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Mechanochemical treatment for degradation of ciprofloxacin (CIP) in solutions

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ABSTRACT

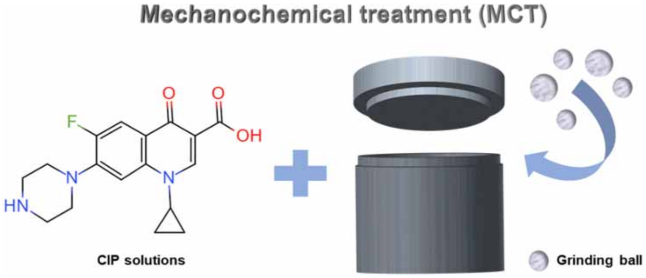
Ciprofloxacin (CIP) is a kind of widely used fluoroquinolone antibiotic, and the widespread presence of CIP in aquatic environment has become a serious issue. Mechanochemical treatment (MCT), as an effective approach to degrade persistent organic pollutants, has many advantages of low cost, simplicity, and being environmentally innocuous. However, little attention has been paid to employing MCT to treat effluents containing CIP. In this study, MCT was introduced to degrade CIP in aquatic solutions. A series of CIP degradation experiments were conducted by a planetary ball mill, and the influences of main parameters on CIP degradation efficiency were investigated. Furthermore, an optimum combination was selected through orthogonal experiments, and CIP degradation efficiency could reach as high as 99% in certain conditions. Besides, the biotoxicity of CIP solution was also studied. MCT exhibits satisfying performance for degrading CIP in solutions, which makes MCT a promising approach to CIP elimination and also encourages further applications in treating effluents containing other organic pollutants.

Key words: ciprofloxacin, degradation efficiency, environmentally innocuous, mechanochemical treatment, planetary ball mill

HIGHLIGHTS

- Mechanochemical treatment was used to degrade ciprofloxacin in solutions.
- Influences of main parameters on degradation efficiency were studied.
- Ciprofloxacin degradation efficiency could reach 99% under optimal conditions.

GRAPHICAL ABSTRACT



INTRODUCTION

Ciprofloxacin (CIP), a broad-spectrum fluoroquinolone antibiotic, has been widely utilized worldwide for treating human and veterinary diseases (Zeng *et al.* 2019; Igwegbe *et al.* 2021). Recently, the residual CIP in natural environments has become a growing environmental issue: more and more CIP is detected in surface water and underground water (Prieto *et al.* 2011; Kutuzova *et al.* 2021). The effluents discharged from hospitals and pharmaceutical factories with high CIP concentration

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will poison organisms in aquatic environment owing to its low biodegradability, which may threaten the health of human body through food chain (Vasconcelos *et al.* 2009; Jin *et al.* 2022). In addition, the widespread presence of low-concentration CIP in aquatic environment can stimulate the generation of resistance genes in microorganisms, leading to the emergence of CIP-resistant pathogens, which will make CIP ineffective (Jia *et al.* 2018; Pu *et al.* 2020). Therefore, it is imperative to find an appropriate approach for CIP degradation to deal with the inevitable concern of high CIP consumption amounts every year.

To address this issue, much effort has been focused on exploring an effective method to degrade CIP, including photocatalytic degradation, Fenton degradation, adsorption degradation, O_3 treatment, etc. (Carabineiro *et al.* 2011; Shehu Imam *et al.* 2018; Wang *et al.* 2019). For example, Tamaddon *et al.* synthesized $CuFe_2O_4$@methyl cellulose (MC) composites as photocatalysts to degrade CIP, and they demonstrated that chemical oxygen demand (COD) removal efficiency was 68.2% (Tamaddon *et al.* 2020). Chen *et al.* used electro-Fenton method to degrade CIP and investigated the effect of chelation between Fe^{3+} and CIP on catalytic behavior (Chen *et al.* 2017). However, all the above-mentioned methods have some drawbacks. Although the photocatalytic approach is easy to operate, the catalysts are hard to recycle and photocatalytic reaction process is quite slow (Wang *et al.* 2018). Regarding the O_3 treatment, the preparation of O_3 is costly; in addition, the storage and transportation procedures are relatively complex. As for the adsorption degradation method with low-cost and high-feasibility advantages, CIP is just immobilized and not actually degraded, so it may be released into surrounding environment over time. Therefore, it is significant to find a low-cost, high reaction rate, easy accessibility approach to meet the demands for CIP degradation.

Mechanochemical treatment (MCT), as a branch of chemistry concerning chemical and physicochemical transformation of substances in all states, has attracted extensive attention since Rowlands *et al.* employed MCT to degrade chlorobenzenes and polychlorinated biphenyls (PCBs) (Rowlands *et al.* 1994; Cagnetta *et al.* 2016; He *et al.* 2020). In a typical MCT process, the mechanical energy provided by electrical machinery is transmitted to substances in the ball mill, triggering some reactions that are unlikely to occur in other conditions (Nomura *et al.* 2012). The transformation of mechanical energy to chemical energy is realized via the effects of squeeze, collision, shearing, and friction; moreover, the whole reaction process is conducted in ball mills (Deng *et al.* 2020). Compared with other degradation methods, MCT has several advantages: (1) the cost of MCT is relatively low because no expensive instruments are needed and no complex operating procedures involved; (2) MCT possesses a relatively high reaction rate, so that pollutants can usually be degraded within hours; (3) MCT is an environmentally innocuous route with minimal hazardous by-products formed in the process (Nie *et al.* 2022). It is noted that MCT is usually employed for treating solid-state pollutants, and in some cases, some kind of liquid pollutants such as tetrachloroethane and oil can also be treated via MCT. Given these advantages, MCT has been utilized for the degradation of persistent organic pollutants (POPs) and exhibits satisfying performance.

Moreover, to the best of our knowledge, using MCT to degrade CIP has not been reported yet. In this study, MCT is introduced to degrade CIP in aquatic solutions, and the effects of various experimental factors such as milling rotational speed, ratio of ball to material, and pH value on degradation performances are investigated.

EXPERIMENTAL

Materials and methods

A planetary ball mill (XGB2, Boyuntong, Nanjing, China) was used to conduct MCT degradation process, with four 100 mL milling pots, and the transmission ratio of revolution to rotation was 1:2, as shown in Figure 1. Ciprofloxacin (purity >98.0%),

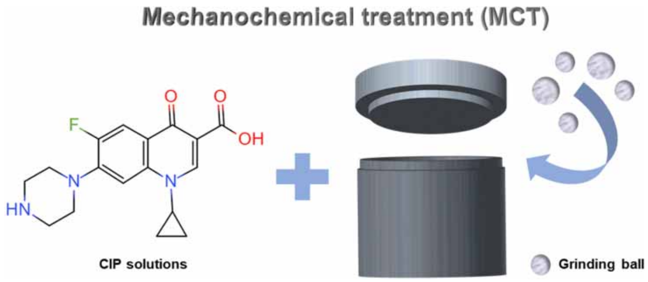

Figure 1 | Illustration of the mechanochemical treatment process for degrading CIP.

HCl, phosphate buffer and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). All chemicals were analytical grade and used without further purification. CIP solutions with various concentrations were prepared and poured into the mill pots, and then the MCT process started. To be on the safe side, the milling pots were placed symmetrically with same weights.

Batch experiments

In this study, five influencing parameters (milling rotational speed; milling time; ratio of grinding ball to material (defined as RGM); ratio of grinding balls (defined as RGB); and grinding ball type) concerning milling process and three influencing parameters (initial CIP concentration; pH value; and co-existing inorganic ions) concerning CIP solutions were studied. Variable-controlling approach was employed and the detailed parameters were set up as shown in Table 1.

As for the 'milling time' parameter, in order to avoid the interruption of ball milling, which would affect the final results, different milling pots corresponding to various sampling times were used. The ratio of grinding balls to material (RGM) is defined as the ratio of weight of grinding balls to volume of CIP solution. Specifically, the 'ratio of grinding balls (RGB)' experiment was set to investigate the influence of weight ratio (weight of Φ10 mm balls to weight of Φ6 mm balls).

Although we could find out the influences of various experimental parameters on CIP degradation efficiencies via variable-controlling approach, there were impacts of interactions between many factors, which would make the single-factor tests unable to accurately analyze the results. Hence, orthogonal experiments were conducted to study the influencing factors. Four experimental factors of milling rotational speed, RGM, grinding ball type, and pH value were set as A, B, C, and D in orthogonal experimental design. Each experimental factor had three values, and Table 2 shows the factors and levels of orthogonal experiment.

CIP degradation measurement

The CIP degradation efficiencies in different experimental conditions were determined by measuring relative CIP concentrations using high performance liquid chromatography (HPLC, Waters, USA), equipped with a C18 column (50 mm × 2.1 mm × 1.7 μm, Waters, USA). The degradation efficiency (DE) was defined as $DE = 1 - C/C_0$, where C represented the measured concentration and C_0 represented the initial CIP concentration, respectively. In addition, the toxicity of liquid supernatant after MCT process was analyzed by a microplate reader (SuperMax 3100, Flash Spectrum, Shanghai, China).

Table 1 | Batch experiments setup

Number	Parameters	Experimental conditions
1	milling rotational speed	100 rpm, 200 rpm, 300 rpm, 400 rpm, 500 rpm
2	milling time	0 min, 5 min, 10 min, 15 min, 20 min, 30 min, 40 min, 60 min
3	ratio of grinding ball to material (RGM)	1:1, 2:1, 3:1, 4:1 , 5:1
4	ratio of grinding balls (RGB)	3:0, 2:1, 1:2, 0:3
5	grinding ball type	agate ball, ceramic ball, steel ball, zirconia ball
6	initial CIP concentration	20 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L
7	pH value	3, 5, 7, 9, 11
8	co-existing inorganic ions	HCO_3^-, Cl^-, SO_4^{2-}, NO_3^-

Table 2 | Orthogonal experiment factor level table

Level	Factor A milling rotational speed (rpm)	Factor B RGM	Factor C grinding ball type	Factor D pH value
1	300	3:1	steel ball	5
2	400	4:1	agate ball	7
3	500	5:1	zirconia ball	9

Furthermore, *Photobacterium phoshporeum* T3 spp was selected as acute toxicity indicator, and the relative inhibition rate (RIR) of luminescence intensity (LI) of bioluminescent bacteria was calculated through Equation (1):

$$RIR = \left(\frac{LI_{relative} - LI_{sample}}{LI_{relative}}\right) \times 100\% \tag{1}$$

It is noted that RIR value was proportional to the toxicity of liquid supernatant; hence the toxicity of solution could be measured by this method.

RESULTS AND DISCUSSIONS

The CIP degradation efficiency is affected by many experimental factors in MCT process, and milling rotational speed is one of the most important factors. As shown in Figure 2(a), when other experimental parameters are maintained the same, the influences of milling rotational speed on CIP degradation efficiency are displayed. Obviously, the CIP degradation efficiency is significantly promoted with the increase of milling rotational speed. Specifically, a degradation efficiency of only 3.9% is observed after 40 min when the milling rotational speed is set to 100 rpm. As for the 200-rpm condition, the degradation efficiency only reaches up to 17.2% after 40 min reaction. In contrast, the CIP degradation efficiency remarkably increases when the milling rotational speed is elevated to 300 rpm, the efficiency reaches 21.8% after only 10 min reaction and a final degradation efficiency of 76.7% is obtained after 40 min. Further increasing the milling rotational speed to 400 and 500 rpm, the CIP degradation efficiency is 94.7 and 98.9%, respectively. It is known that the impact energy of milling balls (E_w) can be calculated by Equation (2):

$$E_w = \sum_{j=1}^{n} \frac{1}{2W} m V_j^2 \tag{2}$$

where W is the sample weight, m is the mass of milling balls, and V_j represents the relative velocity between milling balls or milling balls against the mill walls (Mio *et al.* 2002). The intensities of collisions will be significantly elevated with the increase of milling rotational speed; thus, the V_j value will increase. Since E_w value is proportional to square of the V_j value, higher impact energy will be generated as the milling rotational speed increases. Nevertheless, high milling rotational speed usually costs more energy and excessive rotational speed may lead to the grinding media adhering to the mill walls, which will inhibit the increase of E_w value.

Besides, milling time is another vital experimental parameter that influences the CIP degradation efficiency. As shown in Figure 2(b), little CIP has been degraded in the first 5 min (less than 3%). Further increasing the milling time to 10 min, the degradation efficiency rapidly reaches up to 23.4%; in addition, a satisfying degradation efficiency of 74.7% is observed when the milling time is 20 min. It should be noted that the CIP degradation efficiency slowly increases as time goes on when the

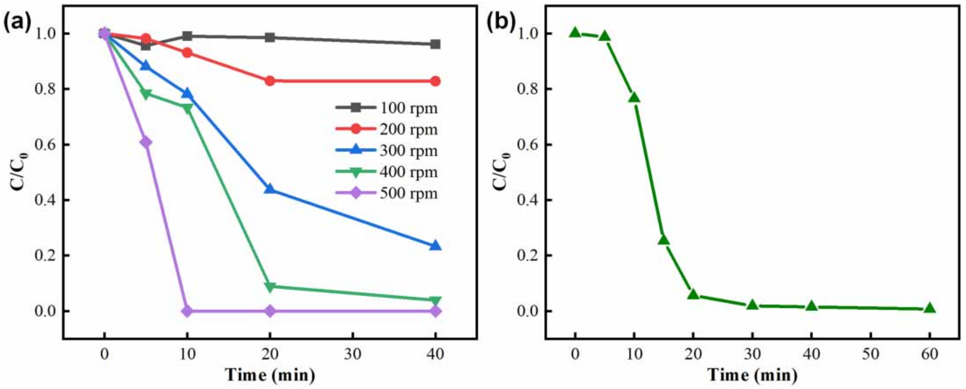

Figure 2 | (a) Influence of milling rotational speed on CIP degradation efficiency, (b) influence of milling time on CIP degradation efficiency, with a rotational speed of 300 rpm.

milling time exceeds 20 min, where the degradation efficiency is 98.1% and 99.3%, corresponding to the 30 and 60 min sample, respectively. Apparently, the CIP degradation efficiency is not a simple linear relationship over time, and it can be divided into three stages. In the first stage, the accumulated energy has not reached the threshold and is not able to degrade CIP effectively. Then, the accumulated energy continues increasing, and CIP degradation efficiency sharply increases by 51% from 10 to 20 min. In the final stage, CIP concentration becomes lower and effective collisions reduce, leading to the decrease of reaction rate. Therefore, we can conclude that milling time is a vital factor influencing degradation efficiency, and 30–40 min is considered as an appropriate milling time in this work, considering both cost and efficiency.

As shown in Figure 3(a), the influence of ratio of grinding balls to material (RGM) on CIP degradation efficiency is studied. Various RGMs ranging from 1:1 to 5:1 are adjusted, maintaining the volume of CIP solution the same, and the weight ratio of Φ10 mm balls to Φ6 mm balls is 1:2. On the whole, the degradation efficiency is promoted with the increase of RGM, where the efficiency is elevated from 36.3% to 78.1% as the RGM increases from 1:1 to 5:1. In addition, there is a huge increase (27%) of degradation efficiency when RGM is elevated from 2:1 to 3:1; however, after that, the increasing rate becomes lower, and only a small increase (8%) is obtained when RGM is elevated from 3:1 to 5:1. Zhang *et al.* demonstrated that the energy per unit mass (D) after a certain milling time can be calculated by Equation (3):

$$D = \frac{1}{2} C_R v_i^2 f t \tag{3}$$

where C_R represents the ratio of grinding balls to material, V_i represents the collision velocity, f represents the collision frequency, and t represents the milling time (Zhang *et al.* 2021). Clearly, D value will increase when RGM (C_R) is elevated. Further increasing the RGM value, however, sliding and scrolling between grinding balls and mill walls grow rapidly, resulting in the decrease of effective collision and finally impacting the V_i value. Moreover, excessive grinding balls will make the milling pot crowded, which may lead to some grinding balls being extremely close to each other, and the f value will decrease. In a word, an appropriate RGM is vital to both improve the CIP degradation efficiency and avoid the energy waste.

Figure 3(b) shows the effects of ratio of grinding ball (RGB) on CIP degradation efficiency. Under the condition when only Φ10 mm balls are employed, that is, the RGB value of 3:0, the CIP degradation efficiency can reach up to 89.7% after 40 min MCT process. Comparatively, the CIP degradation efficiency is 87.6% when only Φ6 mm balls are used (RGB value of 0:3). In contrast, a higher degradation efficiency is observed (96.8%) when both Φ10 mm and Φ6 mm grinding balls (RGB value of 2: 1) are involved. Regarding the sample with RGB value of 1:2, the degradation efficiency is 95.4%. It can be seen that the collocation of different ball sizes can improve the CIP degradation efficiency, while the increasing effect is not significant. What is more, the degradation efficiency in early stages is markedly improved; the efficiency after 10 min increases from 66.5% to 92.1%, corresponding to the RGB values of 3:0 and 2:1. Since total mass of grinding balls is maintained the same, the number of balls will go down when only Φ10 mm balls are used, and the collision frequency will be reduced, finally leading to the decrease of degradation efficiency. On the other hand, the impact energy of Φ6 mm balls is lower compared with that of Φ10 mm balls, resulting from the light weight of grinding balls with small sizes. Therefore, the grinding balls

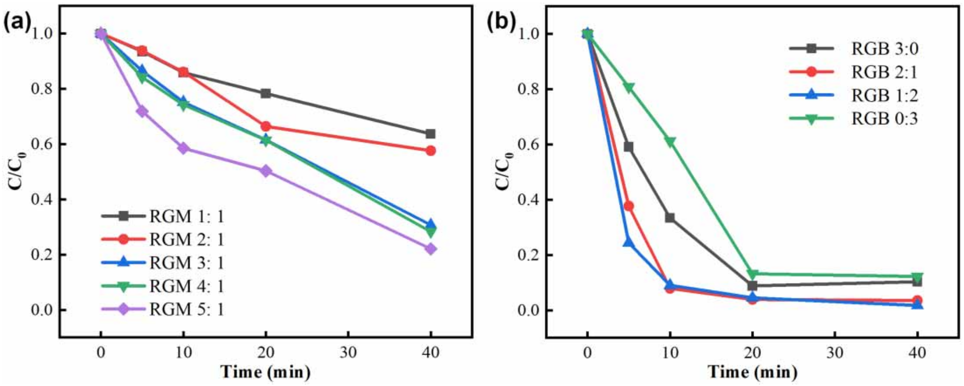

Figure 3 | Influences of (a) RGM value and (b) RGB value on CIP degradation efficiency, with a rotational speed of 300 rpm.

with only a single size are not suitable for improving CIP degradation efficiency, and an appropriate weight ratio of grinding balls is essential in the MCT process.

Generally speaking, there are many types of grinding balls, including agate ball, ceramic ball, steel ball, and zirconia ball, and they have great differences in physical properties such as density, hardness and elastic modulus. As shown in Figure 4, the influences of ball types on CIP degradation efficiency are studied. The grinding balls are composed of Φ10 mm and Φ6 mm balls for all samples, and the weight ratio of Φ10 mm balls to Φ6 mm balls is 2:1. The MCT system containing steel balls exhibits the best performance; a degradation efficiency of 98.3% is obtained after 40 min reaction. In contrast, the degradation efficiency of MCT system containing zirconia balls is only 72.6%. The final CIP degradation efficiency is 80.2% and 91.4%, corresponding to agate and ceramic system, respectively. Based on the typical Hertzian collision theory and research results regarding energy transfer by Lu *et al.*, Zhang *et al.* demonstrated that the elastic impact energy at a time (E_e) can be calculated by Equation (4):

$$E_\mathrm{e} = \frac{1}{12}\pi g_p^2 g_r^2 v_n^{1.6} E_{eff}^{0.2} \rho_b^{0.8} r_b^3 \tag{4}$$

where g_p and g_r are geometrical factors which are determined by the geometries milling pots, v_n represents the vertical velocity of milling ball, E_{eff} represents the effective elastic modulus, ρ_b represents the density of milling ball, and r_b represents the radius of milling ball (Butyagin & Streletskii 2005; Zhang *et al.* 2021). In this work, the density of agate ball, ceramic ball, steel ball, and zirconia ball is 2.6, 3.6, 7.9, and 5.9 g/cm^3, respectively.

Since the density of steel ball is notably higher than that of the rest, the best performance for CIP degradation may be attributed to this. It is noted that density is not the only influencing factor; for example, the density of zirconia ball is higher than that of ceramic ball, while the zirconia system shows a lower degradation efficiency, which may be due to the comprehensive effects of elastic modulus, Moh's hardness, etc. In addition, the number of zirconia balls is lower than that of agate balls and ceramic balls owing to the same weight, which will lead to the decrease of collision frequency and finally reduce the efficiency. Clearly, the grinding ball type can significantly influence CIP degradation efficiency, and it results from the comprehensive factors. Furthermore, it is inevitable that there will be some impurities falling from the grinding balls in the MCT process and they may act as catalysts to some extent, which needs further research in our subsequent study.

Except for the above-mentioned parameters concerning milling process, some features of CIP solution also play vital roles. As shown in Figure 5(a), the influences of initial CIP concentration on degradation performances are studied. The black and red curve shows the degradation efficiency and degradation rate varying with initial CIP concentration, respectively. Obviously, the degradation efficiency is decreasing with the increase of initial CIP concentration. The CIP degradation efficiency is highest (72.3%) when the initial CIP concentration is 20 mg/L; in contrast, the CIP degradation efficiency is only 28.7% when the initial CIP concentration is elevated to 200 mg/L. As for the degradation rate, interestingly, it shows an inverse trend that the degradation rate is increasing with the increase of initial CIP concentration. Specifically, a degradation

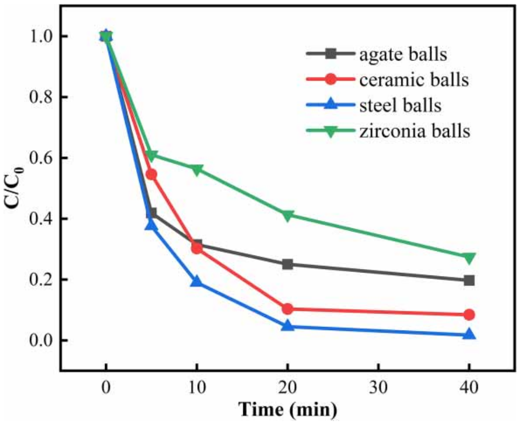

Figure 4 | Influences of ball types on CIP degradation efficiency, under the experimental conditions of rotational speed of 300 rpm, RGB value of 2:1, and RGM value of 3:1.

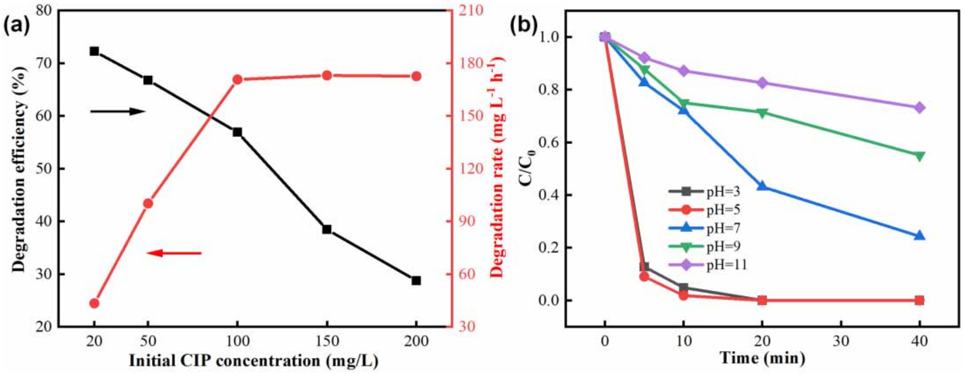

Figure 5 | Influences of (a) initial CIP concentration and (b) pH value on CIP degradation efficiency, with a rotational speed of 300 rpm and RGB value of 2:1.

rate of 43.3 mg/L/h is obtained in the condition of low CIP concentration (20 mg/L), and the degradation rate rapidly increases up to 170.7 mg/L/h when the initial CIP concentration is elevated to 100 mg/L. Moreover, the curve of degradation rate becomes less steep when exceeding the point (100 mg/L). According to the above results, we can conclude that a high degradation rate can be achieved in the condition of high CIP concentration, because the collisions between grinding balls, mill walls and pollutants will dramatically increase. On the other hand, the impact energy provided by planetary ball mill is constant when other conditions are maintained the same; therefore the contents of CIP that can be degraded are fixed, and the degradation efficiency will decrease when more CIP is involved.

Besides, pH value is another key factor influencing solution states, and it can determine the degree of ionization of CIP molecules. In order to investigate the influence of pH value on MCT process, three conditions including acidic, neutral and alkaline environments (pH value = 3, 5, 7, 9, and 11) are set up, and the results are displayed in Figure 5(b). In acid environment, the degradation efficiency can reach as high as 87.3% after only 5 min, and CIP molecules can almost be degraded completely after 40 min (degradation efficiency >99%). However, the degradation efficiency is only 26.7% after 40 min when pH value = 11. In neutral environment, a degradation efficiency of 28.0% can be obtained after 10 min and the final efficiency can reach 75.7%. Obviously, the CIP degradation efficiency is decreasing with the increase of pH value. It is noted that some iron ions will emerge in acid environment (steel milling balls), which will contribute to the CIP degradation. In contrast, the alkaline environment is beneficial to the formation of passive layers on grinding media, finally leading to the decrease of CIP degradation efficiency. Although acid environment can promote the degradation efficiency, the erosion of milling balls and acid wastewater should also be taken into consideration.

Generally speaking, there are always kinds of co-existing ions in CIP solutions, and they may affect the degradation performance. As shown in Figure 6, the influences of HCO_3^-, Cl^-, SO_4^{2-}, and NO_3^- on CIP degradation efficiency are studied. First of all, the existence of these ions will inhibit the degradation process that all the samples containing these ions exhibit lower efficiencies compared with that of control samples without these ions involved. Actually, some previous literature also demonstrated that the co-existing ions would inhibit the CIP degradation performances in most cases (Guo *et al.* 2013; Sayed *et al.* 2016). In particular, a CIP degradation efficiency of 84.8% is detected when 1 mM of HCO_3^- species is introduced into the MCT system, while the efficiency is 97.6% when no HCO_3^- is involved. Further increasing the HCO_3^- concentration to 10 mM, the CIP degradation efficiency decreases to 58.4%. It is acknowledged that HCO_3^- will ionize and hydrolyze in aqueous solution and the degree of hydrolysis is greater than that of ionization, which will make the solution alkaline and finally hinders the CIP degradation. This result is in accordance with that of the literature, in which Lin *et al.* found that the existence of HCO_3^- would increase the pH value and decrease the CIP degradation performance (Lin & Wu 2014). As for the samples containing Cl^-, SO_4^{2-}, and NO_3^- ions, the reduction of degradation efficiency is not significant; the lowest efficiency is still higher than 89.6%. Although there are no obvious hydrolysis or ionization reactions in the above systems, the co-existing ions still have influences on CIP degradation process. In a word, the co-existing ions can influence the degradation performance and should be considered.

In order to make the results more accurate, based on the above findings obtained from single-factor experiments, orthogonal experiments are conducted, since there are impacts of interactions between many factors. It is noted that four factors,

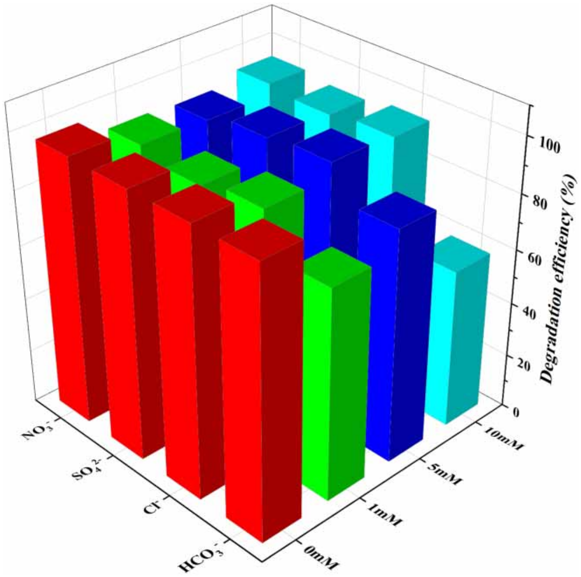

Figure 6 | Influences of HCO_3^-, Cl^-, SO_4^{2-}, and NO_3^- on CIP degradation efficiency, under the experimental conditions of steel balls serving as milling balls, rotational speed of 300 rpm and pH value of 7.

milling rotational speed, RGM, ball type and pH value, have great influences on CIP degradation efficiency, and the results of orthogonal experiments involving these four factors are displayed in Table 3. It can be seen that a highest degradation efficiency of 95.846% is achieved when the milling rotational speed is 300 rpm, RGM is 3:1, grinding media is steel ball, and pH value is 5. As for range analysis (parameter R), the R value is 35.484, 10.191, 29.928, and 26.917, corresponding to factor A, B, C and D, respectively. Therefore, factor A (milling rotational speed) affects CIP degradation efficiency most in MCT process, and factor B (RGM) has less influence on that, while factors C and D have significant influence on that. In addition, through the mean analysis (K1, K2 and K3 values), we can conclude that the optimum combination is A1B3C1D1, that is, the milling rotational speed is 300 rpm, RGM is 5:1, grinding media is steel ball, and pH value is 5. In short, the orthogonal experiments can help us look for the main influencing factors, and guide the CIP remediation work in the real world.

Table 3 | Results and analysis of orthogonal experiments

	Factor				
Number	**A (Milling rotational speed)**	**B (RGM)**	**C (Ball type)**	**D (pH value)**	**Degradation efficiency (%)**
1	1 (300 rpm)	1 (3:1)	1 (steel ball)	1 (5)	95.846
2	1	2 (4:1)	2 (agate ball)	2 (7)	56.349
3	1	3 (5:1)	3 (zirconia ball)	3 (9)	54.469
4	2 (400 rpm)	1	2	3	29.458
5	2	2	3	1	61.651
6	2	3	1	2	86.924
7	3 (500 rpm)	1	3	2	28.939
8	3	2	1	3	32.047
9	3	3	2	1	39.227
K1	68.888	51.414	71.606	65.575	/
K2	59.344	50.016	41.678	57.404	/
K3	33.404	60.207	48.353	38.658	/
R	35.484	10.191	29.928	26.917	/

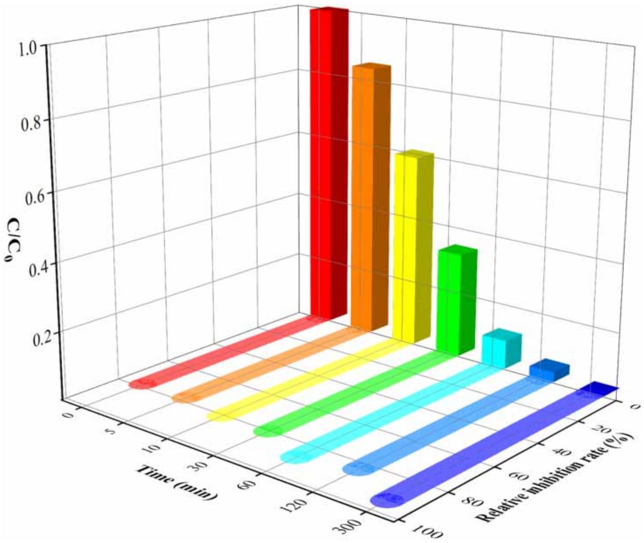

Figure 7 | The toxicity of CIP solution with the increase of reaction time, under the experimental conditions of steel balls serving as milling balls, rotational speed of 300 rpm and pH value of 7.

The toxicity of CIP solution is measured by photobacteria and analyzed through a microplate reader, as shown in Figure 7. The X axis lists different points in time, Y axis is relative inhibition rate, which represents the level of toxicity, and Z axis is C/C$_0$, representing the CIP degradation efficiency. It can be seen that the CIP degradation efficiency rapidly decreases over time, and an efficiency of about 100% is obtained after 300 min. However, the toxicity of solution shows a different tendency. Specifically, the toxicity of solution is comparatively stable in the first 30 min, while the relative inhibition rate is maintained at around 80%, although the CIP degradation efficiency has increased from 0% to 68.7%. In MCT process, CIP is not directly decomposed into some inorganic molecules, and some intermediate products will be produced, such as $C_{17}H_{19}FN_3O_4^+$, $C_{16}H_{19}FN_3O_2^+$, $C_{17}H_{20}N_3O_4^+$, $C_{17}H_{18}N_3O_5^+$, $C_{15}H_{18}N_3O_4^+$, and the specific degradation pathways still need further study. In the early stages of reaction, the contents of intermediate-products are still low and the toxicity increases slowly. Further increasing the milling time, toxicity of solution increases significantly, and the relative inhibition rate reaches as high as 94.6% after 300 min. The increase of toxicity is attributed to the increasing concentrations of some poisonous intermediate products over time, and on the other hand, the leakage of iron from steel balls will also poison the photobacteria and lead to the increase of relative inhibition rate.

CONCLUSION

In this study, mechanochemical treatment was employed to degrade CIP in aquatic solutions. The influences of some experimental parameters including milling rotational speed, milling time, ratio of grinding ball to material, ratio of grinding balls, grinding ball type, initial CIP concentration, pH value, and co-existing inorganic ions on CIP degradation efficiency were investigated and discussed. Based on the results of single-factor experiments, orthogonal experiments were designed and conducted, and the optimum combination is the milling rotational speed 300 rpm, RGM 5:1, grinding media steel ball, and pH value 5. Besides, the toxicity of CIP solution at different times was also studied. In brief, although mechanochemistry in solution is very rare, we believe that this topic is worth studying based on the previous work and our research. And the results in this work show that mechanochemical treatment is an effective approach to degrade CIP in solutions. Moreover, it has many advantages such as simplicity, low cost, and environmentally innocuous nature, which make it a promising candidate for remediation of CIP and other organic pollutants.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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