1   **Fe-based metallic Glass**

2   **Catalyst with Nanoporous Surface for Azo Dye degradation**

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13   **Abstract**

14   In this work, porous structures were introduced to the surface of Fe-based metallic

15 glass ribbons for the first time by chemical treatment in order to increase the catalytic

16 activity in the degradation of azo dyes. The results show that etching treatment in an

17 HF solution with a volume concentration of 20 % for 40 min leads to a porous

18 structure on the Fe-Si-B-Nb metallic glass with a dramatic increase in the specific

19 surface area by 25 times. The much higher specific surface area of the porous ribbons

20 greatly improves the catalytic activity in the degradation of Direct Blue 15 when

21 compared with as-spun metallic ribbons.

22   **Keywords**: Nanoporous surface; Fe-based metallic glasses; Catalytic properties; Azo

1   dyes degradation.

2   **1. Introduction**

3   Nowadays, dye containing wastewater is widely generated in the dyestuff, textile,

4   paper and plastics industries (Mester and Tien 2000, Peralta-Hernández et al., 2008,

5   Wojnárovits and Takács 2008). Dye containing wastewater includes refractory

6   materials and biological toxic substances which can cause serious environmental

7   contamination. Current approaches, such as carbon sorbent absorption (Malik 2004,

8   Santhy and Selvapathy 2006), bacterial degradation (Sarataleet et al., 2011, Baeta et

9   al., 2015) and reduction reaction by zero-valent metals (Lin et al., 2008, Ma and

10   Zhang 2008, Li et al., 2015) have been used to degrade the contaminants, in which

11   reduction reaction by zero-valent metals has attracted a lot of attention due to low cost,

12   simple operation and efficient degradation capability. Among these approaches, zero-

13   valent iron has been successfully applied for wastewater treatment owing to its

14   excellent catalytic properties for dissociating various organic chemicals (Chen et al.,

15   2011, He et al., 2012, Fu et al., 2014, Segura et al., 2015). However, traditional zero-

16   valent iron easily oxidizes or forms a hydroxide on the surface during the reaction

17   process, leading to a lower catalytic activity (Xiao et al., 2015).

18   Amorphous alloys have attracted increasing attention in many fields due to their

19   unique disordered structure (Greer 1995, Wang 2009, Guo et al., 2015, Phan et al.,

20   2015). In addition, the amorphous alloy is an ideal choice for wastewater treatment

21   because of its metastable state (Schroers 2008). Recently, Fe-based amorphous alloys

22   have been reported to show high catalytic activity in the degradation of organic

23   chemicals, such as azo dyes (Wang et al., 2012, Zhang et al., 2012, Liu et al., 2014,

24   Scaglione and Battezzati 2015, Tang et al., 2015). Fe-based metallic glass has a higher

2

1 catalytic activity compared to corresponding crystallize materials, and is attributed to

2 the lower activation energy for electron transfer (Das et al., 2015). On the other hand,

3 Fe-based metallic glasses ribbons also show good stability in degradation processes,

4 and can be recycled at least 4 times with high degradation efficiency (Zhang et al.,

5 2012). However, few studies have been reported that discuss the factors affecting the

6 catalytic activity, such as the morphology or size of the catalyst. It was reported that

7 ball-milled Mg-based amorphous alloy powders have a much better capability in

8 degrading azo dyes due to the ball-milling causing high roughness on the surface in

9 comparison to Fe-based metallic glasses powders (Wang et al., 2012). On the other

10 hand, with the disadvantages of the recycling and thermal stability, ball-milled Mg-

11 based amorphous alloy powders cannot be widely for the industrial wastewater

12 catalysis.

13   It is well known that the rate of chemical reaction is proportional to the rate of

14 electron transfer. Porous structures are widely used for catalysts due to its high

15 specific surface area. However, little work was done on preparing porous Fe-based

16 alloys as catalysts for dye degradation, mainly due to the electrochemical actively of

17 Fe. In this work, a porous Fe-based amorphous alloy was fabricated by dealloying

18 $Fe_{72}Si_2B_{20}Nb_6$ metallic glass. The selection of this metallic glass as an etching

19 precursor is based on the fact that Nb is both a glass forming element for Fe-based

20 alloys and an element which has a much lower standard electro potential than any

21 other elements in the Fe-Si-B system (Nd^{3+}/Nd: -2.323 V, Fe^{2+}/Fe: -0.44 V SiO_2/Si: -

22 0.92 V $B(OH)_3$/B: -0.89 V). During the etching treatment, the Nd element is

23 preferential leached. Since the remaining Fe-Si-B is a good glass former and an ideal

24 system for dye degradation, a porous amorphous Fe-Si-B alloy with higher catalytic

25 activity can be obtained. To the best of our knowledge, this is the first time that a

3

1 porous amorphous Fe-based alloy has been prepared and it exhibits high catalytic

2 activity in the dye degradation.

3

4 **2. Experimental details**

5 The master alloy ingots, with a nominal composition of $Fe_{72}Si_2B_{20}Nb_6$, were

6 synthesized by arc melting a mixture of pure Fe, Si, B and Nb elements in a WK-Ⅱ

7 vacuum arc melter under an Ti getter purified argon atmosphere. Subsequently, the

8 prepared ingots were remelted eight times to guarantee a uniform distribution of the

9 elements. Metallic glassy ribbons were then fabricated by injecting the melted master

10 alloy onto a spinning copper roller under an argon atmosphere. The glassy state of the

11 as-spun ribbons was confirmed by standard X-ray diffraction (XRD) analysis with

12 Cu-K$_\alpha$ radiation. Glassy ribbons with porous surfaces were prepared by an etching

13 technique: the as-spun ribbons were immersed in hydrofluoric acid (HF) solution for

14 free corrosion. The volume concentrations of the HF solution and etching duration

15 were used to further tailor the porous structure. After the etching treatment, all

16 samples were rinsed with distilled water and dehydrated alcohol before the catalytic

17 tests. A Jeol JSM-6490 scanning electron microscope was used to examine the surface

18 morphology of the specimens. The specific surface area of the as-spun and etched Fe-

19 Si-B-Nb ribbons was measured by the Brunauer-Emmett-Teller (BET) method using a

20 Belsorp-Mini-II analyzer.

21 Direct Blue 15 (DB 15) solid reagent was directly dissolved in deionized water to

22 form a simulated azo dye solution with a concentration of 100 mg/L. Hydrogen

23 peroxide with a dosage ranging from 2.9 mM to 58.2 mM was added into the azo dye

4

1   solution and the ribbon samples were then immersed in a DB 15-containing solution

2   for degradation testing. The dosage of the ribbons was kept at 0.03 g/L. About 4 mL

3   of the solution was taken out and filtered in a 0.45 μm membrane over a time interval

4   of 5-10 min during the degradation tests. The filtered samples were subjected to UV-

5   vis spectrum scanning where an excitation wavelength of 598 nm was used. The DB

6   15 solution degradation rate (R) was calculated by $R=(C_t/C_o)$ x100%, where C_0 is the

7   original DB 15 concentration and C_t is the DB 15 concentration at a given time,

8   respectively.

9   **3. Results and Discussion**

10   Fig. 1 shows the XRD patterns of the as-spun $Fe_{72}Si_2B_{20}Nb_6$ ribbons and the

11   samples treated with HF solutions. The as-spun ribbon exhibits only a broad

12   diffraction peak centered at a 2θ of about 45°, indicating the formation of an

13   amorphous structure in the original ribbon. The ribbons immersed in the HF solutions

14   for different durations show similar XRD patterns as the as-spun sample,

15   demonstrating that the etched ribbons are still amorphous after the HF treatment.

16   Fig. 2(a) and (b) show the surface morphologies of the $Fe_{72}Si_2B_{20}Nb_6$ ribbon which

17   are etched in the 20 % HF solution for 20 min and 40 min, respectively. After 20 min

18   of etching treatment, a uniform nanoporous structure with a pore size ranging from

19   100 nm to 200 nm forms on the surface of the ribbons. The longer etching time (eg.

20   40 min) leads to smaller pores, i.e. 50-100 nm. This phenomenon is related to the

21   different corrosion rates across the thickness direction of the ribbons. During the melt

22   spinning process, the ribbon surface which is contacted with the copper roller

23   undergoes the fastest cooling rate, whereas the other side of the ribbon experiences

24   the slowest one. The stress across the thickness direction of the ribbon changes from

<div align="center">5</div>

1   compressive to tensile, resulting in a higher stress concentration on the surface of the

2   ribbons. As a consequence, the corrosion rate is higher on the surface of the ribbons.

3   At the beginning of the etching process, the first several atomic layers on the ribbon

4   surface are attacked by pitting corrosion where the Nb element is preferentially

5   leached, followed by the further sacrificial anodic corrosion of Si, B and Fe nearby.

6   Thus the pores grow and become connected until these layers are totally etched off.

7   Since the corrosion rate is higher on the ribbon surface, when the upper layers near

8   the ribbon surface are etched off gradually, more underlying smaller pores can be seen,

9   giving the appearance of the pore size decreasing with increasing etching time.

10   Fig. 3 shows a typical UV-vis spectra development as a function of the degradation

11   time (the ribbons etched in 20 % HF for 40 min are used as the catalyst). The original

12   DB 15 solution has a strong absorption peak at 599 nm and the intensity of the peak

13   becomes weaker during the degradation treatment. After 60 min, the solution is fully

14   transparent and no characteristic peak can be found in the UV absorption spectrum.

15   The DB 15 solutions treated by other Fe-based alloys have similar UV-vis spectra

16   development with degradation time. Based on the UV-vis results, the DB 15

17   degradation rate was calculated and summarized in Fig.4. As can be seen, all the

18   solutions follow the first order kinetic model: $C_t/C_0=\exp(-kt)$, where k is the reaction

19   rate and t is the degradation time. When the solution is treated for 60 min, the one in

20   which no catalyst is added (control sample) exhibits the lowest degradation rate of

21   about 80%. In contrast, the solutions that contain as-spun or porous Fe-based ribbon

22   catalysts show a degradation rate of 80 % after only 10-30 min and a full

23   decomposition can be obtained after 30-60 min. The degradation speed of the

24   solutions with different catalysts is in the following order: as-spun $Fe_{72}Si_2B_{20}Nb_6$

25   amorphous ribbon＜porous ribbon treated in 10% HF for 40min＜porous ribbon

6

1   treated in 20% HF for 20min ＜porous ribbon treated in 20 % HF for 40min. It should

2   be noted that the porous ribbon treated in 20 % HF for 40min has significantly higher

3   catalytic activity than the as-spun ribbon, i.e. after 30 min of degradation, the DB 15

4   solution with the porous ribbon is almost fully decomposed while the one with the as-

5   spun ribbon decomposed after 60 min. To clarify the origin of the much higher

6   catalytic activity of the porous amorphous ribbon, the specific surface area of several

7   selected samples is measured. The results show that the ribbons etched in 20 % HF for

8   0 min, 20 min and 40 min have specific surface areas of about 0.025 m^2/g, 0.092 m^2/g

9   and 0.647 m^2/g, respectively. When compared with the as-spun ribbons, it can be seen

10   that the etching treatment for 40 min leads to a dramatic increase in the specific

11   surface area by 25 times. The much higher specific surface area of the ribbon etched

12   for 40 min is shown to contribute to the notable improvement of the catalytic activity.

13   Since it shows the highest catalytic activity among all the samples in this work, the

14   ribbon which experienced 40 min of etching treatment in 20 % HF solution was

15   chosen for further experiments. Firstly, we studied the reaction kinetics of this porous

16   ribbon by measuring the degradation rate dependence on the reaction temperature.

17   Fig. 5(a) shows the degradation rate of DB 15 at various temperatures. Temperature

18   has a great effect on both the degradation rate and speed, demonstrating that the

19   reaction is a thermally activated process. The activation energy of the process can be

20   obtained according to the Arrhenius equation (Herney-Ramirez et al., 2008): In k = -

21   E_a/RT + In A, where k is the reaction rate constant, E_a is the activation energy, R is the

22   gas constant, and A is a constant. The Arrhenius plot is presented in Fig. 5(b) by

23   plotting In k against $1/T$. The E_a for the degradation process is 34.6 kJ/mol, which is

24   much lower than that of a similar reaction (60-250 kJ/mol) using hydroxyl-Fe pillared

25   bentonite or as-spun Fe-based metallic glass as catalyst (Chen and Zhu 2007, Wang et

7

1   al., 2014).

2   Fig. 6 shows the effect of H_2O_2 dosage on the decolorization of DB 15 with the

3   porous amorphous ribbon. The reaction rate is sensitive to the H_2O_2 dosage. It first

4   increases greatly with the increasing H_2O_2 dosage (from 2.9 mM to 5.8 mM). Further

5   increase in H_2O_2 dosage (from 5.8 mM to 58.2 mM) leads to a decrease of the

6   reaction rate. The results suggest that Fenton-like degradation is the dominant reaction

7   where the reactions $Fe^0 + H_2O_2$ to $Fe^{2+} + 2OH^-$ and $Fe^{2+} + H_2O_2$ to $Fe^{3+} + HO\cdot + OH^-$

8   (Wang et al., 2014) take place. In this case, the amount of $HO\cdot$ which exhibits

9   stronger activity with azo dye plays a critical role on the degradation rate and speed.

10   When the H_2O_2 concentration is low, the solution cannot provide sufficient $HO\cdot$,

11   leading to a lower reaction rate and speed. However, when the H_2O_2 concentration is

12   too high, the reaction $\cdot OH + H_2O_2$ to $H_2O + HO_2\cdot$ (Liao et al., 2009) can take place

13   and reduces the effective $\cdot OH$ amount. Thus the solution containing 5.8 mM of H_2O_2

14   shows the highest catalytic activity. Though the dominant reaction is a Fenton-like

15   one, it may not be able to exclude the possible effects of the reduction-type reactions

16   in this work. It has been reported that Fe-based metallic glass can react directly with

17   azo dye, i.e. the Fe atoms lose 2 or 3 electrons and form Fe^{2+} or Fe^{3+} ions , while the -

18   N=N- bonds of the azo dye are broken by reduction, and form $-NH_2$ (Wang et al.,

19   2014). Further work is needed to fully understand this effect of the reduction-type

20   reaction in the system.

21   Fig. 7 shows the degradation rate of the solution with different DB 15

22   concentrations versus reaction time. It can be seen that in a wide DB 15 concentration

23   range (100-500 mg/L), the degradation rate can reach 90 %, suggesting that the

24   porous Fe-Si-B-Nb amorphous ribbon has great potential to be used in dye wastewater

8

1   degradation.

2   The stability and reusability of the porous ribbon have been evaluated by

3   degradation cycles and the results are shown in Fig. 8. There is a slight decrease in the

4   degradation speed. During the first use of the porous catalyst, the DB 15 solution

5   decomposes after 30 min. The second use of the catalyst delays the complete

6   degradation time by 10 min. Further reuse of the porous ribbons makes the complete

7   degradation time approach a stable duration of about 60 min. Though the degradation

8   speed decreases after second time of reuse, the degradation rate does not change

9   greatly, even after the 5th cycle of use. All the DB 15 solutions can be completely

10   decomposed within 60min and the degradation rate and speed is higher than the as-

11   spun ribbon sample, indicating that the porous metallic glass ribbon has good

12   reusability with no activity loss.

13   The ribbons subjected to the 1st and 2nd degradation tests were chosen for further

14   SEM observation. When compared with the as-etched porous ribbon (Fig. 9 (a)), the

15   sample used one time for degradation displays an irregular surface morphology (Fig. 9

16   (b)). Instead of fine pores, some loose oxidation products distributed on the surface

17   are observed. The EDS pattern (Fig. 9 (c)) shows that the main chemical compositions

18   of the sample are Fe, B, Si Nb and O. The high O content in the sample further

19   confirms that the irregular patterns and island-like areas are the oxidation products.

20   After the 2nd use in degradation tests (Fig. 9 (d)), the oxidation layer becomes much

21   thicker, and maintains a loose structure. The formation of the oxidation layer might be

22   the main reason that leads to the decrease in the degradation speed. Since the

23   oxidation products are of loose structure, the ribbon surface is still able to be exposed

9

1 to the DB 15 solution such that the degradation rate can still approach 100% for the

2 amorphous ribbons, even after several cycles of reuse.

3

4 **5. Conclusions**

5 In summary, as-spun Fe-based metallic glassy ribbons and etched porous ribbon

6 samples were used to degrade DB 15 azo dye. The degradation rate and speed for the

7 sample which was etched in 20% HF for 40min was higher than the as-spun glassy

8 ribbons, indicating that the porous glassy ribbon has much higher catalytic aciditivity

9 in the decomposition of azo dyes. The dramatic enhancement of the specific area of

10 the porous metallic glass by etching may contribute to the improvement of the

11 catalytic activity.

15

16

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13

1   **Figure captions**

2   **Figure 1** XRD patterns of as-spun Fe-based metallic glass ribbon and samples after

3   etching treatment.

4

5   **Figure 2** The surface morphology of the Fe-based amorphous ribbons after etching

6   treatment in 20% HF solution for 20 min (a) and 40min (b)

7

8   **Figure 3** Typical UV-vis absorption spectra of Direct Blue 15 solution treated by the

9   porous Fe-Si-B-Nb ribbon which was etched in 20%HF solution for 40min (DB 15 :

10   100 mg/L, H_2O_2: 5.8 mM, 333 K)

11

12   **Figure 4** The degradation rate as a function of the reaction time (DB 15 : 100 mg/L,

13   H_2O_2: 5.8 mM, 333 K)

14

15   **Figure 5** The effect of temperature on the degradation rate of Direct Blue 15 solutions

16   (a) and the corresponding fitting plot of lnk versus 1/T (b), a porous Fe-Si-B-Nb

17   ribbon which was etched in 20%HF solution for 40min was used as the catalyst, (DB

18   15 : 100 mg/L, H_2O_2: 5.8 mM)

19

20   **Figure 6** Effect of initial H_2O_2 concentration on the degradation rate of Direct Blue15,

21   a porous Fe-Si-B-Nb ribbon which was etched in 20%HF solution for 40min was used

22   as the catalyst (DB 15 : 100 mg/L, 333 K)

23

14

1   **Figure 7** Effects of initial DB15 concentrations on the degradation rate of Direct Blue

2   15 solutions, a porous Fe-Si-B-Nb ribbon which was etched in 20%HF solution for

3   40min was used as the catalyst (H_2O_2: 5.8 mM, 333 K)

4

5   **Figure 8** Cycle degradation test on Direct Blue 15 solutions, a porous Fe-Si-B-Nb

6   ribbon which was etched in 20%HF solution for 40min was used as the catalyst (DB

7   15 : 100 mg/L, H_2O_2: 5.8 mM, 333 K)

8

9   **Figure 9** Surface morphology of the porous Fe-Si-B-Nb ribbon which was etched in

10   20%HF solution for 40min in as-spun state (a), after 1th of degradation test(b) and

11   after 2nd of degradation test(d), the EDS result of the sample in b (c)

Fig. 1

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(a)

(b)

Fig. 6

Legend:
- 2.9mM H_2O_2
- 4.3mM H_2O_2
- 5.8mM H_2O_2
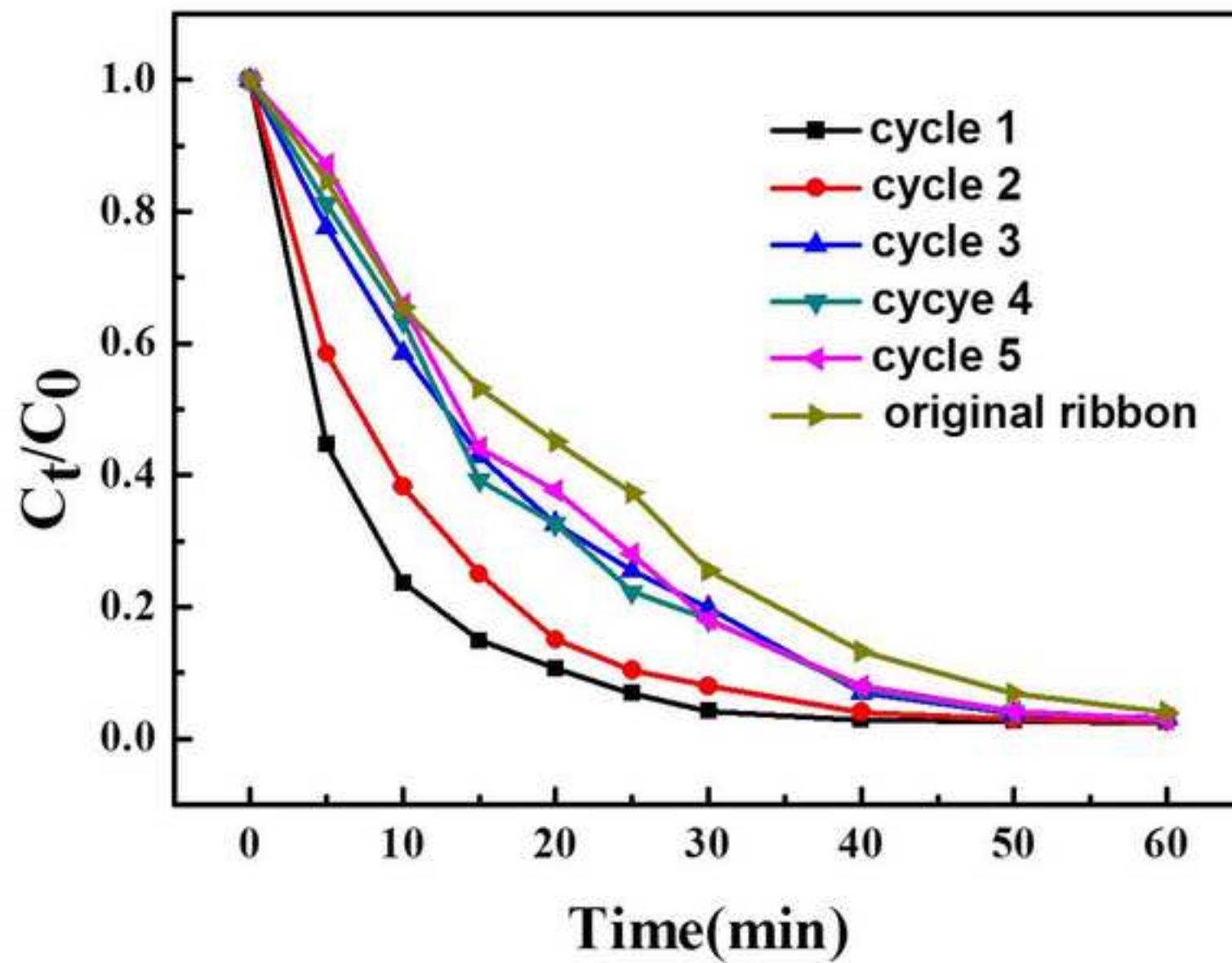- 29.1mM H_2O_2
- 58.2mM H_2O_2

X-axis: Time(min)
Y-axis: C_t/C_0

Fig. 9
[Click here to download high resolution image](#)