nZVIs-modified PET fabric shows a significant reduction in the characteristic pink color of RhB.

The reusability of materials was investigated using optimal conditions such as pH = 5, color dye removal time is 30 minutes and the ratio of 4 mL of nZVIs for modifying 0.3 g PET fabric. After each RhB treatment, the PET/Alginate/nZVIs fabric was removed from the treated solution and rinsed with distilled water. Then, it was used to treat a new RhB color dye solution under the same condition. To compare the color dye removal ability of nZVIs before and after covering on the PET fabric, 4mL of the nZVIs was directly used to treat RhB solution under the same experimental conditions.

Based on the calculated results, the Rhodamine B (RhB) dye removal efficiency through multiple reuse cycles is depicted in Fig. 10. It shows that the RhB dye removal efficiency of the PET-Alginate-nZVIs fabric in the first cycle reached 97%, and after 5 reuse cycles, the treatment effectiveness approached 70%. Meanwhile, RhB dye removal efficiency of nZVIs reached 92% and insignificantly lower than the dye removal efficiency of PET/Alginate/nZVIs fabric in the first use. However, as mentioned above, retrieving to reuse of nZVIs is difficult.

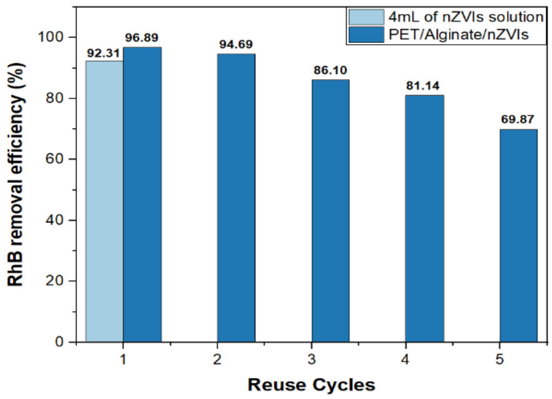

Fig. 10. Treatment efficiency of 5 mg/L RhB solution by PET/Alginate/nZVIs Fabric and nZVIs after five recycle

The perfect combination of carrier material, non-woven PET fabric, along with alginate and nZVIs has demonstrated excellent dye removal capabilities and easy recovery and reusability of the material.

4. Conclusion

Non-woven polyester fabric functionalized with zero-valent iron nanoparticles synthesized using green chemistry and alginate has been successfully developed through a simple process. The nZVIs are anchored onto the fabric using evenly distributed alginate, with no chemical interaction between the fabric, alginate, and nZVIs. FTIR analysis, and AAS characterizations have demonstrated the presence of nZVIs on the material. This allows us to conclude that the polyester fabric material functionalized with nZVIs and alginate can be used as catalyst in an advanced oxidation process for environmental organic pollutant treatment.

The PET/Alginate/nZVIs fabric exhibits excellent dye removal capabilities and can be reused multiple times. When treating a RhB dye solution with a concentration of 5 mg/L, at pH 5, and a treatment time of 30 minutes, the material achieved a treatment efficiency of 98% and could be reused up to 5 times with an efficiency exceeding 70%. The PET/Alginate/nZVIs fabric demonstrates thorough dye removal capabilities. Furthermore, non-woven polyester fabric is commonly used in the market due to its affordability, good mechanical and physical properties, and widespread applications in geotextiles. Alginate, a safe natural compound, finds extensive use in medical, food, and other industries. The zero-valent iron nanoparticles (nZVI) are synthesized using a green chemistry approach with reducing agents from the Cleistocalyx operculatus Leaf Extract, which are abundant in our country and often used to make beverages. This fabric material holds promising potential for future environmental pollution treatment, offering high efficiency, safety, cost-effectiveness, ease of fabrication and multiple reusability.

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