



A new catalyst material from electrospun PVDF-HFP nanofibers by using magnetron-sputter coating for the treatment of dye-polluted waters

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Abstract

In this study, polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP)-based nanofibers were produced by electrospinning technique on aluminum substrate and coated with magnetron sputtering technique by using Cu₂O photocatalyst target material. Resulting materials were characterized by SEM, EDX, and UV diffuse reflectance spectroscopy. Photocatalytic activity of the material was tested against methylene blue decolorization under 105 W tungsten light bulb. Methylene blue concentration was followed up by UV visible spectrophotometer at 664 nm. Kinetic modeling of the photocatalytic reaction was found suitable to the first-order kinetics. Reaction rate constants were 0.0037, 0.0044, and 0.0050 min⁻¹ respectively with corresponding half-life times of 187, 158, and 139 min. Thanks to the genuine design of the catalyst, it allowed easy removal of the material from the solution without any residue by simple tweezers which is a promising step for getting rid of heavy and low yield of filtration processes in the separation of particulate catalysts from the treated water.

Keywords Photocatalysis · Electrospinning · PVDF-HFP · Magnetron sputtering

1 Introduction

Electrospinning is a unique method of producing nanofibers from polymer solutions or melts using an electrostatic field [1]. Many parameters can influence the conversion of polymer solutions into nanofibers via electrospinning. These parameters include solution properties such as viscosity, elasticity, conductivity and surface tension, hydrostatic pressure in the capillary tube, electrical potential at the capillary end, and distance between the needle tip and the collector screen and the ambient parameters such as solution temperature, humidity, and air velocity in the electrospinning chamber [2]. The fibers produced by the electrospinning method have a thinner diameter and a very large surface area than the fibers obtained using conventional methods such as wet spinning, dry spinning, melt spinning, and gel spinning [3].

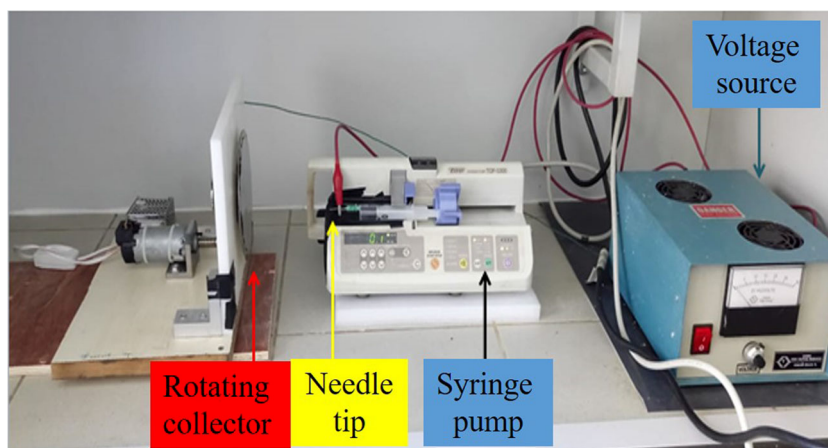
PVDF (polyvinylidene fluoride) is a thermoplastic polymer with high mechanical strength and durability, and high wear resistance and chemical resistance towards many chemicals. To benefit from these properties, several studies have been attempted by many researches. Hwang et al. aimed to prepare the porous PVDF nanoseparators with improved mechanical properties and increased electrolyte uptake. For this purpose, they reported a dimethylacetamide (DMAc):acetone (3:7) solvent system for preparing a PVDF electrospinning solution at a concentration of 19% which resulted in 10–30-μm fiber diameter [4]. Zhou and Wu have done a study aiming to produce super-hydrophobic PVDF membranes in a single step by electrospinning method with DMF: acetone solvent mixture; their reported fiber diameter was between 570 and 4820 nm [5]. In a study carried out by Wu and Chou, two solutions of 22% PVDF and 0.5% CNT added PVDF were prepared with 6:4 ratio of DMF:acetone solvent system. Diameters were determined to be 156 nm and 138 nm for PVDF and CNT added PVDF fibers, respectively. They concluded that the addition of carbon nanotubes reduced the fiber diameter of PVDF, thus achieving high surface area/volume [6]. PVDF-HFP is the derivative of PVDF polymer having the same properties which can be electrospun for different applications such as composite membranes, antimicrobial mats, piezoelectric nanogenerators, and nanocomposite membrane electrodes [7–9].

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Fig. 1 The photograph of electrospinning device



However, the studies benefiting of electrospun PVDF-HFP in the photocatalysis area are not very common. As an abundant p-type semiconductor having a band gap of about 2.0 eV, copper oxide (Cu_2O), with unique optical and magnetic properties, is promising in the areas such as solar energy conversion, lithium-ion battery development, photocatalytic decomposition of organic contaminants, and water splitting [10]. Zheng et al. reported the loading of Cu_2O nanoparticles by a simple solvothermal method on RGO (reduced graphene oxide) in an easy and efficient way. This material, which was prepared as photocatalyst, was used for degradation of rhodamine B dye under visible light [11]. Miao et al. investigated the photocatalytic activity of RGO/PANI/ Cu_2O composite hydrogel and the photocatalytic degradation of Congo red (CR) dye [12]. But many of similar studies use Cu_2O in powder or nanoparticle form. Magnetron sputtering coating method is a very powerful technique to obtain very fine thin films. Films obtained by magnetic sputtering method show better performance compared with films obtained by other physical deposition methods such as solution casting, electrochemical deposition, spray coating, and sol-gel growth [13–16]. Main disadvantages of these techniques when compared with the magnetron sputtering are non-uniform distribution over the surface, grain size of the particles, and the film thickness cannot be reduced as much as the magnetron sputtering does. Also due to the atomic size of sputtered particles, penetration ability of the magnetron sputtering technique is superior [17, 18]. The magnetic sputtering method is of great interest in

areas such as hard, wear-resistant coatings, decorative coatings, corrosion-resistant coatings, and coatings with special optical or electrical properties [19–23].

By taking the advantage of these properties of magnetron sputtering coating, very useful nanoarchitecture may be obtained with Cu_2O catalyst in case of coating on electrospun nanofibers which is not encountered in the literature to the best of our knowledge. In the present study, polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) has been used to prepare nanofibers by electrospinning method and coated with Cu_2O photocatalyst material for the first time with magnetron sputtering technique to obtain a homogeneously coated surfaces and its photocatalytic activity was tested with decolorization of methylene blue (MB) as a model dye to represent the polluted wastewaters which can cause heart palpitations, vomiting, shock, cyanosis (bruising of the skin and mucous membranes), jaundice, quadriplegia (paralysis of arms and legs), and tissue necrosis (tissue deaths) as a result of prolonged exposure [24].

2 Material and methods

Polyvinylidene fluoride-co-hexafluoropropylene (PVDF-HFP) and N,N-dimethylformamide were obtained from Sigma and acetone from VWR International; methylene blue was from Merck. Disc-shape Cu_2O target material was purchased from Goodwill Metal Tech. Company with 99.9% purity. Diameter of the disc and its thickness are 2 in. and 0.125 in. respectively.

Table 1 Magnetron sputtering parameters for PVDF-HFP nanofibers

Sample name	Catalyst	Mat	Power (W)	Vacuum level (mTorr)	Coating thickness (nm)	Coating rate (angstrom/s)
PVDFHFPC 100	Cu_2O	PVDF-HFP nanofiber	60	10	100	0.7
PVDFHFPC 200	Cu_2O	PVDF-HFP nanofiber	60	10	200	0.7
PVDFHFPC 300	Cu_2O	PVDF-HFP nanofiber	60	10	300	0.7

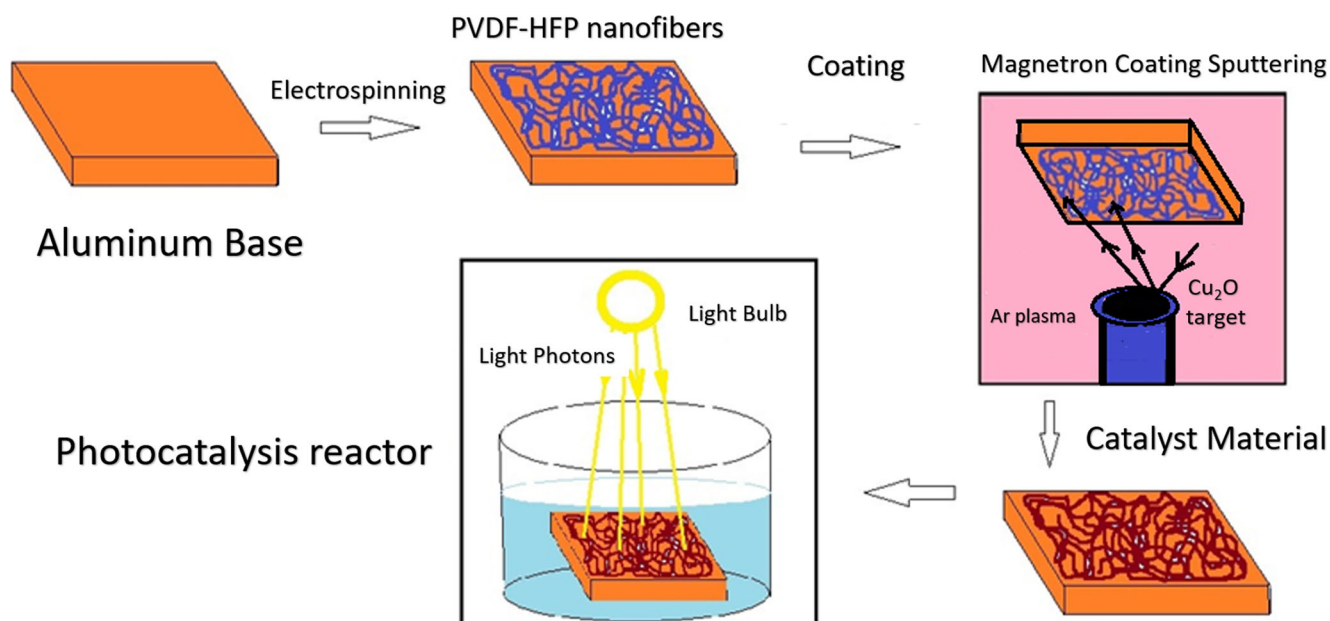


Fig. 2 Production route for catalyst material

Target material was provided with a backing plate to prevent any damage that may stem from arc discharges.

2.1 Nanofiber production by electrospinning technique

The device consisting of syringe pump, voltage source, needle tip, and rotating collector plate used for the production of nanofiber is given in Fig. 1. The TOP-5300 syringe pump is used to ensure controlled solution flow in the electrospinning process.

2.2 Preparation of catalysts by magnetic sputtering coating

Magnetic sputtering was carried out by Nanovak on the NVTH-350 model PVD system. Cu₂O, which is selected as target material, has been deposited in different thicknesses on PVDF-HFP nanofiber mat produced by electrospinning method and supported on 5 × 5 cm² aluminum base. The coating thicknesses were chosen as 100 nm, 200 nm, and 300 nm. The parameters of the Cu₂O coating are given in Table 1. Representative picture of the catalyst production is given in Fig. 2.

Table 2 The optimum electrospinning parameters for the production of PVDF-HFP nanofibers

Polymer	Concentration (%)	Voltage (kV)	Distance (cm)	Flow rate (mL/h)
PVDF-HFP	5	15	10	0.3

2.3 Photocatalytic decolorization of methylene blue

Photocatalysis experiments were performed under visible light emitted by a 105 W tungsten bulb. The change in methylene blue concentration during photocatalysis was followed by the absorbance intensity measured with UV-Vis spectrophotometer at 664 nm, the maximum absorption wavelength of the dye.

2.4 Theory of decolorization kinetics

Decolorizing efficiency of methylene blue was calculated using Eq. 1:

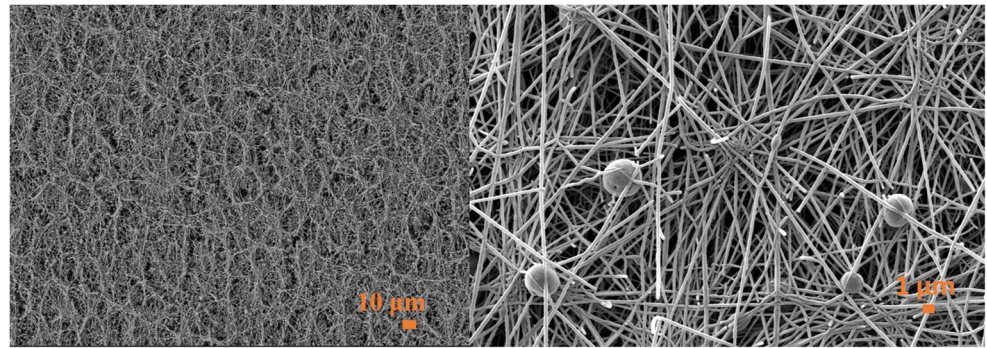
$$(D_e) = \frac{C_i - C_t}{C_i} \times 100 \quad (1)$$

where C_i is the dye concentration at the beginning and C_t is the time-dependent concentration of MB.



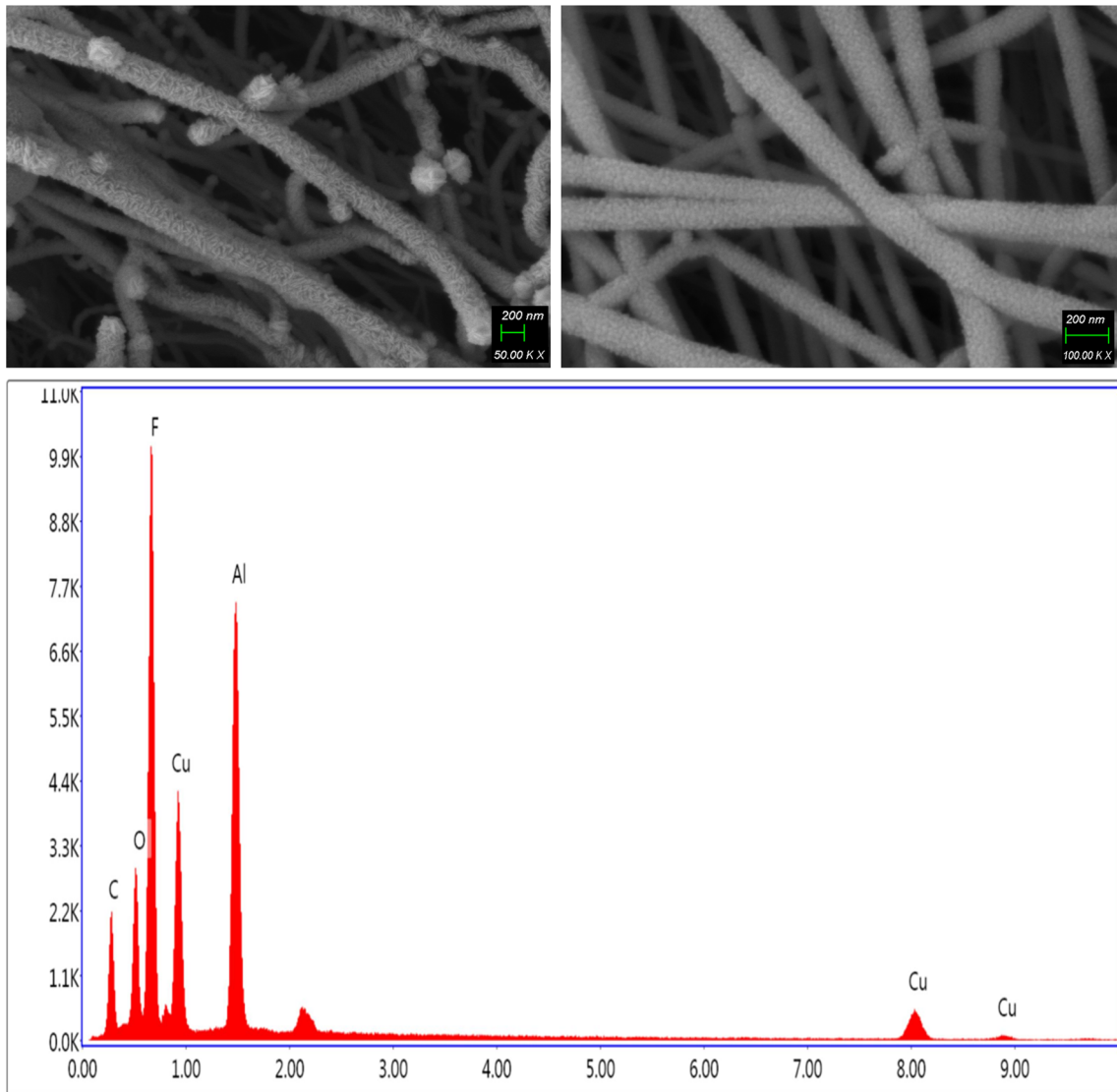
Fig. 3 Photograph of PVDF-HFP nanofiber structure deposited on the surface of the collector plate

Fig. 4 FE-SEM image of PVDF-HFP nanofiber structure



The kinetics of heterogeneous photocatalysis generally conforms to the first-order kinetic model, wherein r , reaction rate; k , rate coefficient; K , adsorption coefficient; and C , refers to the concentration of the reactant as given below:

$$r = \frac{dC}{dt} = \frac{kKC}{1 + KC} \quad (2)$$



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Fig. 5 SEM images and EDX spectrum of 300-nm Cu_2O -coated PVDF sample by magnetic sputtering method

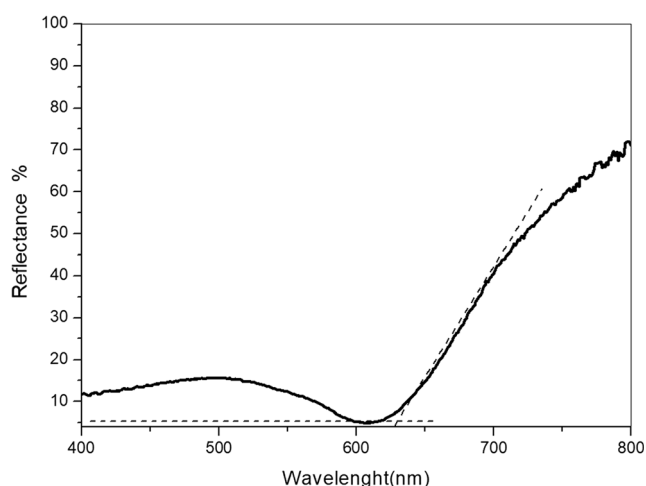


Fig. 6 Diffuse reflectance spectroscopy of 300-nm Cu₂O catalyst

If the methylene blue concentration is kept sufficiently low and the adsorption of the dye to the catalyst surface is not too high, the reaction is expected to behave in accordance with the 1st degree reaction kinetics. If the adsorption is too strong, the photocatalytic reaction must match the zero-degree reaction kinetics. The first-order kinetic equation can be used for highly dilute dye solutions. In Eq. 2, if the adsorption is weak and $1 + KC$ is considered to be equal to 1 for low dye concentration, the simplified equation is obtained as in Eq. 3.

$$r = \frac{dC}{dt} = -kC \quad (3)$$

Integration of this equation between the C and C_0 gives the linear plot equation for 1st-order kinetics as given below:

$$\ln\left(\frac{C}{C_0}\right) = -kt \quad (4)$$

From this equation, by simply replacing C with $C_0/2$, half-life time ($t_{1/2}$) is obtained as the following equation:

$$t_{1/2} = \frac{0.693}{k} \quad (5)$$

3 Results and discussions

For PVDF-HFP (Mw: 400000 g/mol), optimum experimental conditions for the production of nanofibers by electrospinning were investigated. As a result, suitable conditions for electrospinning of PVDF-HFP solution prepared with acetone:DMF (6:4) solvent system are given in Table 2.

When the concentration of the polymer solution fell below 5%, it was observed that the solution dripped from the needle tip and the solution blocked the syringe when it was more than 5%. When the parameters given in Table 2 were used, polymer fibers having an average diameter of less than 150 nm and a

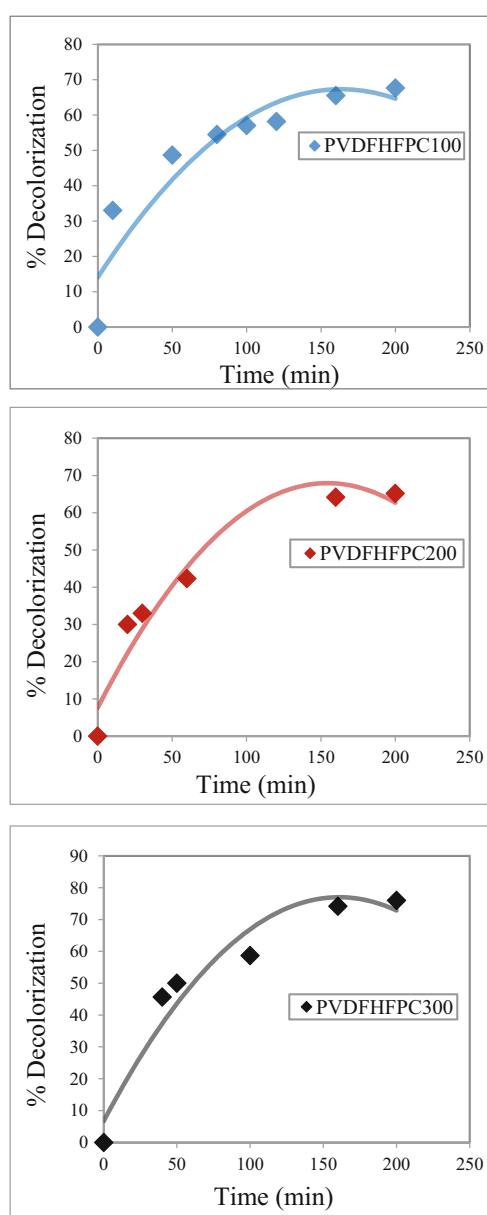


Fig. 7 Photocatalytic decolorization efficiencies of methylene blue with 100-nm, 200-nm, and 300-nm Cu₂O-coated PVDF-HFP nanofibers by magnetic sputtering

continuous structure could be produced. In the examined FE-SEM images, it is seen that they are formed as somewhat beaded nanofiber structures which is inevitable and yet negligible if the diameter is desired to be under 500 nm. The photos of these fiber mats are shown in Fig. 3, and FE-SEM image of nanostructures is shown in Fig. 4.

The SEM image and corresponding energy dispersive X-ray (EDX) spectrum of the Cu₂O-coated samples by magnetic sputtering method are given in Fig. 5.

The nanofiber surfaces, which were coated using magnetic sputtering technique, were observed to be very homogeneous with Cu₂O, including the surfaces of the inner nanofibers. When the EDX spectra are examined, it is clearly seen from

Table 3 Kinetic parameters for methylene blue decolorization

Sample	R^2	Rate constant obtained from graph $k(\text{min}^{-1})$	Rate constant from substitution $k(\text{min}^{-1})$	Half-life time (min)
PVDFHFPC100	0.9754	0.0037	0.0036	187
PVDFHFPC200	0.9844	0.0044	0.0046	158
PVDFHFPC300	0.9803	0.0050	0.0051	139

the peaks given by the Cu and O elements that the catalyst material attaches to the nanofiber surface. The fluorine and carbon peaks observed in the spectrum are due to the PVDF-HFP polymer. Absorption of photocatalysis material was collected as transmittance spectrum by UV-diffuse reflectance measurement by using DRA-EV-600 diffuse reflectance accessory and given in Fig. 6. From the spectrum, approximate band gap of the material was calculated as 1.98 eV which corresponds to the

625 nm. From 625 nm to the lower wavelengths, adsorption of the visible light takes places with 10% loss and above 625 nm, the loss gradually increases to 70% up to 800 nm. This shows that material effectively absorbs the visible light.

In the study, decolorization efficiency of methylene blue was calculated according to Eq. 1 mentioned before. Decolorization efficiencies of methylene blue were plotted against time. Dark adsorption was not observed for samples which were kept in the dark for 10 min. The graph of decolorization of methylene blue is given in Fig. 7. The photocatalysts were found to have a maximum yield of 76% for methylene blue decolorization. This value is very promising when taking account of the catalyst coated on nanofibers which is nearly one thousandth of a milligram. Normally, many of the studies use 0.1–0.5-g powder catalyst [25–28].

The kinetic parameters of methylene blue decolorization were evaluated with 1×10^{-5} M methylene blue solution in different catalyst amounts prepared with 100-nm, 200-nm, and 300-nm Cu_2O coating. In the study, the adsorption values were found to be low. The linearity with high R^2 values obtained in the graph drawn by using Eq. 4 showed that the decolorization of methylene blue was compatible with the 1st-order kinetic model and this was also supported by the k values calculated using the method of substitution into the equation. The parameters obtained from the kinetic study are given in Table 3.

The rate constant of the 1st-degree decolorization reaction was calculated from the slope of the $\ln C$ graph plotted against time (Fig. 8). It was determined that the decolorization reaction was accelerated with increasing amount of catalyst which is also inferred from the decreasing values of half-life time from 187 to 139 min.

Another important point in this study is that photocatalyst material was prepared as sputter-coated electrospun fibers on a hard aluminum base; therefore after the end of catalysis reaction, the base is taken from the solution with no residue as depicted in the Fig. 9.

Conventional, low-efficiency methods for filtration of catalyst particulates from the reaction medium will be completely replaced by this method.

4 Conclusion

The activities of the photocatalysts were monitored by decolorization of the methylene blue solution under visible light.

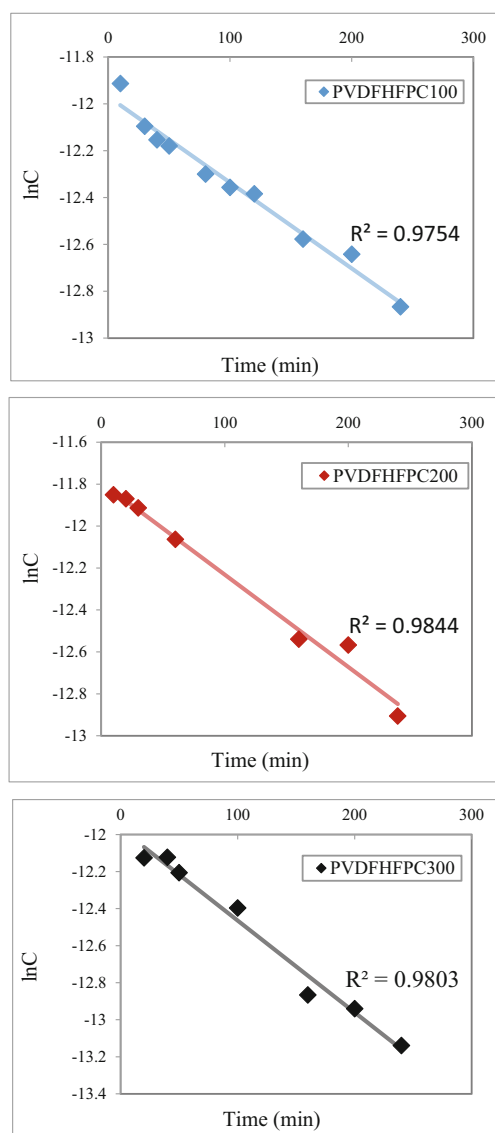
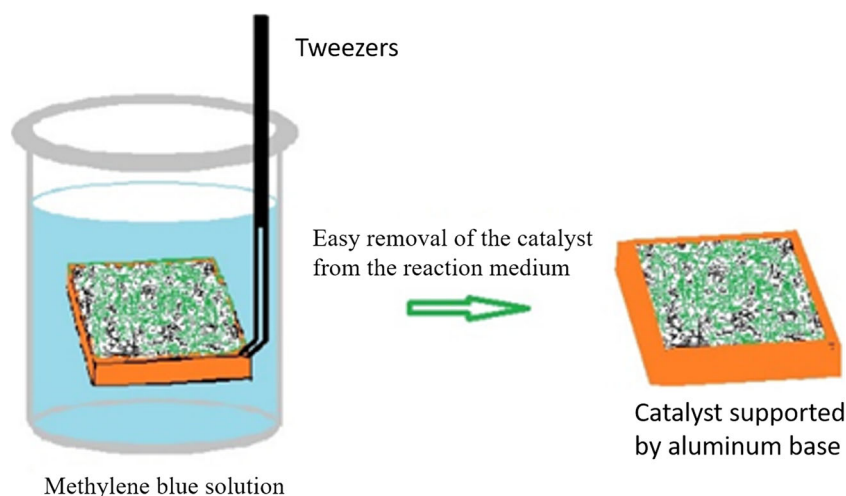
**Fig. 8** Linear fitting of methylene blue decomposition to first-order kinetic model

Fig. 9 Removal of the catalyst from the solution



Catalysts produced with 100-nm, 200-nm, and 300-nm Cu_2O coating did not show dark adsorption. Kinetic studies have shown that the photocatalytic reaction is in accordance with 1st-degree kinetics. It has been determined that the half-life time has decreased from 187 to 139 min with increasing catalyst thickness. This study showed that the PVDF-HFP nanofiber structures could be produced successfully by electrospinning technique resulting in very fine fibers whose diameters are under 200 nm and coated homogeneously with the magnetic sputtering technique. Photocatalyst material introduced in this study will provide a cost-effective option in the process of cleaning wastewater by using solar energy.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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