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Evaluating treatment options for wastewater generated from production of metal complex dyes

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ABSTRACT

Dye manufacturing process wastewater (DMPW) generated from production of metal complex dyes might be mainly consisted of organic chelates. It is hypothesized that these organic chelates might form complex with metal ions. As the result, coagulation, frequently employed for dyeing wastewater treatment through sweep-floc mechanism, might not be an effective process to treat DMPW, since Fe(III) or Al(III) might be chelated by organic dye molecules instead of precipitated as metal hydroxides. In this study, carbon/chelated Fe^{3+} molar ratio (C/Fe ratio) is used to represent the content of organic chelates in DMPW and is subsequently used to explore destruction of these chelates after various treatment processes. Finally, the treatment options for DMPW are proposed based on C/Fe ratio after various treatment processes. The C/Fe ratio of biologically treated DMPW is almost two times higher than that of raw DMPW, indicating that biological treatment process is very effective for destroying chelating functional groups and could be employed as a pretreatment process to improve coagulation efficacy subsequently. On the other hand, the C/Fe ratio of the advanced oxidation process-treated DMPW is quite close to that of raw DMPW, indicating that destruction of chelating molecules by heat-activated persulfate is a non-selective process.

Keywords: Metal complex dye; Chelating; Coagulation; Adsorption; Biological treatment

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1. Introduction

Due to their excellent lightfastness property, metal complex dyes are widely used in dyeing industries [1–4]. Metal complex dyes are broadly classified into two classes, namely 1:1 and 1:2 metal complexes. The former has one metal atom coordinating to a dye molecule, while the latter has one metal atom coordinating to two dye molecules. These dye molecules contain mono-azo structure and additional functional groups such as hydroxyl, carboxyl, or amino groups. These functional groups are the ones forming strong coordination complexes with transition metal ions, such as chromium, cobalt and copper. Carbon to chelated metal molar ratio in metal complex dyes

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depends on the molecular structure of dye. For example, it is 40:1 for Acid Black 172 and is 20:1 for Neutral blue BNL [5].

High chemical stability and low biodegradability of metal complex dyes make conventional biological process frequently employed for dye wastewater treatment ineffective [6]. As the result, physical or chemical processes are commonly applied for the treatment of wastewater containing metal complex dyes [6,7]. Several studies [1–5,8], mainly using adsorption and advanced oxidation processes (AOPs), reported treatment of metal complex dye. AOPs are frequently applied before biological treatment to reduce toxicity and improve biodegradability of recalcitrant dye-containing wastewater [9]. It should be noted that the most of aforementioned studies focus on the treatment of dye-containing wastewater generated from textile finishing industries, and synthetic wastewaters prepared in the laboratory were used to simulate these wastewaters.

To our best knowledge, no study reports treatment of wastewater generated from dye manufacturing process. Dye manufacturing process wastewater (DMPW) is high in COD and color, containing mainly organic chelates, i.e. precursors for making metal complex dye, which might readily form complex with metal ions. According to Chen and Yuan [5], metal ions in metal complex dyes are highly soluble and as the result it is very difficult to remove these metal ions by precipitation. The same reason might apply if coagulation was used to treat DMPW through sweep-floc mechanism in which metal ions, Fe(III) or Al(III), added as coagulant might be chelated by organic dye molecules instead of precipitated as metal hydroxides. Consequently, coagulation process which is frequently used for the treatment of dyeing effluent [10–12] might be ineffective for the treatment of DMPW.

Based on the discussion above, it is desired to evaluate the treatment options for this particular type wastewater and to explore the chelating property of DMPW. Other than coagulation process, adsorption process, biological process and AOPs are also investigated for treatment of DMPW. Since DMPW discharged from production line is in elevated temperature (~40–60℃), heat-activated persulfate process [13–16] is chosen to explore the capability of AOP treatment on degradation of chelating functional groups in DMPW.

2. Experimental section

2.1. Chemical and materials

All chemicals used were of reagent grade. Ferric chloride of powder form was added as coagulant. Sodium persulfate of powder form was used in heat-activated persulfate process. NaOH and H_2SO_4 with concentration of 1 N were used for pH adjustment. Several batches of DMPW collected from a plant manufacturing Cr-based metal complex dyes were mixed and stored in 4℃ before used.

2.2. Experimental methods

Coagulation experiments were conducted with pH values varying from 3 to 7 using a jar test apparatus. In one liter of DMPW, pre-determined amount of ferric chloride (500 and 1,000 mg-Fe^{3+}/L) was added and pH was adjusted while DMPW was stirred at 100 rpm for 1 min. The solution was then mixed at 40 rpm for 10 min while pH was maintained at the desired value. After solution being allowed to settle for 30 min under quiescent condition, the supernatant was taken and filtered immediately using 0.45-μm filter. The filtrate was analyzed for iron content, DOC, and color.

DMPW was also treated with adsorption process using pre-formed ferric hydroxide adsorbent. Ferric hydroxide adsorbent was prepared by adding 9 g of ferric chloride to 0.25 L of deionized (DI) water. The pH value of the mixture was raised to 7.0 to induce precipitation of ferric hydroxide. After ferric hydroxide sludge being settled on the bottom of beaker, supernatant was decanted, and DI was added to the original volume. A small sample was taken and digested [17] to measure the iron content. Adsorption experiments were conducted by adding pre-determined amount of ferric hydroxide adsorbent to the DMPW. The mixtures were mixed for 10 min with pH fixed at the desired level (pH 3, 5, and 7). After mixing, samples were taken and filtered immediately using 0.45-μm filter before DOC and color analyses.

A laboratory scale attached growth biological reactor with an effective volume of 4.8 L was employed to evaluate the potential of biological process for degradation of organic chelates in DMPW. The reactor was seeded with activated sludge (MLSS of ~3,000 mg/L) obtained from the wastewater treatment plant located in the campus. The reactor fed with DMPW was operated at recirculation mode for the first several days for reclamation of activated sludge and for attachment of activated sludge onto support material before being changed to continuous feeding mode. Due to the high COD content, biological process was operated at hydraulic retention time of 2 d. After COD of biologically treated effluent became stable, effluent was collected and filtered with 0.45-μm filter for DOC and color analyses. After treatment, DOC is around 560 mg/L. Since the purpose of the experiment is to explore the ability of biological treatment on degradation of chelating functional groups in DMPW, biological treated filtrate was diluted to various concentrations ranging from 140 to 420 mg/L and subjected to the analysis to be described later for the evaluation of the amount of chelating groups.

Heat-activated persulfate process is chosen to explore the ability of AOP treatment on degradation of chelating functional groups in DMPW. Four times dilution of raw DMPW (with DI water) was dosed with sodium persulfate of 0, 500, 5,000, and 10,000 mg/L, respectively. After dosed with persulfate, solutions were heated at 90℃ at stirring hot plates for 270 min. After cooled with in an ice-water bath, DOC of AOP-treated samples was analyzed and was ranging from 300 to 1,200 mg/L (corresponding to DOC removal efficiencies of 0–75%). The samples were then subjected to the analysis for the evaluation of the amount of chelating functional groups.

2.3. Analyzing the content of organic chelates

It is hypothesized that that DMPW might contain many organic chelates. These chelates might form complexes with ferric ions, preventing the precipitation of ferric hydroxide. To quantify the amount of organic chelates, solutions with various DOC were obtained by diluting raw DMPW and biologically treated DMPW with DI water, and by treating DMPW under various persulfate dosages. These solutions were dosed with ferric chloride under various dosages with fixed pH of 3.0 and were mixed using the protocol identical to that of coagulation experiment mentioned above. After solution being allowed to settle for 30 min under quiescent condition, the supernatant was taken and filtered immediately using 0.45-μm filter, and the dissolved iron concentration was determined. It is hypothesized that in samples containing organic chelates, dissolved iron concentration will increase with increasing dosage of ferric chloride until all of iron ions added forming complexes with organic chelates. While all of organic chelates were chelated, additional ferric chloride added will be precipitated as ferric hydroxide, and dissolved iron concentration should be stable at certain level, i.e. the saturated dissolved iron concentration. For the samples with different dilution ratios, the higher the organic carbon content, the higher the saturated iron concentration while the ratio between the organic carbon content and saturated dissolved iron concentration remains constant. Therefore, the molar ratio between carbon to chelated Fe^{3+} (C/Fe ratio) can be determined and is used to represent the content of organic chelates in the sample. The lower the value, the higher the organic chelates per carbon in the sample.

2.4. Analytical methods

Color analysis followed the ADMI methods (Method 2120E in Standard Method) [18]. A UV–vis spectrophotometer (ThermoSpectronic, Helios Beta) was used to scan the light absorbance, and data were recorded by personal computer for color calculation. BOD_5 and COD analyses followed the 19th edition Standard Methods. The residual DOC was analyzed using a total organic carbon analyzer (Aurora 1030, O.I. cooperation, USA). Iron and chromium concentrations were determined by Flame atomic Absorption Spectrophotometer (GBC 932 plus, Australia).

3. Results and discussion

3.1. Treatment of DMPW with coagulation and adsorption processes

Characteristics of DMPW are listed in Table 1. DMPW is very biodegradable as indicated by BOD_5 to COD ratio of 0.5–0.6, showing very different characteristics from that of metal complex dyes which contain both toxic metals and azo structure and are believed to be chemical stable and non-biodegradable [6]. As indicated in Table 1, DOC, COD, and color are much higher than those reported in other studies for the treatment of metal complex dyes [1,5,8,19]. For example, DOC is in the range of 3,000–4,000 mg/L for DMPW, and it is only 25–30 mg/L reported in the study for removal of metal complex dye by AOPs (see Ref. [5]). According to the manufacturer, C to Cr molar ratio of the finished metal complex dye product is 34:1, which is within the range reported for various metal complex dyes, e.g. 40:1 for Acid Black 172 and 20:1 for Neutral blue BNL. Based on DOC and Cr analysis, carbon to Cr molar ratio in DMPW is

Table 1
Characteristics of DMPW collected

Parameters	Value
COD	6,500–7,500 mg/L
DOC	3,000–4,000 mg/L
Color	3,000–7,000 ADMI
C:Cr molar ratio	6,225:1
pH	7–9
BOD_5/COD	0.5–0.6

calculated to be around 6,225:1 and is much higher than that in the final metal complex dye product, indicating that the majority of metal complex dyes are recovered during manufacturing process.

It is hypothesized that many organic chelates, i.e. the precursors for making the dyes, still remain the DMPW, and might form complex with Fe ions being added as coagulant, resulting in elevated dissolved iron concentration in coagulated water. Consequently, coagulation might not be an effective process to treat DMPW. To test this hypothesis, coagulation experiments were conducted at various pH values ranging from 3 to 7 with coagulant doses of 500 and 1,000 mg/L as Fe^{3+}, respectively.

As indicated in Fig. 1(A), COD removal is only marginal for two coagulant dosages at all pH conditions tested. COD removal efficiencies are 1.7–10.6% for pH values of 3–7 with 500 mg/L Fe added and are 7.8–20.3% with 1,000 mg/L Fe added. ADMI of treated water are higher than that of original DMPW except experiments conducted at pH of 7.0. Increases in treated water color might be related to the elevated dissolved iron in the treated water. As indicated in Fig. 1(B), dissolved iron concentrations in the filtered coagulated DMPW range from 453 to 95 and 774 to 32 mg/L for experiments with 500 and 1,000 mg/L Fe added, respectively. Without the organic chelates, i.e. DI water only, soluble concentrations of Fe are marginal, ranging from 53 to 0 mg/L and decreasing with increasing pH values. These results confirm that DMPW might contain many organic chelates which are readily to form complex with Fe ions, and tendency of these chelates to form complexes with Fe ions is higher at acidic pH values.

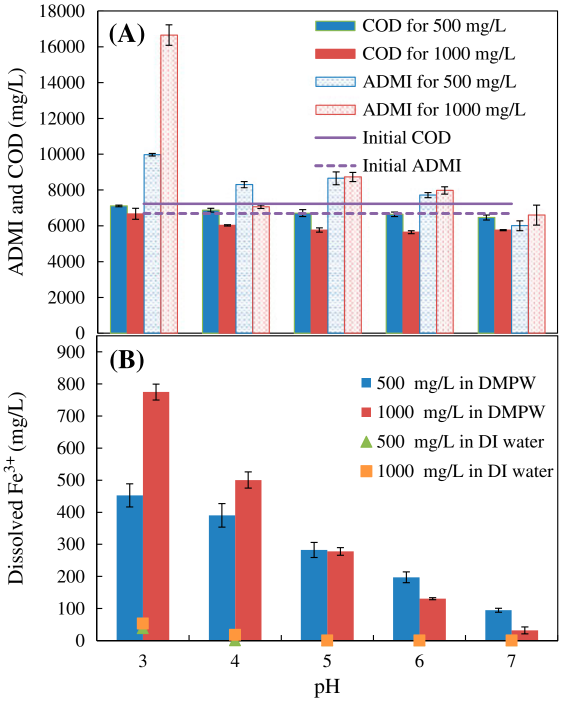

Fig. 1. COD and ADMI (A) and dissolved iron concentration (B) of coagulated DMPW (Initial COD of 7,500 mg/L and ADMI of 5,800) with different coagulant dosage (1,000 and 500 mg/L as Fe) under various pH values. Error bars represent the standard deviation of triplicate experiments.

It is interesting to note that at pH values of 6 and 7, the dissolved iron concentrations in the treated samples with coagulant dosage of 1,000 mg Fe/L are less than those treated with coagulant dosage of 500 mg Fe/L. It is possible that un-complexed Fe ions are ready to from iron hydroxide precipitate, and iron-chelated molecules are removed (adsorbed) by the precipitated iron hydroxide. Since much more iron hydroxide precipitates formed with coagulant dosage of 1,000 mg Fe/L than that with coagulant dosage of 500 mg Fe/L, the adsorption of iron-chelated dye molecules by the precipitated iron hydroxide is more pronounced with coagulant dosage of 1,000 mg Fe/L, resulting in lower dissolved iron concentrations in these samples.

To test the hypothesis of adsorption on dye removal, pre-formed iron hydroxide absorbent was used to treat DMPW. Since iron hydroxide added is already in solid state, negligible iron–organic chelates complexation will occur. As indicated in Fig. 2, both ADMI and DOC decrease with increasing iron hydroxide absorbent dosage. Removal efficiencies range from 5 to 50% and 12 to 49% for DOC and ADMI, respectively. Unlike the result of coagulation test that color is not removed at all, color removal by adsorption is much more effective.

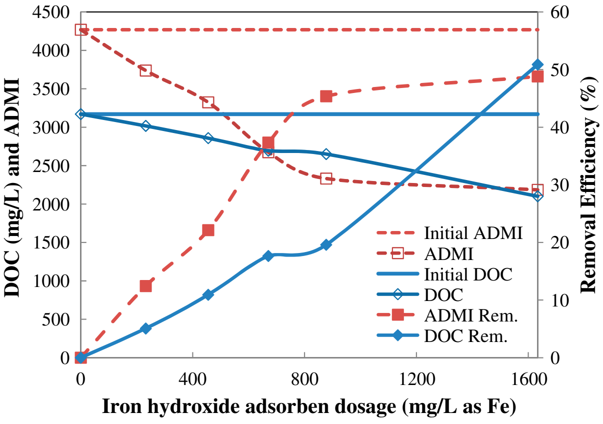

Fig. 2. DOC and ADMI removed vs. dosage of iron hydroxide adsorbent for adsorption test. pH 7.0.

Data from adsorption and coagulation were compiled and shown in Fig. 3 by plotting the amount of precipitated iron versus DOC removed. Data for coagulation test were deduced from Fig. 1(A) and (B) where the amount of precipitated iron was calculated from the difference between added coagulant concentration and dissolved iron concentration. It clearly indicates that the amount of DOC removed is linearly correlated to the amount of precipitated iron in the solution with 0.68 mg of DOC removed per mg of Fe(III) added or 37.98 mg of DOC removed per mmol of Fe(III) added. This value is in the range reported or calculated from other studies. For example, Lee et al. [11] studied adsorption and coagulation of reactive dyes, Black 5 and Orange 16. Under the optimal conditions, around 30.08 and 21.45 mg of DOC removed per mmol Al(III) added. The value is 31.7 mg DOC removed per mmol Al(III) added for Acid Blue 292 study by Hasani Zonoozi et al. [20] and is 68 mg DOC removed per mmol Al(III) added for EBT study by Cañizares et al. [21] by assuming efficiency of DOC removal is the same as efficiency of color removal.

From these results, we can conclude that adsorption is better than coagulation for DMPW treatment since the former can avoid the formation of unwanted metal organic chelate complexes.

3.2. *Chelating properties of raw DMPW, biologically treated DMPW, and AOP-treated DMPW*

The results from previous section indicate that DMPW indeed contains many organic chelates, and the tendency of organic chelates to form complexes with Fe ions is much more pronounced at acidic pH values. In this section, chelating properties of raw DMPW, biologically treated DMPW, and AOP-treated DMPW were quantified using coagulation test described above with fixed pH of 3.0. Samples with various DOC were obtained by dilution of DMPW with DI water and were added with various dosages of Fe coagulant at fixed pH of 3.0. Samples were taken and filtered at the end of coagulation for analysis of dissolved iron concentration. Fig. 4 shows dissolved iron concentration as a function of coagulant dosage for diluted DMPW samples of various DOC. As expected, in DI water system (i.e. data points with legend labeled as DOC = 0), dissolved iron concentration is very low (less than 40 mg/L) due to precipitation of $Fe(OH)_3$ at pH of 3. In samples containing organic chelates molecules, i.e. samples with no-zero DOC, dissolved iron concentration increases initially with increasing dosage of iron coagulant, and the points are located alone the 45-degree line, indicating that almost all of Fe ions added form complexes with organic chelates and dissolve in the solution. After all of organic chelates forming complexes with added Fe ion, the points start deviate from the 45° line. The point after all of organic chelates forming complexes with added Fe ion is denoted as saturation point. It is noteworthy that further increase of coagulant dose after saturation point causes precipitation of iron hydroxide which adsorbs iron/organic chelates molecules, resulting in decreasing the dissolved iron concentration.

Fig. 5 shows the amount of chelated iron concentration at the saturation point as a function of DOC of DMPW, clearly indicating the existence of linear relationship between DOC and dissolved iron

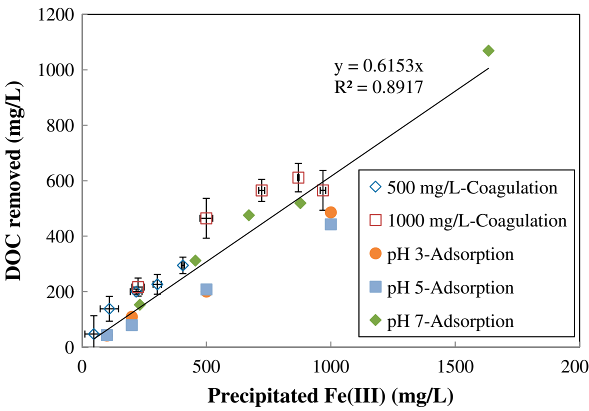

Fig. 3. DOC removed vs. amount of precipitated Fe(III) for coagulation and adsorption test. Error bars represent the standard deviation of triplicate experiments.

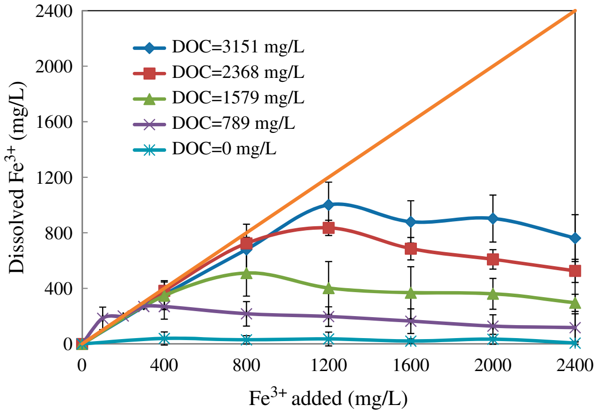

Fig. 4. Dissolved iron concentration as a function of iron added initially under various DOC of raw and diluted DMPW. Error bars represent the standard deviation of triplicate experiments.

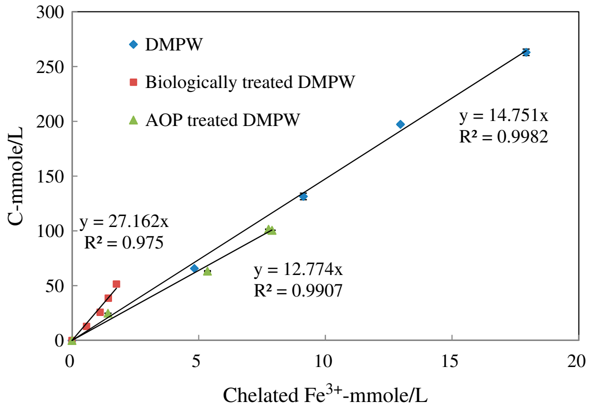

Fig. 5. Chelated iron concentration for raw (data extracted from Fig. 4), biologically treated, and AOP-treated DMPW. Error bars represent the standard deviation of triplicate experiments.

concentration with R^2 of 0.9981. The slope indicates the carbon to chelated Fe molar ratio, and is around 14.8 as shown in Table 2. As indicated earlier, according to the manufacturer C to Cr molar ratio of the finished metal complex dye is 34. The ratio for the finished metal complex dye products is about two times that of the DMPW. The reason might be due to the finished metal complex dye products are 1:2 metal complexes dyes where one Cr atom being coordinated to two dye molecules, and only one Fe atom being coordinated with one dye molecule in DMPW.

The same procedures were conducted for biologically and AOP-treated DMPW to determine the content of organic chelates and to investigate the tendency of biological and AOP treatment on destruction of chelating property of DMPW. As stated previously, high chemical stability and low biodegradability of dyes make conventional biological treatment process ineffective for treating colored wastewater [6], and physical or chemical processes are commonly used to treat dye wastewater [6,7]. However, our results indicate that characteristics of DMPW are quite different from effluent related to the textile finishing industry and are quite biodegradable. Table 2 shows that after biological treatment DOC of treated water is around 600 mg/L, corresponding to around 75–80% of removal efficiency. The DOC removal efficiencies are around 75 and 35%, respectively, with persulfate dosages of 10,000 and 5,000 mg/L for treating diluted DMPW.

As shown in Fig. 5 and Table 2, carbon to chelated Fe molar ratio of the biologically treated DMPW is around 27, indicating that the chelating functional groups are effectively degraded by biological process. Chelating property of AOP-treated DMPW is also shown in Fig. 5 and Table 2. The carbon to chelated Fe molar ratio of the AOP-treated DMPW is around 12.8 which is quite close to that of raw DMPW. The result indicates that destruction of dye molecules by heat-activated persulfate is a non-selective process [16].

Table 2.
Carbon to chelated Fe ratio

Sample	DOC (mg/L)	C/Fe molar ratio
DMPW	3,151–789	14.8
Biological treated	618	27.2
AOP treated	300–1,200	12.8

4. Conclusions

DMPW mainly consists of organic chelates, showing very different characteristic from wastewater generated from textile finishing industry. Coagulation process is shown to be ineffective for treating DMPW because iron coagulant added is chelated by organic chelates in DMPW. COD removal is only marginal (1.7–20.3%) for two coagulant dosages (500 and 1,000 mg/L Fe) at all pH conditions tested. Due to the elevated dissolved iron in the treated water, ADMI of treated water are higher than that of original DMPW except experiments conducted at pH of 7.0. Dissolved iron concentrations in the filtered coagulated DMPW range from 453 to 95 and 774 to 32 mg/L for experiments with 500 and 1,000 mg/L Fe added, respectively, confirming that DMPW indeed contain many organic chelates. These organic chelates molecules are readily to form complex with Fe ions, and tendency of dye molecules to form complexes with Fe ions is higher at acidic pH values.

The carbon/chelated Fe^{3+} molar ratio is employed to explore the destruction of organic chelates after various treatment processes. The carbon/chelated Fe^{3+} molar ratios is 27.2 for biologically treated DMPW and is almost two times higher than that of raw DMPW, indicating that biological treatment process is very effective for destroying chelating functional groups and DOC. The biological treatment process could be employed as a pretreatment process to improve coagulation efficacy subsequently. On the other hand, the carbon/chelated Fe^{3+} molar ratios of the AOP-treated DMPW is around 12.8 and is quite close to that of raw DMPW, indicating that destruction of dye molecules by heat-activated persulfate is a non-selective process.

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