



Kinetics and mechanistic study of oxidation of paracetamol: an accelerated catalytic approach

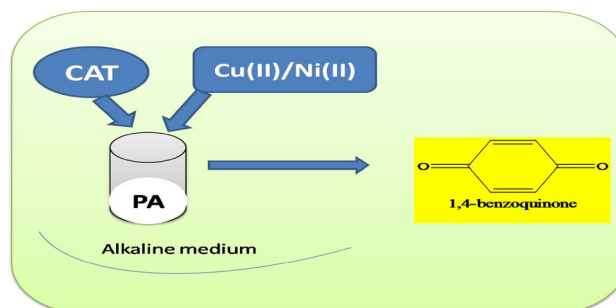
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Abstract

In the present paper, a simple, and novel method for the abatement of paracetamol (PA) in aqueous system into environmental friendly compound benzoquinone at 308 K has been described, and was accelerated by simple, and inexpensive catalyst Cu(II)/Ni(II). A comparative assessment between Cu(II) and Ni(II) catalyzed, abatement of PA by CAT was performed. It has been determined that there are very little change in rate of reaction for both Cu(II)/Ni(II) catalyzed degradation of PA. All the kinetics parameters, i.e. the effect of change in concentrations of chloramine-T (CAT), sodium hydroxide, paracetamol, catalyst, added *p*-toluenesulfonamide, electrolyte etc. have been studied, and measured carefully. Reaction had been studied in the range of temperature 303–323 K. On the basis of kinetic data obtained a satisfactory mechanism has been proposed. And it was deduced that, presently used process was a tenable technique for the degradation of PA. Main abatement product was confirmed by GC–MS analysis technique.

Graphic abstract



Keywords Kinetics · Degradation · Chloramine-T · Paracetamol · Ni(II)/Cu(II) chloride catalysis

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1 Introduction

Sometime, water contains an unwanted substance that makes it no longer suitable for use. Its existence make threaten to drinking water, and finally harsh the living organism [1, 2]. It will affect the liver, kidney, lung etc. [3, 4]. These days, due to increases of civilization uses of drugs, fertilizers, cosmetics, paints continuously pollute the water [5]. Different contaminants that comes from various industries i.e. pharmaceutical [6, 7], petroleum [8], textile [9], steel [10], pulp and paper mill [11] etc. are generally dispose into the water, which finally make water for unfit for domestic utilization.

Among which, we have been found that pharmaceutical waste generated by industries; expel its waste in water bodies, and sometime people through non-used medicine into open land or in garbage. So, the pharmaceutical wastes that mix into water convert into many toxic substances, and had toxic effect on both human and aquatic life. Some of real wastewater sample i.e. drug present in German ground water, and synthetic drug containing wastewater such as amoxicillin, ciprofloxacin, ofloxacin and atanolol, and captopril were degrade by various oxidation process [12–16].

Paracetamol (*N*-acetyl-*p*-aminophenol) has a significant role because of analgesic and antipyretic action. This non narcotic analgesic drug can alternatively used as in place of aspirin. It is most widely used medicine for the relief of pain i.e. headache, backache, and postoperation. On the other hand, when it consumed in overdose, it may result in severe hepatic toxicity or even death. Its determination process includes various spectroscopic methods [17–19]. However, less attention has been given the choice to use an oxidizing agent for its determination [20–26]. Paracetamol has been reported to be present in sewage treatment plant effluents up to a concentration of 6.0 $\mu\text{g}/1$ [27].

N-haloamine compounds have halonium ions and nitrogen anions, so it acts as both the base, and nucleophile [28–33]. The well known leading member of *N*-halonium-compounds is sodium-*N*-chloro-4-methylbenzenesulfonamide, it is also known as chloramine-T (CAT). This reagent has been turned to account as an oxidant for various substrates [34–40]. As a result, these compounds are capable for molecular changes.

The elements, which can easily form cation, and have partially filled d-orbitals are reported as efficient catalyst in various organic oxidation reactions [41–50], copper compound are abundance in nature, biological media, so it consider a major role in oxidation chemistry and it also act as catalyst in many oxidation reaction [51]. In 1961, Corey reported that cis hydrogenation of olefins was possible in the presence of hydrazine, hydrogen peroxide, and trace

amounts of Cu(II) [52]. Interestingly, he reported that the reaction occurred “instantaneously”. Thus, the rate of reaction in the presence of Cu(II) would have to be much faster [53–60]. An iodometric determination of CAT employing copper(II) as catalyst has also been reported [61]. Since Cu(II) is known to form Cu(III), if oxidized and stabilized by suitable ligands in alkaline solutions, we thought the mechanistic study involving Cu(II) as a catalyst in oxidation with CAT might enable us to know more of the chemistry of Cu(III). Another catalyst nickel used in present work is a low cost catalyst with high activity [62], in comparison with the more active palladium or platinum [63, 64], that could mask to some extent the role of the support. Amine is be synthesized by Hydrogenation of nitriles bears industrial interest, given their wide spectrum of industrial application, which can be involved in the synthesis of surfactants, fungicides, chelating agents, surfactants etc. [65]. The result from laboratory, on the self decomposition of Ni(II)-peroxomonosulfate in the pH range of approximately 3.4–5.9, suggest that the metal ion-catalyzed reaction proceeds through a molecular mechanism with a metal peroxide intermediate. Metallopeptides of the type Ni(II)-Xaa-Xaa-His, where Xaa is any amino acid, have been shown to mediate cleavage of DNA [66–74]. Thendral et al. [75] have shown the role of Ni(II) in the oxidation of glycylglycine dipeptide by peroxomonosulfate. For the analytical chemists kinetic methods are of best option for drug analyses because it provides the sensitive determination by using very simple instruments. Thus, the basic principle of kinetic method is to measure, the change in concentration of reactants with time, catalyst can increase the reaction rate. Recent advance in analytical techniques have facilitated measurements of very low concentration of drug [76].

By close look over the literature, we endow that there are no reports available for the oxidation of PA by CAT in the presence of either Cu(II) or Ni(II) catalyzed reaction in alkaline medium, and its comparative studies, so we prepared this manuscript.

2 Experimental

2.1 Materials and instrumentation

Pharmaceutical wastewater was synthetically prepared every day, by dissolving, an appropriate amount of recrystallized PA sample in deionized water. Similarly, stock solutions of CAT (Loba, AR), Cu(II) and Ni(II) of E. Merck, were prepared, and standardized idometrically. Sodium perchlorate, NaOH (E. Merck) was used without further purification by preparing their solutions. Analytical reagent grade chemicals, and doubly distilled water were used throughout the investigation. Degradation processes

were recorded using UV–Vis spectrophotometer computer controlled, and λ_{\max} for PA was obtained at 240 nm. And product of reaction was determined by GCMS.

2.2 Oxidation method

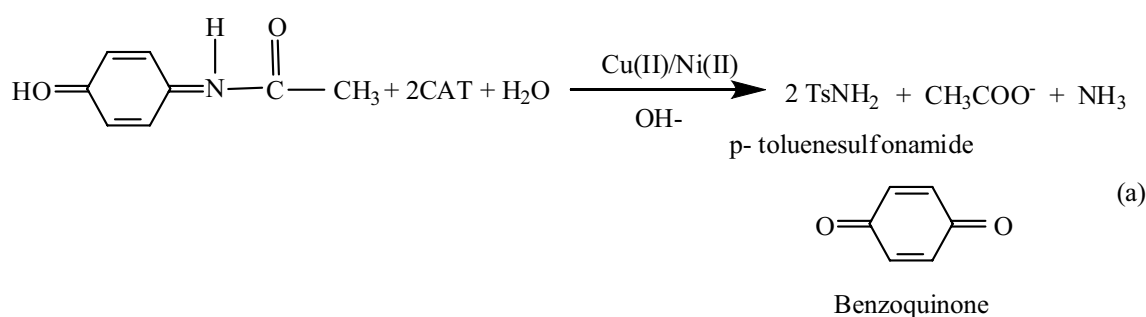
To sum up, synthetic pharmaceutical wastewater was oxidize by CAT at laboratory (bench) scale. A probe study of oxidation of PA in alkaline medium in the presence of catalyst (Cu(II)/Ni(II)) were placed in a dark (black) vessel at constant temperature, 308 K with all reactants in required concentrations. A kinetic studies had been done under pseudo first-order conditions with $[PA] \gg [CAT]$. The reaction was initiated by rapid addition of pre-equilibrated PA to the reaction mixture containing all reactants in appropriate amount. The reaction was monitored by idometric determination of unconsumed [CAT] at various time intervals.

In view of the ubiquitous contamination of basic solutions by carbonate, the rate of reaction was studied by the addition of carbonate. Added carbonate had no effect on the reaction rate. Fresh solutions were always used during the experiments.

3 Results and discussion

3.1 Stoichiometry and product analysis

Concentration of CAT required 2 mol for the oxidation of 1 mol of PA when taking into account the following reaction.



The main reaction product was identified as Benzoquinone. It was further confirmed by GC–MS analysis, which has been done by JEOL-JMS (Mate-MS system, Japan). The mass spectrum showed a molecular peak confirming

Benzoquinone product (Fig. S9 supporting document). Benzoquinone is mainly used for the synthesis of hydroquinone. Presence of PTS was confirmed by addition of xanthinol to yield the corresponding *N*-xanthyl-*p*-toluenesulfonamide and detected by TLC [57, 58].

3.1.1 Effect of CAT

At constant concentrations of all the reactants i.e. [PA], [NaOH], [catalyst], and temperature, where $[PA] \gg [CAT]$, plot of $\log[CAT]$ versus time were linear, indicated a first order dependence of rate on [CAT] for alkaline medium. The order of reaction in each reactant was determined using a log–log plot of k versus concentration of the reactant. The linearity of the plots of $(-dc/dt)$ versus [CAT] (Table 1, Figs. S2 and S3) was linear passing through the origin shows the order in [CAT] was found to be unity in the reactions.

3.1.2 Effect of PA

At lower concentration of [PA], the rate of reaction followed first order kinetics and shifted to zero order at its higher concentration. This is also obvious from the plot of $(-dc/dt)$ versus [PA] (Tables 1, 2, Figs. S3 and S4), indicating first order at their lower concentration and tending towards zero order at their higher concentration.

3.1.3 Effect of catalyst

To obtain the optimal Cu(II)/Ni(II) concentration, experiments were conducted at several combination of catalyst,

and it was observe that rate of reaction increases as the concentration of catalyst increases. So, both Cu(II) (Table 1, Fig. S1) and Ni(II) (Table 1, Fig. S4) followed first order kinetics.

Table 1 Effect of variation of [CAT], [PA], [Ni(II)], and [OH⁻] on the rate of oxidation of paracetamol at 308 K

[CAT] × 10 ³ (mol dm ⁻³)	[PA] × 10 ² (mol dm ⁻³)	[Ni(II)] × 10 ⁵ (mol dm ⁻³)	[OH ⁻] × 10 ³ (mol dm ⁻³)	$k_1 \times 10^4$ (s ⁻¹)	$k_{(cal)} \times 10^4$ (s ⁻¹)	$k_{(exp)} \times 10^4$ (s ⁻¹)
0.20	1.00	8.00	1.00	2.00	–	–
0.40	1.00	8.00	1.00	2.00	–	–
0.60	1.00	8.00	1.00	2.03	–	–
0.80	1.00	8.00	1.00	2.06	–	–
1.00	1.00	8.00	1.00	2.20	–	–
1.20	1.00	8.00	1.00	2.18	–	–
1.00	0.20	8.00	1.00	0.63	0.60	0.69
1.00	0.40	8.00	1.00	1.31	1.15	1.07
1.00	0.60	8.00	1.00	1.47	1.66	1.37
1.00	0.80	8.00	1.00	1.89	2.13	1.64
1.00	1.00	8.00	1.00	2.20	2.56	1.89
1.00	1.20	8.00	1.00	2.63	2.96	2.12
1.00	1.60	8.00	1.00	2.84	3.69	2.54
1.00	1.00	2.00	1.00	0.52	0.64	0.46
1.00	1.00	4.00	1.00	1.05	1.28	0.93
1.00	1.00	6.00	1.00	1.47	1.90	1.41
1.00	1.00	8.00	1.00	2.20	2.56	1.89
1.00	1.00	12.0	1.00	3.26	3.84	2.85
1.00	1.00	16.0	1.00	4.52	5.12	3.82
1.00	1.00	20.0	1.00	5.20	6.40	4.79
1.00	1.00	8.00	0.50	7.00	4.30	5.93
1.00	1.00	8.00	0.60	3.79	3.80	4.10
1.00	1.00	8.00	0.80	2.52	3.06	2.65
1.00	1.00	8.00	1.00	2.20	2.56	1.89
1.00	1.00	8.00	1.20	1.66	2.20	1.43
1.00	1.00	8.00	1.60	1.05	1.72	0.93
1.00	1.00	8.00	2.00	0.71	1.40	0.66

Bold values define effect of various concentrations of reactants while other being constant

3.1.4 Effect of NaOH

With increasing the concentration of [OH⁻] the value of reaction rate decreased, which is also evident from the plot of (–dc/dt) versus [OH⁻] in both catalyzed system (Tables 1, 2, Figs. S1 and S2). This shows negative effect of [OH⁻] on the oxidation of paracetamol.

3.1.5 Effect of PTS

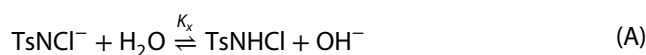
Addition of the *p*-toluene sulphonamide (PTS) in the reaction mixture showed that the rate of reaction decreased with increasing [PTS] (Tables S1 and S2, Figs. S1 and S2).

Variations of ionic strength of the medium, and [Cl⁻] suggesting an unchanged form to degrade PA under the constant experimental conditions. The rate of reaction increased with increasing in dielectric constant of the medium (Tables S1 and S2). The reaction was performed at different temperatures and the activation energies (E_a) were calculated for both Cu(II) and Ni(II) catalyzes system. With the help of the energy of activation, values of the

other activation parameters such as enthalpy of activation (ΔH^\ddagger), entropy of activation (ΔS^\ddagger), Gibbs free energy of activation (ΔG^\ddagger) and Arrhenius factor (A), were also calculated.

3.1.6 Reactive species of CAT and catalyst

The reactive species of CAT, responsible for the oxidation of PA is HOCl, because it is successfully capable to explain all the kinetic results obtained among all other reactive species of CAT i.e. TsNCl₂, H₂OCl⁺ in acidic medium, and TsNHCl, HOCl and TsNCl⁻ in alkaline medium [17, 18].



$$K_y = 4.21 \times 10^{-3} \text{ at } 298 \text{ K.}$$

While, Cu(II) and Ni(II) exist as same.

In reaction scheme 1, Firstly reactive oxygen species HOCl (C₁) was generated with the PTS, this HOCl (C₁) reacts

Table 2 Effect of variation of [CAT], [PA], [Cu(II)], and [OH⁻] on the rate of oxidation of paracetamol at 308 K

[CAT] × 10 ³ (mol dm ⁻³)	[PA] × 10 ² (mol dm ⁻³)	[Cu(II)] × 10 ⁶ (mol dm ⁻³)	[OH ⁻] × 10 ³ (mol dm ⁻³)	k ₁ × 10 ⁴ (s ⁻¹)	k _(cal) × 10 ⁴ (s ⁻¹)	k _(exp) × 10 ⁴ (s ⁻¹)
0.20	1.00	8.00	1.00	2.00	2.43	–
0.40	1.00	8.00	1.00	2.20	2.50	–
0.60	1.00	8.00	1.00	2.33	2.43	–
0.80	1.00	8.00	1.00	2.06	2.58	–
1.00	1.00	8.00	1.00	2.17	2.50	–
1.20	1.00	8.00	1.00	2.08	2.53	–
1.00	0.20	8.00	1.00	0.52	0.57	0.65
1.00	0.40	8.00	1.00	1.05	1.12	1.25
1.00	0.60	8.00	1.00	1.47	1.59	1.80
1.00	0.80	8.00	1.00	1.89	2.10	2.32
1.00	1.00	8.00	1.00	2.24	2.34	2.80
1.00	1.20	8.00	1.00	2.42	2.50	3.27
1.00	1.60	8.00	1.00	2.52	2.75	4.00
1.00	1.00	2.00	1.00	0.63	0.52	0.81
1.00	1.00	4.00	1.00	1.47	0.97	1.51
1.00	1.00	6.00	1.00	1.84	1.91	2.23
1.00	1.00	8.00	1.00	2.20	2.34	2.80
1.00	1.00	10.0	1.00	2.63	2.84	3.31
1.00	1.00	14.0	1.00	3.15	3.21	4.42
1.00	1.00	16.0	1.00	3.36	3.41	4.88
1.00	1.00	20.0	1.00	3.51	3.70	5.71
1.00	1.00	8.00	0.20	8.31	11.8	8.80
1.00	1.00	8.00	0.40	5.68	7.54	5.81
1.00	1.00	8.00	0.60	3.79	3.45	4.32
1.00	1.00	8.00	0.80	2.84	2.50	3.45
1.00	1.00	8.00	1.00	2.18	2.34	2.80
1.00	1.00	8.00	1.20	2.00	1.84	2.45
1.00	1.00	8.00	1.60	1.47	1.30	1.91
1.00	1.00	8.00	2.00	0.94	0.82	1.50

Bold values define effect of various concentrations of reactants while other being constant

with PA to form a complex between involves chlorine transfer through the intermediacy of HOCl. The protonated oxidant species HOCl formed from TsNHCl reacts with the substrate in a fast equilibrium step to form the substrate-CAT complex (C₂) with the elimination of hydroxide ion. The inverse negative order in [OH⁻] might also be due to this reason. In the pre rate determining step, this C₂ complex, combines with a molecule of catalyst (Cu(II)/Ni(II)) to give an intermediate complex C₃, which decomposes in a slow step to produce the intermediate species by the regeneration of catalyst and no intervention of the free radical was observed. One more molecule of CAT further reacts with an intermediate in a fast step to yield products.

3.2 Spectral evidence

UV-VIS spectra of paracetamol, CAT and mixture of both, verified the complex formation between oxidant (CAT) and

substrate (PA). Maximum absorption occurred at 245 nm for paracetamol, 225 nm for CAT, and 230 nm for PA-CAT. It was further confirmed by 15 nm of hypsochromic shift from 245 to 230 nm of paracetamol (Figs. 1, 2). The formation of complex between catalyst and CAT-PA mixture was also evidenced spectra of both CAT-paracetamol and CAT-PA-catalyst in which a shift of CAT-PA from 230 to 225 nm.

According to the reaction scheme 1 (supporting document) and considering the fact that 1 mol of PA is oxidized by 2 mol of CAT, the rate expressed as:

$$\text{rate} = (R) = -\frac{d[\text{CAT}]}{dt} = 2k[\text{C}_3] \quad (1)$$

$$R = \frac{2kK_1K_2K_3[\text{PA}][\text{catalyst}][\text{CAT}]_T}{[\text{OH}^-][\text{TsNH}_2] + K_1[\text{OH}^-] + K_1K_2[\text{PA}] + K_1K_2K_3[\text{PA}][\text{catalyst}]} \quad (2)$$

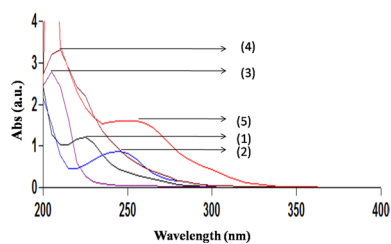


Fig. 1 Reaction conditions: (1) $[CAT]=1 \times 10^{-4} \text{ mol dm}^{-3}$, (2) $[PA]=1 \times 10^{-4} \text{ mol dm}^{-3}$; (3) $[Cu(II)]=8 \times 10^{-6} \text{ mol dm}^{-3}$, $[OH^-]=1 \times 10^{-3} \text{ mol dm}^{-3}$; (4) $[CAT]=1 \times 10^{-4} \text{ mol dm}^{-3}$, $[PA]=1 \times 10^{-4} \text{ mol dm}^{-3}$; (5) $[CAT]=1 \times 10^{-4} \text{ mol dm}^{-3}$, $[PA]=1 \times 10^{-4} \text{ mol dm}^{-3}$, $[Cu(II)]=8 \times 10^{-6} \text{ mol dm}^{-3}$, $[OH^-]=1 \times 10^{-3} \text{ mol dm}^{-3}$

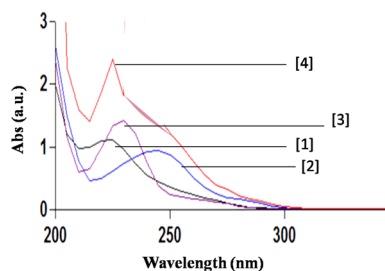


Fig. 2 Reaction conditions: (1) $[CAT]=1 \times 10^{-4} \text{ mol dm}^{-3}$, (2) $[PA]=1 \times 10^{-4} \text{ mol dm}^{-3}$; (3) $[Ni(II)]=8 \times 10^{-5} \text{ mol dm}^{-3}$, $[OH^-]=1 \times 10^{-3} \text{ mol dm}^{-3}$; (4) $[CAT]=1 \times 10^{-4} \text{ mol dm}^{-3}$, $[PA]=1 \times 10^{-4} \text{ mol dm}^{-3}$; (5) $[CAT]=1 \times 10^{-4} \text{ mol dm}^{-3}$, $[PA]=1 \times 10^{-4} \text{ mol dm}^{-3}$, $[Ni(II)]=8 \times 10^{-5} \text{ mol dm}^{-3}$, $[OH^-]=1 \times 10^{-3} \text{ mol dm}^{-3}$

where, catalyst = Cu(II)/Ni(II).

Equation (2) is the rate law on the basis of which observed kinetic orders with respect to each reactant of the reaction can very easily be explained.

On reversing Eq. (2), we have Eq. (3)

$$\frac{[CAT]_T}{\text{rate}} = \frac{[OH^-][TsNH_2]}{2kK_1K_2K_3[PA][Catalyst]} + \frac{[OH^-]}{2kK_2K_3[PA][Catalyst]} + \frac{1}{2kK_3[Catalyst]} + \frac{1}{2k} \tag{3}$$

Equation (3), indicates that if a plot is made between $[CAT]_T/\text{rate}$ and $[OH^-]$ or $[TsNH_2]$ or $1/[PA]$ or $1/[Cu(II)/Ni(II)]$ straight lines with positive intercepts on y-axis will be obtained (Figs. S5, S6, S7, S8), and prove the proposed reaction scheme on the basis of which the rate law (2) has been derived. From the values of the intercept and slope of the plots, the values of k , K_1 , K_2 and K_3 have been calculated and found to be $5.05 \times 10^{-4} \text{ s}^{-1}$, $1.83 \times 10^{-4} \text{ mol dm}^{-3}$, $9.9 \times 10^{-2} \text{ mol}^{-1} \text{ dm}^3$ and 339.59 respectively.

4 Comparative study

Present paper is compared the experimental findings with earlier work done in the presence of Ir(III), Ru(III), Pd(II) catalyst in acidic and alkaline medium for the degradation of paracetamol. The reactive species of CAT is HOCl in Ir(III), and Ru(III) catalysts, but TsNHCl was the reactive species of CAT in the Pd(II) catalyzed oxidation of PA in an acidic medium. All catalysts have first- to zero-order kinetics with respect to the concentration of PA. The order with respect to the catalyst in present paper followed first order.

Furthermore, efforts were made to compare the finding of this paper with the results reported for the Ir(III) [17], Ru(III) [18], and Pd(II) [25] catalyzed oxidation of PA by CAT in an acidic, and alkaline medium. It can be seen from Table S3, that the activation energy is the highest for the slowest reaction in the Pd(II) catalyzed oxidation of PA in an acidic medium. From the given rate constants and energies of activation, the relative reactivity of the catalysts for the oxidation of PA by CAT is in the order: Ir(III) acidic > Cu(II) alkaline > Ru(III) acidic > Pd(II) alkaline medium > Ni(II) alkaline > Pd(II) acidic medium. Pd(II) has d^8 electronic configuration, and is expected to have the least catalytic efficiency among the catalysts used.

5 Conclusions

Oxidation of paracetamol by CAT in catalytic system and in alkaline medium at 308 K was successfully carried out. In the absence of catalyst reaction is sluggish but catalyst helps to increase the oxidation process. Above results also reveal that both the catalyst Ni(II) and Cu(II) showed same catalytic behavior for oxidation of paracetamol. Obtained results have been clearly demonstrated by conceivable mechanism and the related law has been deduced. Three results i.e. experimental (k_1), calculated from rate law (k_{cal}) and by use of regression analysis (k_{exp}), support the rate law and reaction mechanism.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, I states that there is no conflict of interest.

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