applied sciences

MDPI

Article

Removal of Cu(II) from Aqueous Solutions Using Amine-Doped Polyacrylonitrile Fibers

Kay Thwe Aung [1], Seung-Hee Hong [1], Seong-Jik Park [1,*] and Chang-Gu Lee [2,*]

[1] Department of Bioresources and Rural System Engineering, Hankyong National University, Anseong 17579, Korea; kaythweag11@gmail.com (K.T.A.); trea1568@naver.com (S.-H.H.)
[2] Department of Environmental and Safety Engineering, Ajou University, Suwon 16499, Korea
* Correspondence: parkseongjik@hknu.ac.kr (S.-J.P.); changgu@ajou.ac.kr (C.-G.L.); Tel.: +82-31-670-5131 (S.-J.P.); +82-31-219-2405 (C.-G.L.)

Received: 4 February 2020; Accepted: 24 February 2020; Published: 3 March 2020

Abstract: Polyacrylonitrile (PAN) fibers were prepared via electrospinning and were modified with diethylenetriamine (DETA) to fabricate surface-modified PAN fibers. The surface-modified PAN fibers were used to evaluate their adsorption capacity for the removal of Cu(II) from aqueous solutions. Batch adsorption experiments were performed to examine the effects of the modification process, initial concentration, initial pH, and adsorbent dose on the adsorption of Cu(II). Kinetic analysis revealed that the experimental data fitted the pseudo-second-order kinetic model better than the pseudo-first-order model. Adsorption equilibrium studies were conducted using the Freundlich and Langmuir isotherm models, and the findings indicated that the PAN fibers modified with 85% DETA presented the highest adsorption capacity for Cu(II) of all analyzed samples. Moreover, the results revealed that the Freundlich model was more appropriate than the Langmuir one for describing the adsorption of Cu(II) onto the modified fibers at various initial Cu(II) concentrations. The maximum adsorption capacity was determined to be 87.77 mg/g at pH 4, and the percent removal of Cu(II) increased as the amount of adsorbent increased. Furthermore, the surface-modified PAN fibers could be easily regenerated using NaOH solution. Therefore, surface-modified PAN fibers could be used as adsorbents for the removal of Cu(II) from aqueous solutions.

Keywords: polyacrylonitrile; electrospun fibers; Cu(II) removal; batch experiments; adsorption models

1. Introduction

Environmental problems affect humans, animals, and plants worldwide. In particular, rapid industrialization has increased water pollution, and thus water sanitation has become a significant global concern. Owing to the increasing environmental and economic impacts of heavy metal ions, their removal from industrial wastewater has been studied in depth [1]. Heavy metals, such as Cr, Cu, Fe, Pb, Ag, Ni, and Zn, which are highly toxic and nonbiodegradable, could cause problems for both the environment and living organisms [2]. The presence of heavy metal pollutants in water could lead to serious health problems, such as stomach aches, nausea, dehydration, dizziness, nervous system damage in young children, skin rashes, vomiting, abdominal pain, lung irritation, eye irritation, and liver damage [3].

Cu is not only an essential nutrient but also a water contaminant. Moreover, Cu has many commercial and industrial applications; it can be used to manufacture pipes, valves, and fittings, and could also be a constituent of different types of alloys and coatings. Copper(II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) is sometimes added to surface waters to control the growth of algae [4]. The typical oxidation states of Cu are +1 and +2, and the corresponding compounds are referred to as cuprous and cupric, respectively [5]. Cu compounds, whether organic complexes or organometallics, could be

used to promote or catalyze numerous chemical and biological processes [6]. Copper(I) and copper(II) sulfides are important examples of copper sulfides. $CuSO_4 \cdot 5H_2O$ is the most frequently used Cu compound in the laboratory. Highly toxic amounts of Cu are present in the industrial wastewaters of the metal cleaning and plating facilities, refineries, paper and pulp plants, fertilizer mills, and wood preservative factories [7]. Furthermore, exposure to environmental sources of Cu could cause vomiting, headaches, stomach cramps, nausea, liver and kidney damage, and even death [8]. Cu is found in drinking water at concentrations in the range of 0.005 to 30 mg/L, and it mainly originates from the corrosion of Cu plumbing [9]. The concentration of Cu in treated water often increases during distribution, particularly in systems where the pH of the water is acidic or basic, or where the water is high in carbonates [4]. According to the U.S. Environmental Protection Agency, the maximum allowable limits for Cu in drinking and industrial waters are 1.3 and 3.0 mg/L, respectively [10].

Several methods could be used to reduce the amounts of heavy metal from effluents, including chemical precipitation, electrodialysis, reverse osmosis, ion exchange, evaporation, and adsorption [8]. Of these, adsorption is an effective and economical method of wastewater treatment [2]. Many adsorbents, such as activated carbon, biosorbents, illite–smectite, natural zeolites, natural bentonites, oxide minerals, polymer materials, resins, and synthetic hydroxyapatite have been used for the removal of metal ions from wastewaters [11–13]. Recently, electrospinning has attracted significant attention in academic research circles and for industrial applications because it (1) could be used to fabricate continuous fibers with diameters as small as a few nanometers; (2) could be applied to a wide range of materials, such as synthetic and natural polymers, metals, and ceramics and composite systems; and (3) could be a low-cost and high-yield method for the preparation of nanofibers [14]. Modified electrospun nanofibers have been developed as adsorbents for metal ions from solutions because they have high porosity, high specific surface area, and controllable surface functionality [15].

In this study, polyacrylonitrile (PAN) fibers were prepared via electrospinning, and diethylenetriamine (DETA) was used to modify the PAN fibers. The purpose of the study was to fabricate surface-modified PAN fibers for the removal of heavy metals from aqueous solutions. The effects of the pH, contact time, and initial concentration of the Cu(II) solution on the adsorption capacity of the surface-modified PAN fibers for Cu(II) ions were examined. Adsorption kinetics and isotherm experiments were performed to analyze the experimental data.

2. Materials and Methods

2.1. Reagents

PAN powder (Sigma-Aldrich, Mw = 150,000 g/mol) and dimethylformamide (DMF, Sigma-Aldrich, Steinheim, Germany, 99.8%) were used to prepare the polymer spinning solution, and DETA (ACROS Organics Co., Geel, Belgium, 98.5%) and aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$, Sigma-Aldrich, 99%) were used as the modifying agent and catalyst, respectively. Analytical grade $CuSO_4 \cdot 5H_2O$ (Daejung Co., Siheung, Korea, 99%), NaCl (Samchun Co., Seoul, Korea, 99%), and $CaCl_2$ (Samchun Co., 95%) were used for experiments. The pH of the test solution was adjusted using HCl (Samchun Co., 36%) and NaOH (Samchun Co., 99%) solutions, and deionized (DI) water was used throughout the experiments.

2.2. Preparation of Electrospun PAN Fiber

PAN powder (4% (*w*/*v*)) was dissolved in DMF solution and the mixture was magnetically stirred at 60 °C for 10 h to obtain a clear solution. Then, the mixture was continuously stirred overnight at room temperature to obtain a homogeneous blend. The prepared polymer solution was converted into PAN fibers using an electrospinning device that featured a 10-mL injection syringe with a stainless steel needle. PAN fibers were collected by rotating a metal drum wrapped with Al foil. The flow rate of the syringe pump was 1 mL/h and the speed of the rotating drum was 120 rpm. The distance between the rotating drum and needle tip was 12 cm, and the applied high DC electrospinning voltage was 17 kV.

2.3. Modification of PAN Fibers

To prepare surface-modified PAN fibers, the PAN fibers were added to recipients that contained different concentrations of DETA (40%, 55%, 70%, and 85% (*v*/*v*)) solutions. Then, the mixtures were heated in a reflux system at 100 °C for 1 h using Al as the catalyst until the fibers became yellow. Afterward, the fibers were washed with 0.1 M HCl, 0.1 M NaOH, and DI water in sequence to achieve neutral pH. The washed fibers were dried in a vacuum oven at 60 °C for 18 h to obtain the surface-modified PAN fibers, and the resulting fibers were stored in a desiccator for further use. A field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan) was used to observe the surface morphologies of the surface-modified PAN fibers. Fourier-transform infrared spectroscopy (FTIR, Nicolet iS10, Thermo Scientific, USA) was employed to identify functional groups of the samples.

2.4. Adsorption Experiments

Adsorption experiments were conducted in batch systems. The required concentrations of Cu(II) were prepared by diluting the stock Cu(II) solution (1000 mg/L). Cu(II) solutions of different concentrations (50, 100, 150, 200, 300, and 500 mg/L) were stirred with 1.0 g/L surface-modified PAN fibers at 100 rpm and 25 °C. Then, the samples were filtered and their residual Cu(II) concentrations were determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 5100, Agilent Technologies, USA). Kinetics experiments were conducted on the system and were obtained by adding 0.04 g adsorbent to 40 mL of 100 mg/L Cu(II) test solution at different reaction times (0.25, 0.5, 1, 2, 3, 6, 12, and 24 h). To analyze the effect of the pH on the adsorption process, the pH of the solution was adjusted to 2, 3, and 4 using 1 M HCl or 1 M NaOH solutions. For the adsorbent dosage experiments, 0.02, 0.04, 0.06, 0.08, and 0.1 g surface-modified PAN fibers was added to 40 mL of 100 mg/L Cu(II) solution and the mixtures were shaken for 24 h at 100 rpm. Regeneration experiments were also carried out to observe the removal of Cu(II) ions using the surface-modified PAN fibers after they were subjected to a few regeneration cycles. Adsorption experiments were performed using 0.04 g surface-modified PAN fibers and 40 mL of 100 mg/L Cu(II) solution at pH 4. After 2 h, the adsorbed Cu was desorbed using 50 mL of 0.1 M NaOH followed by washing with DI water. Further adsorption tests were carried out under the same conditions.

The adsorption capacity (q) and removal percent of Cu (%) were calculated using the following equations:

$$q = (C_i - C_f)\frac{V}{w} \quad (1)$$

and

$$Removal\ (\%) = (C_i - C_f) \times \frac{100}{C_i} \quad (2)$$

where q (mg/g) is the amount of Cu(II) adsorbed per unit of adsorbent, C_i and C_f (mg/L) are the initial and final Cu(II) concentrations, respectively, V (L) is the volume of Cu(II) solution, and w (g) is the amount of adsorbent.

2.5. Adsorption Model Analyses

The kinetic data were fit using pseudo-first- and pseudo-second-order kinetic models (Equations (3) and (4), respectively), and the best fit was determined using the Sigma Plot 10 software.

$$q_t = q_e\left(1 - e^{-k_1 t}\right) \quad (3)$$

and

$$q_t = \frac{k_2 {q_e}^2 t}{1 + k_2 q_e t} \quad (4)$$

where q_t and q_e (mg Cu/g) are the amounts of Cu removed at time t and at equilibrium, respectively, and k_1 (1/h) and k_2 (g/(mg Cu h)) are the pseudo-first- and pseudo-second-order rate constants, respectively.

The most common mathematical models used to analyze isotherm data are the Langmuir and Freundlich models. The Langmuir model was derived to describe adsorption on homogeneous adsorbent surfaces, where each adsorptive site could be occupied only once. Mathematically, the Langmuir model can be described as follows [16]:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{5}$$

where q_m (mg/g) is the maximum sorption capacity of the metal ions on the adsorbent, and K_L (L/mg) is the Langmuir adsorption equilibrium constant.

The Freundlich model is used to describe the adsorption of an absorbate on heterogeneous adsorbent surfaces, and its mathematical expression could be written as follows [16]:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{6}$$

where K_F and n are the Freundlich constants.

3. Results and Discussion

3.1. Effect of DETA Concentration on Surface Modification of PAN Fibers Used for Cu(II) Removal

The adsorption capacities of the surface-modified PAN fibers obtained using four different DETA concentrations (40%, 55%, 70%, and 85%) were analyzed. As presented in Figure 1, the adsorption capacity of the fibers for Cu(II) increased as the concentration of DETA increased, and the highest adsorption capacity of 78.17 mg/g was achieved when the PAN fibers modified using 85% DETA were used. This was attributed to the number of nitrile groups converted to amine groups on the surface of PAN, which increased as the amount of DETA increased [17]. These results were similar to those previously reported in the literature, where the DETA concentration of 70–80% was reported to be the optimal concentration for the modification of modacrylic fibers that contained 40% acrylonitrile [18]. Therefore, the surface-modified PAN fibers treated with 85% DETA were used for further tests.

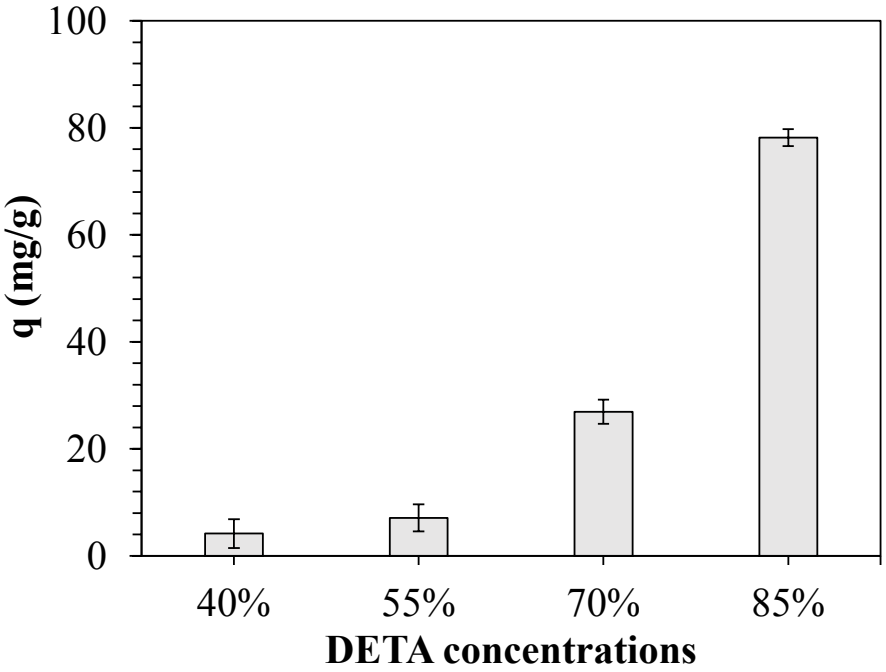

Figure 1. Adsorption capacities (q) of surface-modified polyacrylonitrile fibers with different concentrations of diethylenetriamine (DETA) for Cu(II) removal.

3.2. Characterization of Surface Modification of PAN Fibers

The surface morphologies of the surface-modified PAN fibers were observed by FE-SEM (Figure 2). The surface of pure PAN fiber was smooth and uniform, while the surface roughness increased as it reacted with DETA. The thickness of the fibers also increased due to the reaction between DETA and the PAN fibers [8,19]. The reaction was also confirmed by the FTIR spectra (Figure 3). The pure PAN fiber showed adsorption peaks of stretching vibrations at 1070 cm^{-1} (C-O), 1450 cm^{-1} (CH_2), and 2936 cm^{-1} (CH stretching in CH, CH_2, and CH_3 groups) [1,20]. The FTIR spectra of the PAN fibers showed the most distinctive bonds of the nitrile (C≡N) vibration at 2242 cm^{-1}, which decreased with increasing DETA concentration and almost disappeared with 85% EDTA [19,21,22]. The peaks of the amine modified at 1561–1571 cm^{-1} (Figure 3c–e) correspond to the stretching bending vibration of NH groups, demonstrating the presence of primary amine groups [20]. The broad band around 3300 cm^{-1} was attributed to the O-H spectrum [23].

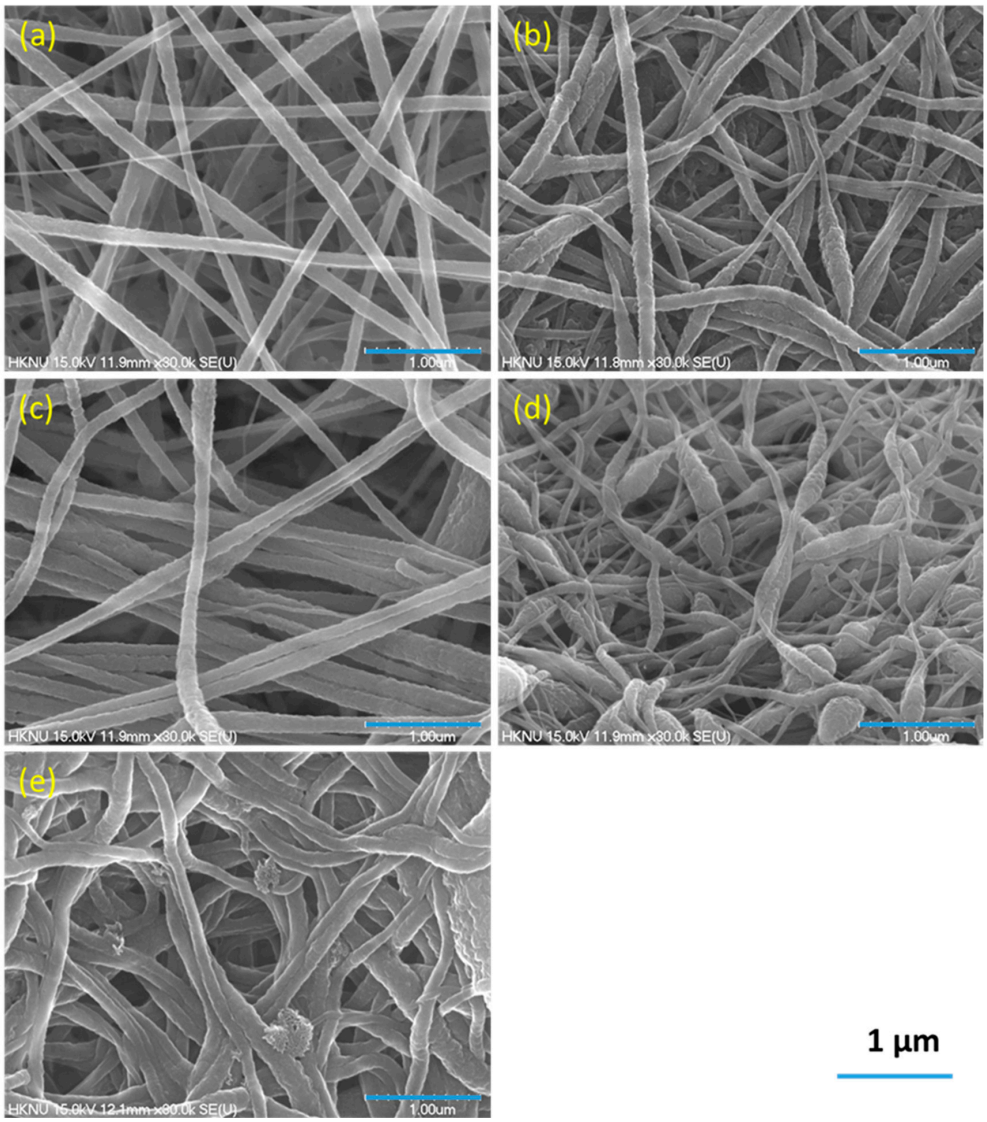

Figure 2. Field emission-scanning electron microscope (FE-SEM) images of (**a**) unmodified polyacrylonitrile (PAN) fiber and PAN fiber with different concentrations of DETA: (**b**) 40% DETA, (**c**), 55% DETA, (**d**) 70% DETA, and (**e**) 85% DETA.

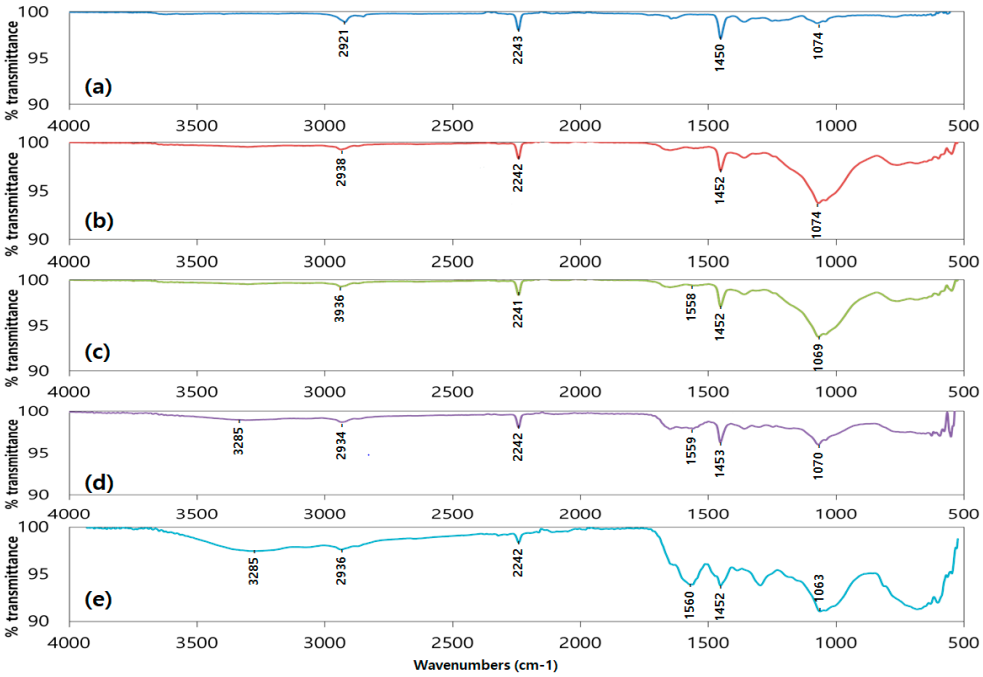

Figure 3. Fourier-transform infrared spectroscopy (FTIR) spectra of (**a**) unmodified PAN fiber and PAN fiber with different concentration of DETA: (**b**) 40% DETA, (**c**) 55% DETA, (**d**) 70% DETA, and (**e**) 85% DETA.

3.3. Adsorption Kinetics

The kinetics of the Cu(II) adsorption on the surface-modified PAN fibers were analyzed using pseudo-first- and pseudo-second-order kinetic models. Figure 4 depicts the plot of the experimental data for the initial Cu(II) solution concentration of 100 mg/L. The calculated kinetic parameters are summarized in Table 1. The experimental data fitted the pseudo-second-order kinetic model better than the pseudo-first-order one. These results indicated that the adsorption rate of Cu(II) on the surface-modified PAN fibers depended on the adsorbate concentration and the number of active sites of the adsorbent [24]. Previous studies have also revealed that the adsorption of Cu(II) on amine-modified PAN fibers followed the pseudo-second-order kinetic model [2,8,25].

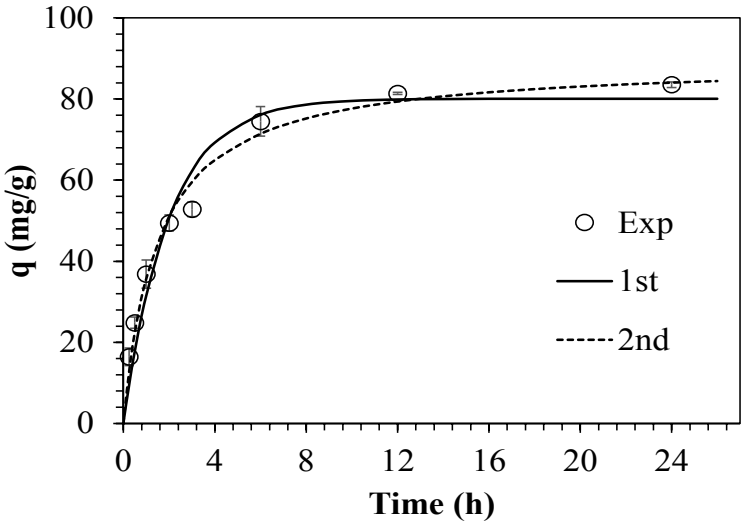

Figure 4. Pseudo-first-order and pseudo-second-order kinetic models (1st and 2nd, respectively) for adsorption of Cu(II) ions onto surface-modified polyacrylonitrile fibers. Here, q and t denote the adsorption capacity and time, respectively.

Table 1. Kinetics parameters for adsorption of Cu(II) ions onto surface-modified polyacrylonitrile fibers. Here, k_1, k_2, q_e, and R^2 denote the pseudo-first- and pseudo-second-order rate constants, amount of Cu(II) removed at equilibrium, and determination coefficient, respectively.

Pseudo-First-Order Kinetic Model			Pseudo-Second-Order Kinetic Model		
k_1 (1/h)	q_e (mg/g)	R^2	k_2 (g/(mg h))	q_e (mg/g)	R^2
0.500	80.06	0.968	0.007	89.36	0.984

3.4. Adsorption Isotherms

The effect of the equilibrium concentrations of Cu(II) ions in the testing solutions on the adsorption capacities of the surface-modified PAN fibers is illustrated in Figure 5. The figure presents the fitting of the equilibrium data, and the obtained parameters of the adsorption isotherms are listed in Table 2. The adsorption capacity of the fibers increased gradually as C_e increased. This was attributed to the mass transfer being the driving force of the process at higher C_i values [26]. The determination coefficient of the Freundlich model was higher than that of the Langmuir model, which indicated that the Freundlich model fitted the adsorption data better than the Langmuir one. It was inferred that the Cu(II) ions were collected in multiple layers on the heterogeneous surface of the surface-modified PAN fibers [24]. The maximum experimental adsorption capacity on the surface-modified PAN fibers was 112.3 mg/g, which was in the range with the values reported in the literature (45–151 mg/g) for the Cu(II) adsorption capacity on amine-modified PAN fibers (Table 3) [2,8,25].

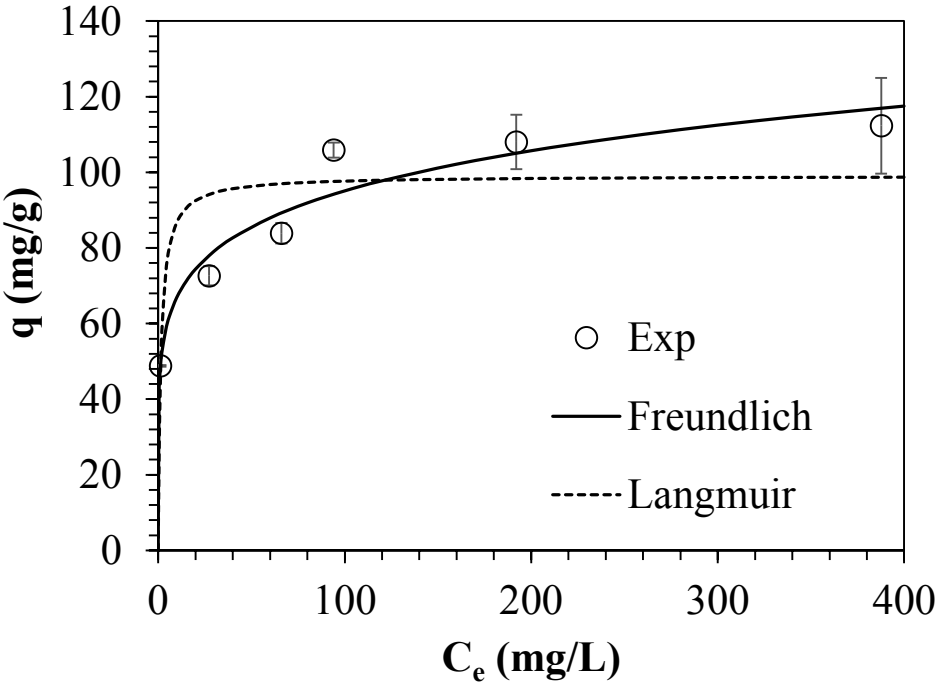

Figure 5. Adsorption isotherms of Cu(II) ions onto surface-modified PAN fibers. Here, q and C_e denote the adsorption capacity and Cu(II) equilibrium concentration, respectively.

Table 2. Parameters of Langmuir and Freundlich models for adsorption of Cu(II) on surface-modified PAN fibers. Here, K_L, K_F, q_m, n, and R^2 denote the Langmuir and Freundlich equilibrium adsorption constants, maximum sorption capacity of metal ions on adsorbent, Freundlich constant, and determination coefficient, respectively.

Langmuir Model			Freundlich Model		
K_L (L/mg)	q_m (mg/g)	R^2	K_F (L/g)	1/n	R^2
0.703	99.06	0.679	47.06	0.153	0.928

Table 3. Comparison of the adsorption capacity (q) of different fibrous ion exchangers and adsorbents for Cu(II) adsorption.

Materials	Conditions	q (mg/g)	Reference
Synthetic hydroxyapatite	Initial concentration = 6355 mg/L; pH = 3	50.2	[12]
Bentonite	Initial concentration = 3177 mg/L; pH = 5	27.6	[13]
Lime sand brick	Initial concentration = 30 mg/L; pH = 5	7.0	[27]
Surface-doped PAN fiber	Initial concentration = 1000 mg/L; pH = 6	143.5	[25]
	Initial concentration = 10 mg/L; pH = 6	45.0	[8]
	Initial concentration = 1000 mg/L; pH = 4	150.6	[2]
	Initial concentration = 500 mg/L; pH = 4	112.3	This study

3.5. Effect of Solution pH on Cu(II) Adsorption

The pH value is considered one of the most important parameters during metal removal processes. The dependence of the adsorption of Cu(II) on surface-modified PAN fibers on the initial pH of the solution is presented in Figure 6. At low solution pH levels, the modified amine groups are protonated and the surface of the adsorbent is more positively charged, which is not favorable for the adsorption of metal cations [19,25]. The amount of Cu(II) ions adsorbed on the surface-modified PAN fibers increased significantly as the number of protonated amine groups decreased, owing to the increase in the solution pH [2]. The optimum solution pH was determined to be 4, and the corresponding adsorption amount was 87.767 mg/g for the initial Cu(II) solution concentration of 100 mg/L.

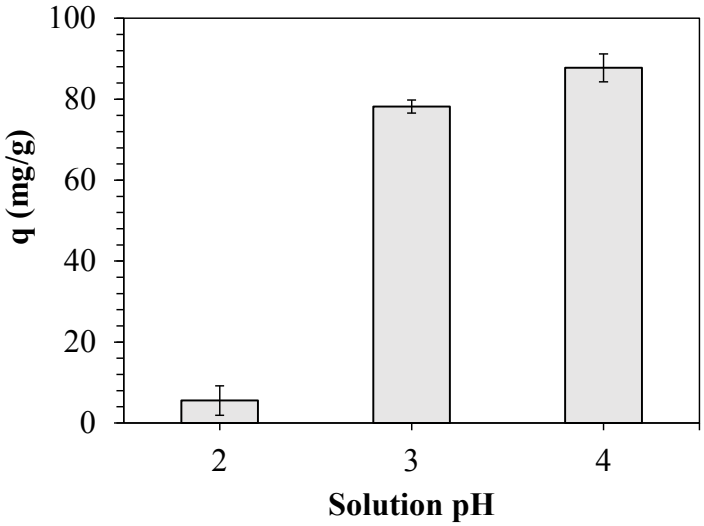

Figure 6. Effect of solution pH on adsorption of Cu(II) ions. Here, q denotes the adsorption capacity.

3.6. Effect of Adsorbent Dosage

The effect of the surface-modified PAN fiber dose on the adsorption capacity of the surface-modified PAN fibers for Cu(II) was evaluated, and the results are illustrated in Figure 7. As the surface-modified

PAN fibers were added to the Cu(II) solution, the mass of adsorbed Cu(II) per unit mass of fiber gradually decreased and the removal percentage increased. The decrease in adsorption capacity per unit mass was attributed to the concentration of Cu(II) being insufficient to match the increasing number of adsorption sites caused by the addition of fibers, and therefore some adsorption sites were unsaturated [28]. The maximum percent removal reached 97.63% when the dose of 0.1 g adsorbent was added to 40 mL of 100 mg/L Cu(II) solution.

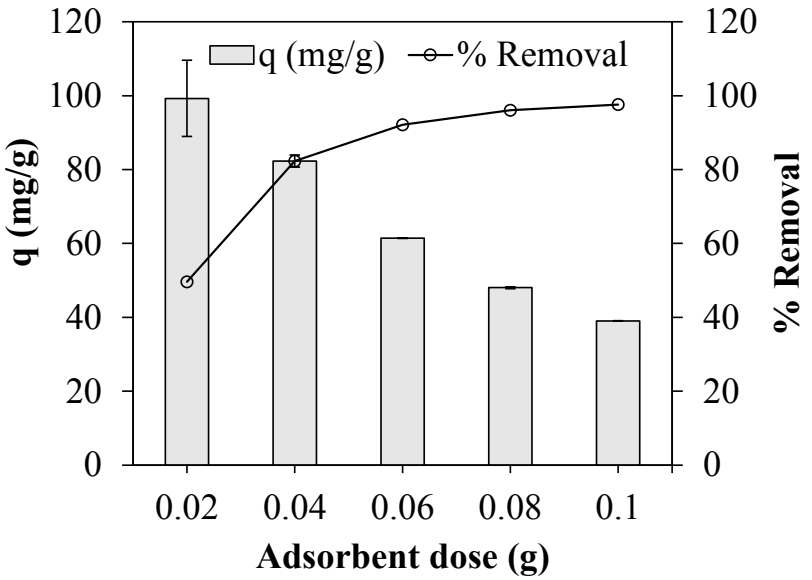

Figure 7. Effect of adsorbent dose on Cu(II) adsorption. Here, q denotes the adsorption capacity.

3.7. Effect of Coexisting Cations

The effects of NaCl and $CaCl_2$ as coexisting cations on the Cu(II) adsorption with the surface-modified PAN fiber are shown in Figure 8. The amounts of adsorbed Cu(II) in the presence of 1 mM of NaCl and $CaCl_2$ were 92.42 and 91.89 mg/g, respectively. When the concentrations of coexisting cations increased to 10 mM, the amounts of adsorbed Cu(II) were 92.80 and 92.26 mg/g, respectively. These increases in the adsorption capacity were due to the salting-out effect of NaCl and $CaCl_2$ [29,30], causing Cu(II) ions to move into the interface of the surface-modified PAN fiber. The adsorption capacity increased with increasing salt concentration, but there was no difference between types of salts at the same molar concentration.

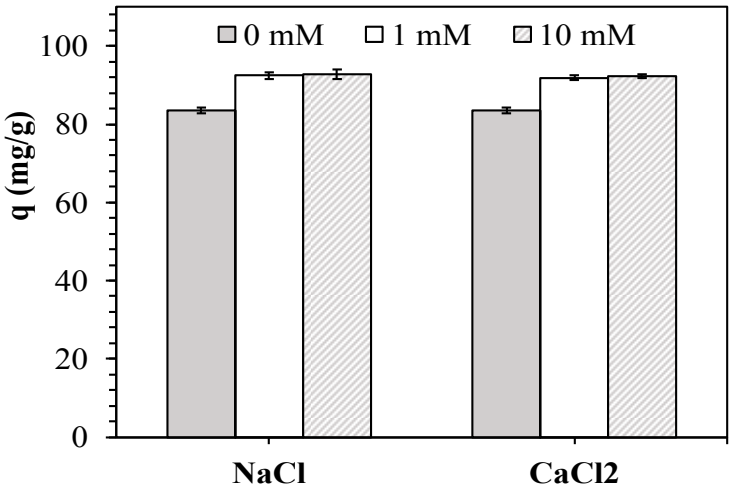

Figure 8. Effect of coexisting cations on Cu(II) adsorption. Here, q denotes the adsorption capacity.

3.8. Regeneration Study

The reusability of the surface-modified PAN fibers was tested during three consecutive regeneration cycles using 0.1 M NaOH and DI water, in sequence. The adsorption capacity of the surface-modified PAN fibers decreased as the number of regeneration cycles increased but remained above 51 mg/g after three cycles (Figure 9). The decrease in adsorption capacity was associated with the degradation of the surface-modified PAN fibers during the regeneration process [19,26]. Nevertheless, the surface-modified PAN fibers could be easily reused for the removal of Cu(II) from aqueous solutions after they were regenerated with NaOH.

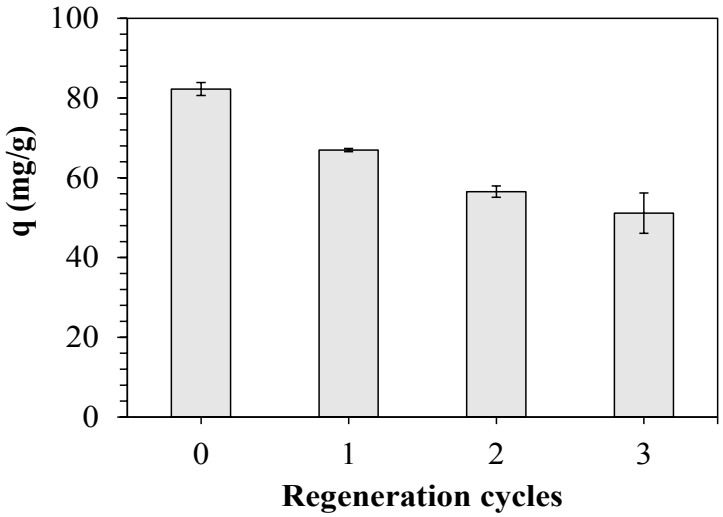

Figure 9. Cu(II) adsorption dependence on number of regeneration cycles. Here, q denotes the adsorption capacity.

4. Conclusions

PAN fibers modified with DETA were used as adsorbents for the removal of Cu(II) from aqueous solutions. The surface-modified PAN fibers that were treated with 85% DETA presented the highest Cu(II) adsorption capacity. The adsorption of Cu(II) followed the pseudo-second-order kinetic model, and the equilibrium data fit the Freundlich isotherm model, which indicated that the adsorption was a multilayer process that occurred on a heterogeneous surface. The maximum adsorption capacity of 87.77 mg/g was achieved at pH 4. The percent removal of Cu(II) was increased from 49.63% to 97.63% as the adsorbent dosage increased from 0.02 to 0.1 g. The surface-modified PAN fibers could be regenerated with NaOH solution. These results indicated that the surface-modified PAN fibers could be used as adsorbent for the removal of Cu(II) from aqueous solutions.

Author Contributions: Conceptualization, methodology, formal analysis, writing—original draft preparation, K.T.A. and C.-G.L.; formal analysis, validation, visualization, S.-H.H.; conceptualization, supervision, writing—review and editing, S.-J.P. All authors have read and agreed to the published version of the manuscript.

Funding: This research was supported by the Basic Science Research Program through the National Research Foundation (NRF) of Korea funded by the Ministry of Education (Grant no. NRF-2017R1D1A1B03030649) and by the National Research Foundation (NRF) of Korea (Grant no. NRF-2018R1C1B5044937).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Abdouss, M.; Shoushtari, M.A.; Haji, A.; Moshref, B. Fabrication of chelating diethylenetriaminated pan micro-and nano-fibers for heavy metal removal. *Chem. Ind. Chem. Eng. Q.* **2012**, *18*, 27–34. [CrossRef]
2. Kampalanonwat, P.; Supaphol, P. Preparation and adsorption behavior of aminated electrospun polyacrylonitrile nanofiber mats for heavy metal ion removal. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3619–3627. [CrossRef] [PubMed]
3. Haider, S.; Park, S.-Y. Preparation of the electrospun chitosan nanofibers and their applications to the adsorption of Cu (II) and Pb (II) ions from an aqueous solution. *J. Membr. Sci.* **2009**, *328*, 90–96. [CrossRef]
4. IPCS; World Health Organization. *International Programme on Chemical Safety*; World Health Organization: Geneva, Switzerland, 1998.
5. Holleman, A.; Wiberg, E. *Inorganic Chemistry*; Academic Press: Berlin, Germany; New York, NY, USA, 2001.
6. Trammell, R.; Rajabimoghadam, K.; Garcia-Bosch, I. Copper-promoted functionalization of organic molecules: From biologically relevant Cu/O2 model systems to organometallic transformations. *Chem. Rev.* **2019**, *119*, 2954–3031. [CrossRef]
7. Rengaraj, S.; Yeon, J.-W.; Kim, Y.; Jung, Y.; Ha, Y.-K.; Kim, W.-H. Adsorption characteristics of Cu (II) onto ion exchange resins 252H and 1500H: Kinetics, isotherms and error analysis. *J. Hazard. Mater.* **2007**, *143*, 469–477. [CrossRef]
8. Yang, C.Y.; Fang, L.; Nguyen, N.T.; Ma, C.M.; Chang, C.T. Preparation of amine-modified polyacrylonitrile fibers: Copper removal in aqueous solution. *J. Nanosci. Nanotechnol.* **2016**, *16*, 1945–1951. [CrossRef]
9. World Health Organization. *Copper in Drinking-Water: Background Document for Development of WHO Guidelines for Drinking Water Quality*; World Health Organization: Geneva, Switzerland, 2004.
10. Adeeyo, R.O.; Edokpayi, J.N.; Bello, O.S.; Adeeyo, A.O.; Odiyo, J.O. Influence of selective conditions on various composite sorbents for enhanced removal of copper (II) ions from aqueous environments. *Int. J. Environ. Res. Public Health* **2019**, *16*, 4596. [CrossRef]
11. Neghlani, P.K.; Rafizadeh, M.; Taromi, F.A. Preparation of aminated-polyacrylonitrile nanofiber membranes for the adsorption of metal ions: Comparison with microfibers. *J. Hazard. Mater.* **2011**, *186*, 182–189. [CrossRef]
12. Rosskopfová, O.; Galamboš, M.; Ometáková, J.; Čaplovičová, M.; Rajec, P. Study of sorption processes of copper on synthetic hydroxyapatite. *J. Radioanal. Nucl. Chem.* **2012**, *293*, 641–647. [CrossRef]
13. Viglašová, E.; Daňo, M.; Galamboš, M.; Krajňák, A.; Rosskopfová, O.; Rajec, P. Investigation of Cu(II) adsorption on Slovak bentonites and illite/smectite for agricultural applications. *J. Radioanal. Nucl. Chem.* **2017**, *314*, 2425–2435. [CrossRef]
14. Wang, H.-S.; Fu, G.-D.; Li, X.-S. Functional polymeric nanofibers from electrospinning. *Recent Pat. Nanotechnol.* **2009**, *3*, 21–31. [CrossRef] [PubMed]
15. Pereao, O.; Bode-Aluko, C.; Ndayambaje, G.; Fatoba, O.; Petrik, L. Electrospinning: Polymer nanofibre adsorbent applications for metal ion removal. *J. Polym. Environ.* **2017**, *25*, 1175–1189. [CrossRef]
16. Gallo-Cordova, A.; Morales, M.d.P.; Mazarío, E. Effect of the surface charge on the adsorption capacity of chromium(VI) of iron oxide magnetic nanoparticles prepared by microwave-assisted synthesis. *Water* **2019**, *11*, 2372. [CrossRef]
17. Almasian, A.; Olya, M.E.; Mahmoodi, N.M. Preparation and adsorption behavior of diethylenetriamine/polyacrylonitrile composite nanofibers for a direct dye removal. *Fiber Polym.* **2015**, *16*, 1925–1934. [CrossRef]
18. Nesteronok, P.V.; Soldatov, V.S. Acid–base properties of ion exchangers: V. Synthesis and properties of ion exchangers on the base of modacrylic polyacrylonitrile–vinylchloride fibers. *React. Funct. Polym.* **2011**, *71*, 1033–1039. [CrossRef]
19. Lee, C.G.; Alvarez, P.J.; Nam, A.; Park, S.J.; Do, T.; Choi, U.S.; Lee, S.H. Arsenic(V) removal using an amine-doped acrylic ion exchange fiber: Kinetic, equilibrium, and regeneration studies. *J. Hazard. Mater.* **2017**, *325*, 223–229. [CrossRef]
20. El-Newehy, M.H.; Alamri, A.; Al-Deyab, S.S. Optimization of amine-terminated polyacrylonitrile synthesis and characterization. *Arab. J. Chem.* **2014**, *7*, 235–241. [CrossRef]
21. Karacan, I.; Erdogan, G. The influence of thermal stabilization stage on the molecular structure of polyacrylonitrile fibers prior to the carbonization stage. *Fiber Polym.* **2012**, *13*, 295–302. [CrossRef]

22. Lim, A.; Song, M.-H.; Cho, C.-W.; Yun, Y.-S. Development of surface-modified polyacrylonitrile fibers and their selective sorption behavior of precious metals. *Appl. Sci.* **2016**, *6*, 378. [CrossRef]
23. Fu, H.; Quan, X. Complexes of fulvic acid on the surface of hematite, goethite, and akaganeite: FTIR observation. *Chemosphere* **2006**, *63*, 403–410. [CrossRef]
24. Chaúque, E.F.; Dlamini, L.N.; Adelodun, A.A.; Greyling, C.J.; Ngila, J.C. Electrospun polyacrylonitrile nanofibers functionalized with EDTA for adsorption of ionic dyes. *Phys. Chem. Earth Part A Solid Earth Geod.* **2017**, *100*, 201–211. [CrossRef]
25. Ren, J.; Yan, C.; Liu, Q.; Yang, Q.; Lu, G.; Song, Y.; Li, Y. Preparation of amidoxime-modified polyacrylonitrile nanofibrous adsorbents for the extraction of copper (II) and lead (II) ions and dye from aqueous media. *J. Appl. Polym. Sci.* **2018**, *135*, 45697. [CrossRef]
26. Lee, C.-G.; Park, J.-A.; Choi, J.-W.; Ko, S.-O.; Lee, S.-H. Removal and recovery of Cr(VI) from industrial plating wastewater using fibrous anion exchanger. *Water Air Soil Pollut.* **2016**, *227*. [CrossRef]
27. Zhang, X.; Guo, S.; Liu, J.; Zhang, Z.; Song, K.; Tan, C.; Li, H. A Study on the removal of copper (II) from aqueous solution using lime sand bricks. *Appl. Sci.* **2019**, *9*, 670. [CrossRef]
28. Lee, J.I.; Hong, S.H.; Lee, C.G.; Park, S.J. Experimental and model study for fluoride removal by thermally activated sepiolite. *Chemosphere* **2020**, *241*, 125094. [CrossRef] [PubMed]
29. Acisli, O.; Khataee, A.; Darvishi Cheshmeh Soltani, R.; Karaca, S. Ultrasound-assisted Fenton process using siderite nanoparticles prepared via planetary ball milling for removal of reactive yellow 81 in aqueous phase. *Ultrason. Sonochem.* **2017**, *35*, 210–218. [CrossRef]
30. Chang, D.T.; Park, D.; Zhu, J.-J.; Fan, H.-J. Assessment of an MnCe-GAC treatment process for tetramethylammonium-contaminated wastewater from optoelectronic industries. *Appl. Sci.* **2019**, *9*, 4578. [CrossRef]