

## Synthesis and Development of Novel Aminated Chelating Resin and its Application in Industrial Waste Water Treatment

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**Abstract:** An investigation was undertaken regarding the adsorption of different heavy metal ions from aqueous solutions using novel tertiary aminated cellulose (TAC) having different amine extents, which was prepared by reacting amine epoxide formed from epichlorohydrin and various amounts of diethyl amine with cellulose pulp as a starting substrate. This was done to obtain three levels of TAC having different amination extent (expressed as % N) with increasing order and designated as (TAC I, TAC II and TAC III). The different factors affecting metal ions adsorption on this substrate such as metal ion concentration, pH, treatment time and temperature as well as extent of amination were studied in detail. It was found from the obtained results that; the adsorption % increased with (a) increasing the metal ions concentration up to 50 mmol/l then levels off, (b) increasing the pH value within the studied range, (c) increasing the treatment time up to 2 hour then levels off, (d) increasing the extent of amination reaction within the range studied, and (e) decreasing the temperatures from 80°C to 60°C and then to 40°C respectively. Furthermore, tertiary aminated cellulose was selective adsorbent for Hg<sup>2+</sup> at pH 0.5, and the adsorption % of different metal ions on it follows the order: Hg<sup>2+</sup> > Cu<sup>2+</sup> > Zn > Ni<sup>2+</sup> > Co<sup>2+</sup> > Cd<sup>2+</sup> > Pb<sup>2+</sup>. On the other hand, durability of tertiary aminated cellulose derivatives was also examined.

**Key words:** Tertiary aminated cellulose, Epichlorohydrin, Nitrogen %, Heavy metal ions; Adsorption; Durability.

### INTRODUCTION

It is well known that, heavy metal ions and organic compounds remain a serious environmental problem facing the world for water pollution, as a result of their numerous industrial applications. In addition many of them are known to be toxic or carcinogenic even at low concentration, not biodegradable and tend to accumulate in living organisms causing a serious diseases and disorders (Crini, G., 2005). Therefore, their presence in water should be controlled. Different methods such as precipitation, ion-exchange, reverse osmosis, solvent extraction, electro dialysis techniques (Boto, B.A., L. Pawlowski, 1987; Barcicki, J., L. Pawlowski, 1980), biological treatments (Pearce, C.I., J.R. Lloyd, 2003; Fu, Y., T. Viraraghavan, 2001), membrane process (Ning, R.Y., 2002; Bruggen, B.V.D., C. Vandecasteele 2003), advanced oxidation process (Al-Momani, F., E. Touraud, 2002), chemical and electrochemical techniques (Van, 2003) and adsorption procedure (Xu. Shi-Mei, F. Shun, 2005; Li-Ming, Z. and C. Dan-qing, 2002 Gupta, V.K., CK. Jain, 2003) have been developed for the removal and recovery of metal ions and organic compounds from sewage and industrial wastewater. Amongst all the techniques proposed, adsorption-using sorbents is one of the most fascinating and popular methods for high quality treated effluents. Recently, a great attention and faster publications rate on developing cheaper and effective adsorbents containing natural polymers to overcome the non-biodegradability and high cost of the adsorbent resins were reported. Among these, polysaccharides, such as chitin and chitosan (Kumar, M.N.V.R., 2002), cyclodextrin (Crini, G. and M. Morcellet, 2002) as well as starch derivatives (Wurzburg, O.B., 1986; Mostafa, Kh. M. and A.R. Samerkandy, 2004; Sanford, P.A., J. Baird, 1983) deserve particular attention with respect to their ability to remove heavy metal ions from aqueous solutions. In this work, we describe the synthesis and application of novel tertiary amine derivatives based on cellulose pulp and its application for the removal of toxic metal ions such as Hg<sup>2+</sup> > Cu<sup>2+</sup> > Zn<sup>2+</sup> > Ni<sup>2+</sup> > Co<sup>2+</sup> > Cd<sup>2+</sup> > Pb<sup>2+</sup> from their solutions. For this purpose, various factors affecting the adsorption, such as metal ions concentration, pH, treatment time and temperature as well as extent of amination, in addition to durability (sorption and desorption) were investigated.

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## MATERIALS AND METHODS

Cellulose pulp was obtained from Misr Company for Starch and Glucose, Egypt. Epichlorohydrin, diethyl amine, sodium hydroxide, dioxane, ethyl alcohol, methyl alcohol, acetic acid, mercuric chloride, copper sulphate, zinc acetate, nickel chloride, cobalt nitrate, cadmium sulphate, and lead acetate were reagent grade chemicals.

### *Preparation of Tertiary Aminated Cellulose Having 1.95 % Nitrogen (TAC I):*

Tertiary aminated cellulose was prepared by reacting amine epoxide formed from epichlorohydrin and diethyl amine with cellulose pulp as a starting substrate (scheme 1). Unless other indicated, amination condition was adopted as follows:

9.25 g (0.1 moles) of epichlorohydrin was reacted with 7.3 g (0.1 moles) of diethyl amine. A viscous chlorohydrin (I) resulted was treated with 50% solution of 4.0 g (0.1 moles) sodium hydroxide. Amine epoxide (II) so formed was extracted with dioxane and filtered. Thus it was separated from sodium chloride formed during the reaction.

156 g (0.5 moles) cellulose pulp was taken as slurry in dioxane and made alkaline with 0.1 ml of 50% aqueous sodium hydroxide. Then amine epoxide (II) in dioxane was added to cellulose pulp and allowed to react for 4 hours at 50-60°C. The product was then filtered, washed and neutralized with 75% methanol containing acetic acid and finally washed with methanol and air-dried. This tertiary amine derivative of cellulose pulp was named as 3-N-N diethyl amino-2 hydroxy propyl cellulose ether.

### *Preparation of Tertiary Aminated Cellulose Having Different Extents Amination:*

Three levels of tertiary aminated cellulose substrates designated as (TAC I, TAC II and TAC III) were prepared by varying the concentration of diethyl amine from (0.1 to 0.15 to 0.2 mol) and living all other reaction condition constant. This was done to obtain tertiary aminated cellulose having different amine groups expressed as nitrogen %.

**Table I:** Main characteristics of tertiary aminated cellulose and their statistical data.

Substrate	Tertiary amine derivatives of cellulose (TAD)	
	Nitrogen %	Apparent Viscosity (m.pa.s)
TAC I	1.95 ± 0.024	215
TAC II	2.25 ± 0.042	185
TAC III	3.16 ± 0.086	115

Where;

TAC I: Tertiary aminated cellulose having 1.95 N%.

TAC II: Tertiary aminated cellulose having 2.25 N%.

TAC III: Tertiary aminated cellulose having 3.16 N%.

± Values are the standard deviations of nitrogen % samples measured three times for each sample.

Detail of the conditions used is given in the experimental part.

### *Proof of Amination Reaction:*

This was done via measuring the nitrogen % by well-known kjeldahal method (Vogel A.I., 1975) for aminated products three times for each samples, as well as their standard deviation. In other word, both the nitrogen % in addition to the statistical data (standard deviation) for each sample were taken as an evidence for proofing amination reaction onto cellulose pulp as a carbohydrate polymer that is free from nitrogen groups when it has been used as a starting substrate.

### *Adsorption of Metal Ions:*

The procedure adopted to remove of heavy metal ions is as follows: solutions (50 ml) containing different metal ions concentrations (10-100 m.mol/L) were treated with (0.25 g) tertiary amine derivatives of cellulose (added as solid) and in each case pH was adjusted to a specific value (0.5-6.5). The mixture was occasionally shaken and stirred with magnetic stirrer for the desired reaction time. Finally, the solutions were filtered through whatman filter paper (No. 40) and the residual metal ions concentration in the filtrate was measured by using atomic absorption spectrophotometer, (Instrumentation Lab. Aa / ae Spectrophotometer 175, USA).



### Factors Affecting Metal Ion Adsorption:

The different factors affecting adsorption of metal ions in question such as metal ion concentration, pH, treatment time, treatment temperature and degree of amination as well as the durability of the prepared resin will be studied in detail as shown under:

#### 1- Effect of Metal Ion Concentration:

Figure 1 represents the effect of different metal ion concentration on the adsorption % of tertiary aminated cellulose derivatives having 1.95 N % (TAC I). It is shown figure 1 that;

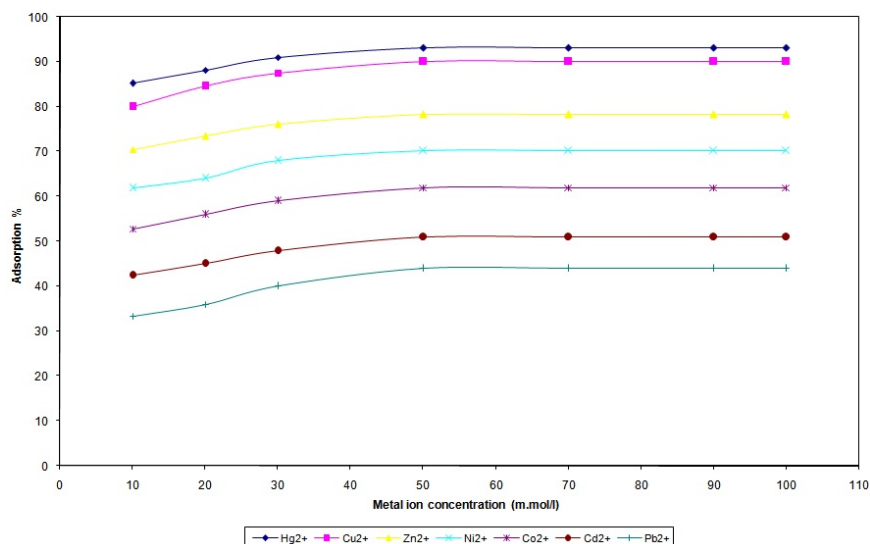
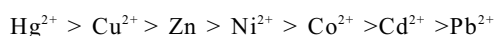


Fig. 1: Effect metal ion concentration versus adsorption % of tertiary aminated cellulose

1. The adsorbed % of metal ions increase by increasing metal ion concentration from 10-50 m.mol/L then levels off.
2. The maximum adsorption % value was 93.1 % for Hg<sup>2+</sup> and the minimum was 44 % for Pb<sup>2+</sup>.
3. The adsorption % value depends on the metal ion in questions and follow the order:

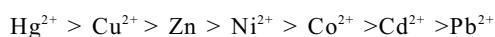


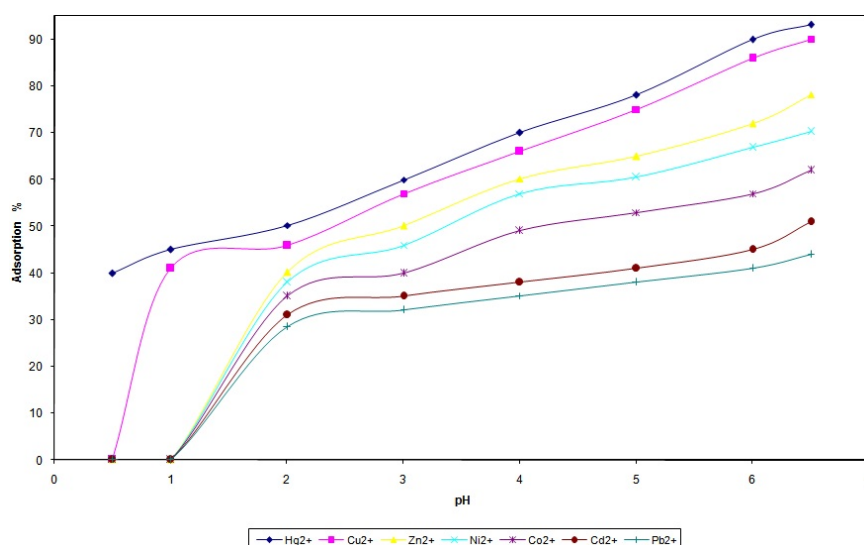
This observation is in full agreement with the published results obtained by Khalil *et al* (1998) for the stability of various ligands with nitrogen and oxygen as coordinating atoms for divalent ions.

#### 2-Effect of pH:

Due to the protonation and deprotonation of the tertiary amine groups on the surface of the cellulose, its adsorption behavior for metal ions is influenced by the pH values, as shown in figure 2. The tests were limited to the pH range of 1.0 to 6.5 because of the precipitation of the metal ions in basic medium. It is found from fig. 2 that at strongly acidic pH the tertiary aminated cellulose has lower adsorption % than that at higher one. This can be explained by the fact that at lower pH values, most of tertiary amine groups are protonated. Then cationic repulsion can occur between metal ion species and protonated aminated cellulose. In addition to the above, the results obtained reflect the following findings:

1. The adsorption % of metal ions in question increases by increasing the pH value within the studied range.
2. At pH 0.5 only Hg<sup>2+</sup> metal ion adsorbed and the adsorption value was 40 %. This reflects the role of the prepared tertiary aminated cellulose derivatives towards Hg<sup>2+</sup> at pH 0.5 (i.e. selective adsorption).
3. At pH value 1 the adsorbed metal ions were Hg<sup>2+</sup> and Cu<sup>2+</sup> and the adsorption value were 45 % and 41 % respectively.
4. At pH 2.0 - 6.5 all metal ions used were adsorbed with different values depending on the nature of metal ion used and the adsorption % follows the order:.

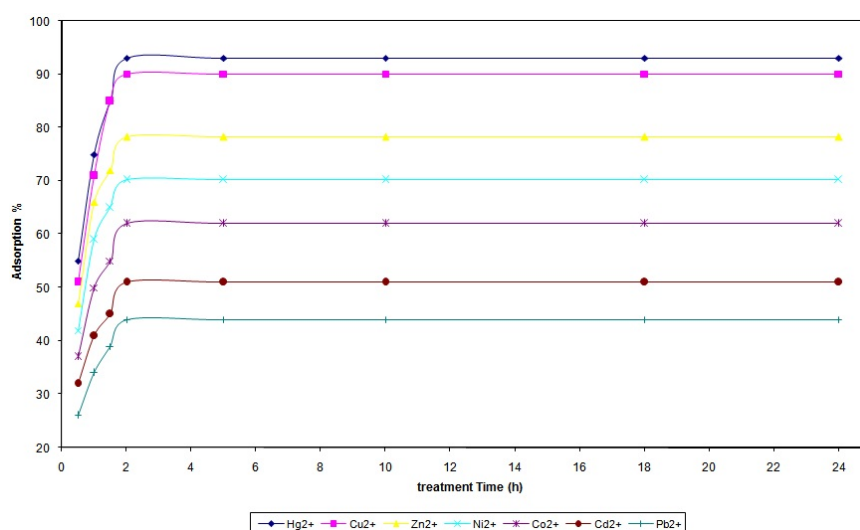




**Fig. 2:** Effect of pH on the adsorption % of different metal ions on tertiary aminated cellulose

**3-Effect of Treatment Time:**

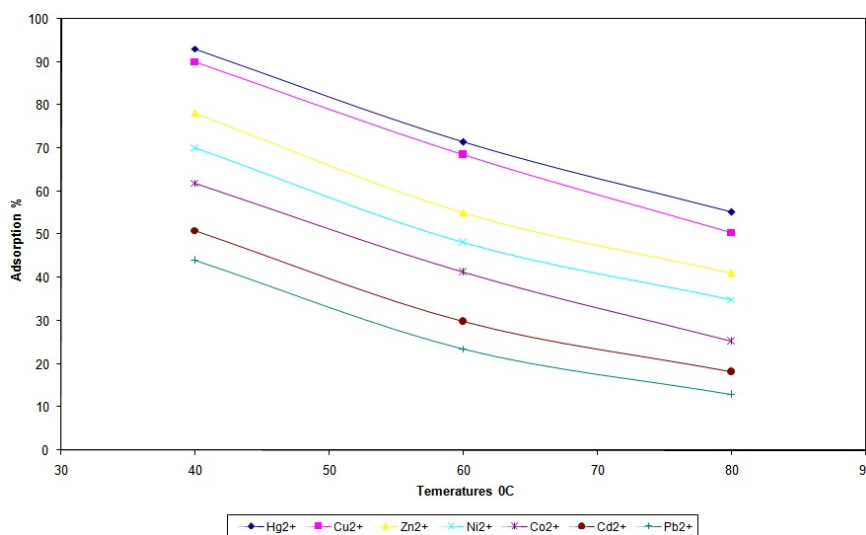
Figure 3 shows the effect of treatment time on the adsorption % of metal ion in question onto tertiary aminated cellulose having 1.95 N% (TAC I). The adsorption % of metal ions increases by increasing the treatment time during the first 2 hour, and then level off by increasing the treatment time to 24 hours. In general, there are three main steps involved in metal ions removal onto TAC: (i) the transport of the metal ions from the bulk solution to the adsorbent surface; (ii) adsorption on the particle surface; and (iii) transport within the adsorbent particles. Because the adsorption is a chemical process, step (ii) is fast. On the other hand, TAC was prepared in solid-state form, so most of the active groups are on the particle surface, which make step (iii) rapid. So, the metal ions in questions were completed within the first 2 hour induction period, which indicate that the metal form chelates or interaction with tertiary amine groups of the prepared substrate. In contrast, the adsorption rate of Hg<sup>2+</sup> is higher than that other metal ion. This may be due to the higher complex formation rate between Hg<sup>2+</sup> ions and the tertiary amine groups on the surface of cellulose.



**Fig. 3:** Effect of changing the treatment time on the adsorption % of different metal ions of tertiary aminated cellulose

#### 4-Effect of Treatment Temperatures:

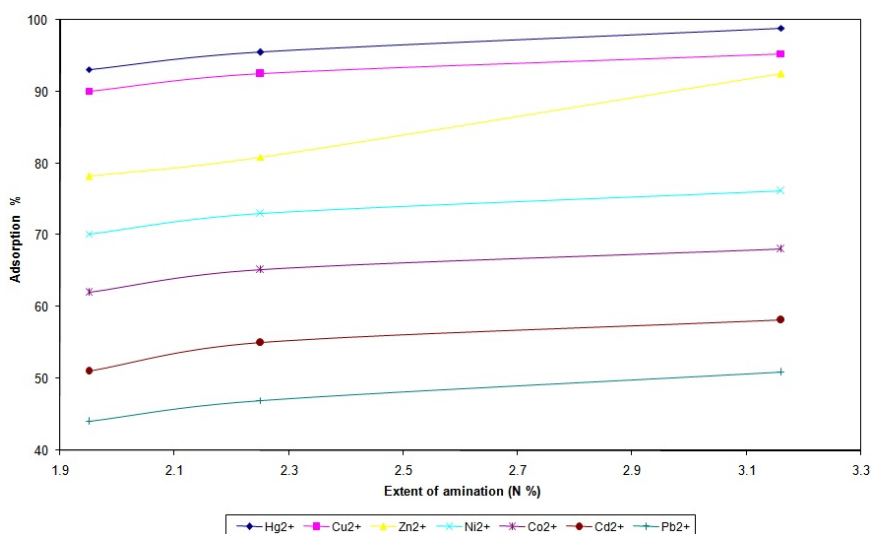
Figure 4 gives the effect of treatment temperatures on the adsorption % of metal ion in question onto tertiary aminated cellulose having 1.95 N% (TAC I). The adsorption % of metal ions decreases by increasing the treatment temperature from 40°C to 60°C and then to 80°C at optimum treatment time 2 hour. This can be explained in terms of higher stability of formed chelates at lower temperatures as generally observed for low molecular weight complexes. This observation is in full agreement also with that obtained with Khalil *et al* (1998).



**Fig. 4:** Effect of changing treatment temperatures on the adsorption % of different metal ions onto tertiary aminated cellulose

#### 5-Effect of Extent of Amination on Metal Removal:

Three levels of tertiary aminated cellulose (TAC I – TAC III) their nitrogen % ranged from (1.95 -2.25 - to 3.16) were used for removing different heavy metal ions from their solutions. The different heavy metal ions used were  $Hg^{2+} > Cu^{2+} > Zn > Ni^{2+} > Co^{2+} > Cd^{2+} > Pb^{2+}$ . The obtained results are set out in Figure 5. It is seen from the figure that, the adsorption % of heavy metal ion removed are governed by the nitrogen % (extent of amination) as well as the nature of metal ion used. So, when the nitrogen % increased from 1.95 to 3.16 the adsorption % of heavy metal increased irrespective of the nature of metal ion used. It is also seen that, the newly synthesized tertiary aminated cellulose are more effective in removing  $Hg^{+2}$  than all other metal ions in question and follow the order:



**Fig. 5:** Effect of extent of amination of tertiary aminated cellulose on the adsorption % of heavy metal ion removal



This can be explained in terms of, the differences between the metal ions in questions with respect to; (a) relative atomic size; (b) ability for metal ion to interact with the tertiary aminated cellulose; (c) metal ion charge density and (d) reactivity of the metal ion. In addition, according to (Khalil, M.I. and S. Farag, 1998; Khalil, M.I. and S. Farag, 1991; Khalil, M.I. and M.G. Abdel-Halim, 2000),  $\text{Hg}^{2+}$  acquires the highest sorption value amongst the variable studied metal ions used i.e.  $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ , hence,  $\text{Hg}^{2+}$  will be used in comparing the sorption behavior of different legends. Furthermore, this is in accordance with the results (Khalil, M.I. and M.G. Abdel-Halim, 2000) also published for the stability of various legends with nitrogen or oxygen as coordinating atoms for divalent transition metal ions. In addition to the metal ions in the solution interact more likely with higher extent with the nitrogen groups of tertiary aminated cellulose, which reflect the role of extent of amination on the heavy metal ions binding activity. The latter was not reported for our knowledge in the literature until now.

### 6-Durability:

Table II shows the absorbency of different metal ions on the tertiary aminated cellulose after 10 cycles (adsorption and desorption). It is seen table II that:

- 1-The adsorbed metal ions was easily desorbed by treatment with 0.1 N  $\text{HNO}_3$  at room temperature,
- 2-The adsorbed amount of the different metal ions decreases after 4 cycles then levels off.

In other word, the decrease in adsorption % of metal ions on tertiary aminated cellulose up to 4 cycles may be due to solubility of some highly substituted tertiary aminated cellulose derivatives (Mostafa, Kh. M. and N.S. Abdel- Aziz, 2001).

**Table II:** The adsorption % of different metal ions on tertiary aminated cellulose (adsorption and desorption)

Metal ions	Adsorption % of different heavy metal ions onto tertiary aminated cellulose after;					
	0 cycle	2 cycles	4 cycles	6 cycles	8 cycles	10 cycles
$\text{Hg}^{2+}$	93.1	90.1	86.1	86.1	86.1	86.1
$\text{Cu}^{2+}$	90.1	87.9	82.3	82.3	82.3	82.3
$\text{Zn}^{2+}$	78.2	75.2	70.5	70.5	70.5	70.5
$\text{Ni}^{2+}$	70.2	66.9	61.8	61.8	61.8	61.8
$\text{Co}^{2+}$	62	59.3	55.6	55.6	55.6	55.6
$\text{Cd}^{2+}$	51	48.3	44.5	44.5	44.5	44.5
$\text{Pb}^{2+}$	44	41.5	38.9	38.9	38.9	38.9

Details of the condition used are given in the text.

### Conclusions:

Tertiary aminated cellulose having different extent of amination was prepared by reacting amine epoxide formed from epichlorohydrin and various amounts of diethyl amine with cellulose pulp as a starting substrate. Their adsorption behavior towards  $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$  ions from aqueous solutions were investigated under different conditions including, metal ion concentration, pH, treatment time and temperature as well as extent of amination in addition to durability. It was found that, this aminated cellulose is effective adsorbents for the removal of different heavy metal ions from aqueous solutions and follows the order:  $\text{Hg}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ . It would be interesting to use these copolymers as sorbents for the economic treatment of effluent containing the aforementioned metal ions. Beside, at pH 0.5 only  $\text{Hg}^{2+}$  metal ion adsorbed and the adsorption value was 40 %. This reflects the role of the prepared tertiary aminated cellulose derivative for selective adsorption of  $\text{Hg}^{2+}$  ions at pH 0.5 which consider as on of the succeeded target of this manuscript.

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