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Research Paper

On The Adsorption And Desorption Of Heavy Metal Ions By Modified Fibers In Industrial Wastewater

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***ABSTRACT**: Utilizing a new type of fiber material that contains amidoxime and carboxylchelating functional groups as sorbent to treating electroplating wastewater that contains heavymetals such as copper, cobalt and cadmium. Related research has been focused on extraction ofuranium in ocean water, this study applies this fiber sorbent to common industrial wastewatercontaining copper and cobalt. Critical parameters including temperature, pH value, concentration ofeluent were examined. In the case of a single metal ion solution, the adsorption capacity is 117 mg/gfor copper(II), 86 mg/g for cobalt(II), and 130 mg/g for cadmium(II). Desorption efficiency can reaches over 99% when using 0.1M HCl. And both adsorption reaction and desorptionreaction can reach the equilibrium within one hour. The impact of fiber reusage was also tested, therewas no significant change in the adsorption and desorption efficiencies within 5 reusage. Thisnovel fiber has significant effectiveness in the adsorption and desorption (under certain conditions) of metal cations, and can be reused with little change in its performance. This novel heavymetal adsorption material is a promising new solution to the remediation of heavy metalpollution.*

***KEYWORDS:** Absorption, fiber sorbent, copper, cobalt, cadmium, wastewatertreatment*

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I. INTRODUCTION

In the high-tech industry, production is often accompanied by the discharge ofindustrial wastewater containing heavy metals. The prevention and control of these heavy metals hasbeen mostly carried out by traditional coagulation and precipitation methods, converting heavymetals in wastewater into metal sludge and transporting away. Technological uncertainty andcost considerations often lead to improper waste-treatment and result in environmental pollution.On the other hand, the international community is advocating the idea of circular economy, whichis that the valuable heavy metals in the wastewater can be recycled and reused. This approachis particularly rewarding in light of the recent rise in the prices of many rare earth metalsand strategic metals. The technology for recovering valuable recently metals from wastewaterhas gradually become the mainstream focus of wastewater treatment, and many newrecycling technologies have beendeveloped. The LCW nano-adsorbing fiber is a polymer material that based on polyacrylonitrilefibre and the nitrile group will be transformed into amidoxime group through reaction. Theamidoxime group is composed of an amine group and a oxime group (-RC=NOH), which is anamphoteric complex formed by a weakly basic nitrogen atom and a moderately acidic hydroxylgroup. Theoretically, amidoxime-based sorbent has superior adsorption properties for heavy metals,and can be applied to the concentration and separation of metal ions. The amidoxime groupcan combine with many metal ions such as copper, lead, cobalt, and nickel ions to form astable complex as shown in

Fig. 1., and can thus be used to treat metal ion-containing wastewater.In addition to being used for industrial wastewater treatment, LCW nano-adsorption fibers canalso selectively desorb adsorbed metals, achieving the purpose of recovering specificmetals.

Fig. 1. Color change of LCW fiber after adsorption of heavymetals

Traditional heavy metal wastewater treatment process including concentrating the metals ina fixed space to increase the concentration, then adding a large amount of alkali or precipitant.The new method explored in this work breaks these traditional limitations on both spaceand concentration, possesses some advantage like fast capture rate, high efficiency, and canprocess large amounts of wastewater. The macroscopic appearance of our material is highly adjustable,the form of which can be filamentous, reticular or granular, and therefore it can be applied tofactory wastewater discharge outfall, or open-surface water bodies including rivers, lakes andoceans. This fiber-sorbent can be regarded as a metal-capturing net that prevents high-pollutionheavy metals from flowing into the environment, and can also remediate the heavy metalsin contaminated rivers. Among the common methods to treat metal wastewater, theadsorption method has many advantages including simple operation, mild adsorption conditions,hardly requires any additional energy and power consumption, reusable, etc. It is anenvironmental protection method that saves energy while adhering to the concept of green circulareconomy.

Fig. 2. LCW fiber cheerleading ball type

II. MATERIAL AND METHOD

Inthisexperiment,chelate-typeadsorptionfiberwereusedfortheadsorptionofheavymetals, and the flame atomic absorption spectrometer was used for inspecting the content. We studythe optimum conditions for adsorption and desorption, and investigate its capacity forreuse.

Using the flame atomic absorption spectrometer, this experiment tests three commonheavy metals (copper, cadmium, cobalt), and measure the adsorption and desorptioneffects. 3

2.1 Basic adsorptiontest

Weigh modified fiber(wet) which equal to 0.1g dry weight into three beakers with 200ml solutions containing respectively 100 ppm Cu(II) ion, 100 ppm Co(II) ion and 100 ppm Cd(II)ion. Stir with magnetic stirrer and take samples after 1, 2, 4, and 24 hours. The concentrations ofCo(II) Cu(II), and Cd(II) ions in solution were determined byAAS. 10

2.2 Temperature dependent fiber performancetest

Weigh modified fiber(wet) which equal to 0.1g dry weight into three beakers with 200 ml solutions containing respectively 100 ppm Cu(II) ion, 100 ppm Co(II) ion and 100 ppm Cd(II) ion. Stir with magnetic stirrer under 10℃, 25℃ and 40℃ environment, and take samples for analysis. The concentrations of Co(II), Cu(II), and Cd(II) ions in solution were determined by AAS.

2.3 pH dependent fiber performancetest

Weigh modified fiber(wet) which equal to 0.1g dry weight into three beakers with 200 ml solutions containing respectively 100 ppm Cu(II) ion, 100 ppm Co(II) ion and 100 ppm Cd(II) ion. And adjust pH value to 3, 4, and 7 with HNO3 and NaOH solution. Stir with magnetic stirrer under and take samples for analysis. The concentrations of Co(II), Cu(II), and Cd(II) ions in solution were determined by AAS.

2.4 Acid concentration of eluent dependent desorptiontest

(1) Prepare 200 ml hydrochloric acid solution which its concentration is 0.5 M, 0.1Mand 0.01M with DIwater.
(2) Add fiber after adsorption process separately into the three differentconcentration hydrochloric acid solution, and stir with magnetic stirrer to facilitate desorptionprocess.
(3) Dilute the solutions for measurement. The concentrations of Co(II), Cu(II), andCd(II) ions in eluent were determined by AAS.

2.5 Repeated adsorption and desorption test

(1) Prepare 100 ppm metal ion solution with DIwater.
(2) Weigh modified fiber(wet) which equal to 0.1g dry weight into three beakers with 200ml solutions containing respectively 100 ppm Cu(II) ion, 100 ppm Co(II) ion and 100ppm Cd(II) ion. And stir with magnetic stirrer to facilitate adsorptionprocess.
(3) After the adsorption reaction finished, separate adsorbing fiber fromsolution by suction filtration and wash fiber with DIwater.
(4) Place the adsorbing fiber into a 0.1M hydrochloric acid solution fordesorption.
(5) Repeat the above procedure five times with the same fiber, to explore how theadsorption and desorption amounts change withrepetitions.

2.6 Real cobalt-containing industrial wastewatertreatment

Weigh 2, 4, 6, 8, and 10 grams of fiber into separate 100ml cobalt-containing industrial wastewater. And stir with magnetic stirrer to facilitate adsorption process for one hour at 25 ℃, to investigate the cobalt-absorption efficiency of the fiber under these conditions.

2.7 Continuous adsorption and desorption of real industrial cobalt-containingwastewater

Weigh 0.5 grams of fiber into 200 ml cobalt-containing industrial wastewater. And stir with magnetic stirrer to facilitate adsorption process for one hour, and then desorb with 0.1M hydrochloric acid. Repeat 15 times with the same fiber, and investigate how the adsorption and desorption amounts will be affected with repetitions.

III. RESULTS AND DISCUSSION

3.1 Basic adsorptiontest

ItcanbeseenfromtheFig.3.thatTheadsorptioncapacityisabout117mg/gfiberfor copper(II), 86 mg/g fiber for cobalt(II), and 130 mg/g fiber for cadmium(II) while adsorptiontime is one hour, but when adsorption time increase to 24 hour, however, there is no significant change on adsorption amount, the adsorption reaction of copper(II), cobalt(II) and cadmium(II)reaches equilibrium within one hour. It was found that the best adsorption time for all metal ionswe interested in is one hour.

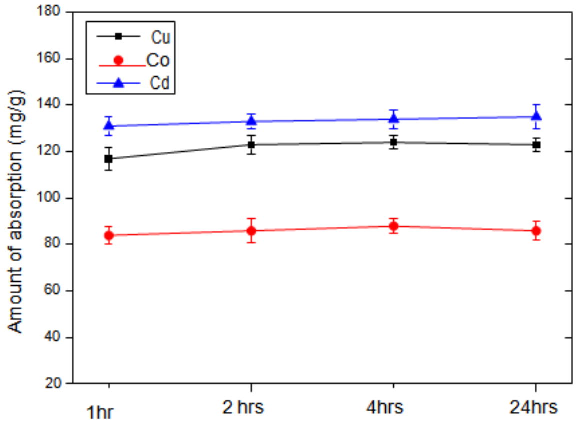

Fig. 3 Effect of adsorption time for Cu(II), Co(II), and Cd(II) adsorptionamount

3.2 Temperature dependent fiber performancetest

Adsorption performance of interested metal ion increasing while adsorption temperature increasing. When adsorption temperature decrease to 10℃, the lower adsorption amount will be. This result also shows that there is a positive correlation between adsorption effect and adsorption temperature, as Fig. 4(a) shown.

3.3 pH dependent fiber performancetest

pH value is a very important variable at this work. As Fig. 4(b) shown, at low pH condition, adsorption amount is reduced due to competition between H+ ions and all three metal ions for active sites on fiber sorbent.

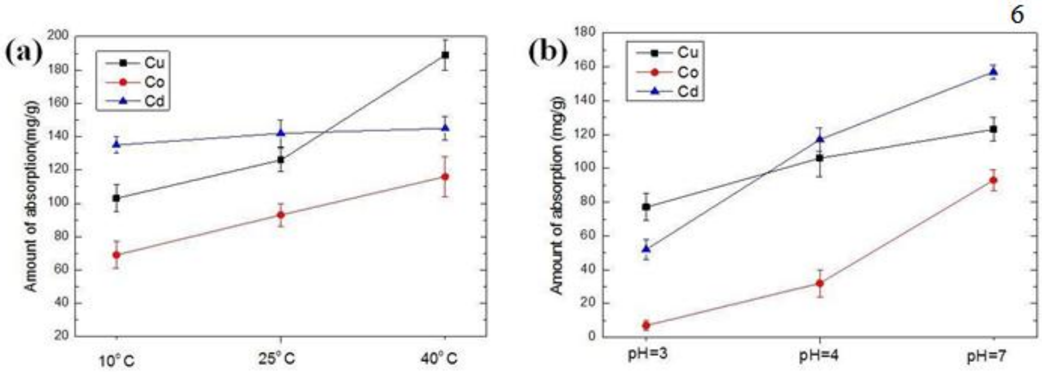

Fig. 4 Effect of (a) temperature and (b) pH value for Cu(II), Co(II), and Cd(II)adsorption amount

3.4 Acid concentration dependent desorptiontest

After adsorption process, we replaced metal ions on sorbent with H+ by using different concentration HCl solution. As shown in Fig. 5. There is over 90% desorption efficiency when using 0.5M and 0.1 M HCl. However 0.01M HCl eluent can't replace metal ions effectively because of the low concentration of H+. The best eluent for desorption we choose is 0.1M HCl.

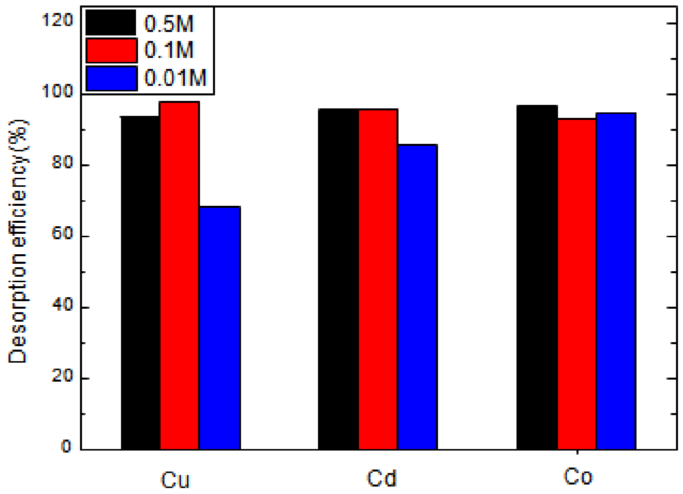

Fig. 5 Effect of concentration of eluent for Cu(II), Co(II), and Cd(II) desorptionefficiency

3.5 Repeated adsorption and desorption test

The result of reusage of fiber sorbent for three metal ions is shown as Fig.6(a). The adsorption efficiency remained still for Co(II) adsorption, but for the Cu(II) and Cd(II) adsorption, there is a slight decrease in adsorption amount.

3.6 Real cobalt-containing industrial wastewatertreatment

The 100 ml industrial wastewater was measured to contain cobalt(II) which the concentration is 984 mg/L. After adding 2, 4, 6, 8, and 10 grams of adsorbing fiber and adsorbing at 25°C for one hour, it was found that the adsorption efficiency of 6 grams of fiber reached 99.7%, and furthermore, the cobalt(II) concentration after the treatment by 8 grams of fiber could no longer be detected by our equipments. The cobalt(II) adsorption capacity for our sample of industrial wastewater was about 42.6 mg/g fiber, which was lower than the original 86 mg/g fiber in model solution, since the cobalt(II) absorption was interfered by other solvents and substrates in the industrial water.

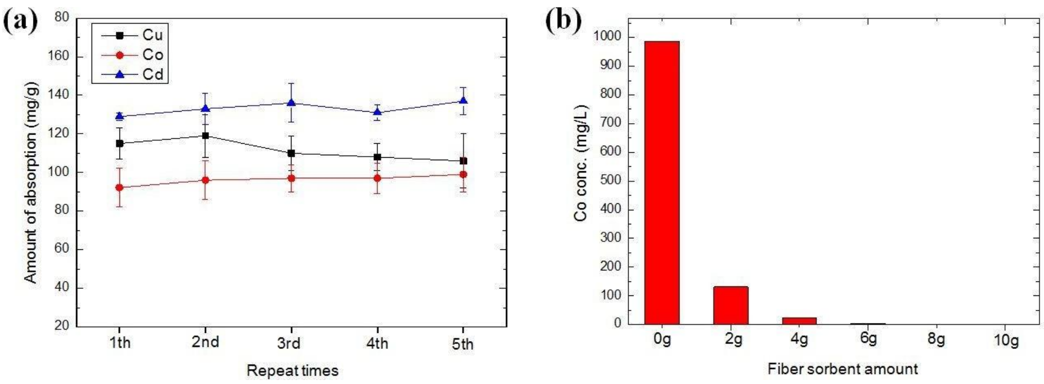

Fig. 6 (a)Effect of reusage for Cu(II), Co(II), and Cd(II) adsorptionamount
(b)Effect of sorbent amount for industrial wastewater adsorptionprocess

3.7 Continuous adsorption and desorption of real industrial cobalt-containingwastewater

The concentration of cobalt(II) in the stock solution was 984 mg/L. It can be seen from the Fig. 7 that there is no effect on fiber sorbent adsorption and desorption efficiency after repeating the adsorption and desorption process about 15 rounds. In fact, the adsorption amount is increased from round to round, because the fiber-to-fiber spacing is enlarged during the continuous adsorption, desorption and reduction process; as a result, the whole fiber complex became fluffier, therefore the hydrophilicity of fiber improved. The average adsorption capacity was 55.2 mg per gram of fiber. 4 In the application of recycled metal, every gram of the adsorbing fiber can be desorbed by 5 ml of acid, so the concentration can reach 55mg/5ml, that is, 11000 mg/L. The concentration is concentrated about 11 times compared to the original stock solution, and the higher concentration improves the metal recovery efficiency of the electroplating and precipitation process.

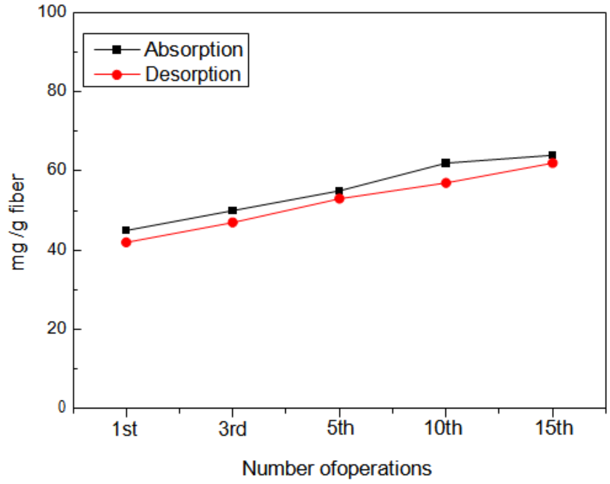

Fig. 6 Repeat test for industrial wastewater adsorption and desorption process 11

IV. CONCLUSIONS

The modified fiber used in this study has significant effect on the adsorption of metal cations. In the case of a single metal ion solution, the adsorption/desorption equilibrium for copper(II), cobalt(II) and cadmium(II) can be reached in one hour. The adsorption capacity is about 117 mg/g fiber for copper, 86 mg/g fiber for cobalt, and 130 mg/g fiber for cadmium. And the desorption efficiency can reach 99% by using 0.1M HCl solution.

As for the dependency on pH, the lower the pH value is, the worse the adsorption efficiency will be. For temperature, he adsorption amount increase along with the temperature increase, showing a positive correlation. In the repetitive test, no significant change in the adsorption and desorption efficiency was found within 5 repetitions for Co(II), and the fiber basically maintained its original efficiency. It's performance did not change significantly in repetitive tests for authentic industrial wastewater sample over 15 times. These results demonstrate that this new type of heavy metal adsorption material is fast, yet very efficient sorbent, and it provides a promising new way to remediate heavy metals pollution. Taiwan's mineral resources are scarce, so the government actively promotes circular economy policies. With the introduction of new technologies for urban mining, Taiwan is developing a model of sustainable resource recycling, that not only solves the problem of heavy metals pollution, but also recycles these valuable metal resources, to achieve the goal of zero waste discharge.

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