Aquatic Toxicity of Hydroquinone and Catechol Following Metal Oxide Treatment to Ceriodaphnia dubia and Pimephales promelas

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Abstract

Metal oxides comprise a large group of chemicals used in water treatment to adsorb organic pollutants. The effects of titanium dioxide (TiO_2) and iron (III) oxide (Fe_2O_3) to reduce the chronic toxicity of (phenolic) $C_6H_6(OH)_2$ isomers, namely hydroquinone (HQ) and catechol (CAT) to *Ceriodaphnia dubia* and *Pimephales promelas* were investigated. The toxic endpoints following metal oxide treatment were compared to endpoints of untreated CAT and HQ. Chronic toxicity testing to HQ resulted in greater toxicity than CAT for both test organisms; the median lethal concentrations (LC_{50}) for CAT were 3.66 to 12.36 mg.L^{-1} for *C. dubia* and *P. promelas*, respectively, while LC_{50}s for HQ were 0.07 to 0.05 mg.L^{-1}, respectively. Despite both treated solutions presented lower toxic endpoints than those in the untreated solutions, Fe_2O_3 had a better potential to reduce the toxic effects of CAT and HQ than TiO_2.

1. Introduction

Over the last decades, the effects of industrialization, urbanization, and population growth have led to the occurrence and magnification of severe pollutants in the environment, including synthetic organic compounds (El Morabet, 2018; Kodavanti et al., 2014). Two common organic pollutants in industrial and domestic effluents are catechol (CAT) (1, 2-dihydroxybenzene) and hydroquinone (HQ) (1, 4-dihydroxybenzene). CAT is used as a reagent for photography, fur dye development, an antioxidant in manufacturing rubber, plastic production, and in the pharmaceutical industry (Amin et al., 2014; Schweigert et al., 2001b). HQ is used in varnishes, oils, and hair dyes (U.S. Food and Drug Administration, 2009), in industry as an agent in photography, stabilizer in paints, and antioxidant in rubber (El Morabet, 2018), and in pharmaceutical and cosmetics as skin brightening products, skin lighteners, and topical treatment for skin disorders (DeCaprio, 1999; Odumosu and Ekwe, 2010).

Industrial wastewater containing phenolic compounds without proper treatment has a severe effect on aquatic life, plants, animals, and humans (Milligan and Häggblom, 1998). Phenol and its derivatives are toxic and carcinogenic and can persist for many years in the environment due to their resistance to biological degradation (Deisinger et al., 1996; Zheng et al., 2013). Several studies have reported the toxicity of CAT for a variety of aquatic organisms (Anku et al., 2017; Duan et al., 2018; Elmenaouar et al., 2017; Neilson et al., 1991). In humans, CAT can irritate skin, eyes, and the upper respiratory tract as well as cause DNA damage provoking mutagenesis and carcinogenesis (Subramanyam and Mishra, 2013). HQ exposure can result in eye pigmentation, corneal effects, and impaired vision (DeCaprio, 1999; Subramanyam and Mishra, 2013). Exposure to phenols can result in severe toxic effects in humans and animals (DeCaprio, 1999; Schweigert et al., 2001a), bacteria (Subramanyam and Mishra, 2013), and aquatic organisms (Enguita and Leitão, 2013; Saha et al., 1999; U.S. Department of Health and Human Services, 2008). Due to their toxicity and impact, the United States Environmental Protection Agency (USEPA) has classified phenols as priority pollutants (Anku et al., 2017).

Treatment approaches for removing organic compounds from wastewater include physical, chemical, and biological processes; however, adsorption process has been found to be economical and effective method of removing organic compounds (Karpińska and Kotowska, 2019; Sophia and Lima, 2018). Adsorption mechanisms were studied to facilitate phenolic removal from polluted water using various materials such as metal oxides, activated carbon, waste materials, biochar, and other oxides (Abugazleh et al., 2020; García-Araya et al., 2003; Sophia and Lima, 2018; Yang et al., 2018).

The importance of metal oxides emerged from their physical, chemical, magnetic, and optical properties (Alias et al., 2020; Lewandowski et al., 2015), and although they are small in size, they exhibit a relatively large and unique surface structure. These properties result in high surface reactivity, leading some metal oxides such as titanium dioxide (TiO_2)

and iron (III) oxide (Fe_2O_3) to be used in industrial and biomedical applications (Lewandowski et al., 2015; Nagpal and Kakkar, 2019). TiO_2 is currently used in electronics, personal care products, paints, coatings, solar cells, and photocatalysis, and has been reported in environmental remediation to effectively remove phenols from contaminated water (Bahri et al., 2011; Rasalingam et al., 2014; Vasudevan and Stone, 1996). Fe_2O_3 is abundant, low cost, environmentally friendly (MacHala et al., 2011; Wu et al., 2014), and has been used in adsorbents for contaminated water remediation (Dave and Chopda, 2014). Attributes of Fe_2O_3 that enable its effective separation of adsorbents include its particle size, magnetic and polymorphism properties (Wu et al., 2014). This has led to studies investigating Fe_2O_3 as a potential adsorbent and detoxifying agent for heavy metals and organic compounds (Anku et al., 2017; Sophia and Lima, 2018; Wu et al., 2014).

The toxicity of phenols and their derivatives has been reported to cause substantial damage to aquatic organisms (Bährs et al., 2013; Enguita and Leitão, 2013; Schweigert et al., 2001; Shadnia and Wright, 2008). The USEPA recognizes the standard freshwater test organisms, *Ceriodaphnia dubia* and *Pimephales promelas*, for short-term chronic toxicity testing (U.S. Environmental Protection Agency, 2002). These 7-d tests are utilized to examine Whole Effluent Toxicity (WET) testing to fulfill requirements for National Pollution Discharge Elimination System, pesticide and industrial chemical registration, and ambient toxicity in surface waters (U.S. Environmental Protection Agency, 2002). They are used in ecotoxicological studies due to their sensitivity to a wide range of pollutants in relevant aqueous ecosystems (Blaise and Férard, 2005). *C. dubia* is recommended as an ideal toxicity test organism due to its sensitivity and rapid generation time (Pakrashi et al., 2013; Versteeg et al., 1997). *C. dubia* is recommended as a bioindicator for environmental risk of many toxic materials in freshwater ecosystems (Brayner et al., 2006; Pakrashi et al., 2013). *P. promelas* (fathead minnows) are small omnivorous fish with a relatively short life span and the ability to survive a wide range of aquatic conditions (Geiger et al., 1986; Watanabe et al., 2007). *P. promelas* are used in many environmental studies to predict toxic effects on resident fishes and their ecosystems (Ankley and Villeneuve, 2006; Babich and Borenfreund, 1987).

In this study, the chronic toxicity induced by CAT and HQ to *C. dubia* and *P. promelas* was investigated before and after adsorption with metal oxides (TiO_2 and Fe_2O_3). Toxicological data in aquatic invertebrates to CAT and HQ is limited with high variability (Bährs et al., 2013; Duan et al., 2018; Warnecke et al., 2014); thus, the lack of information warrants the need to determine the toxicity to standard aquatic test organisms. Additionally, the efficacy of using TiO_2 and Fe_2O_3 to reduce the toxicity of these phenolic compounds is reported.

2. Materials And Methods

2.1 Materials

CAT and HQ were purchased from Alfa Aesar (Heysham, England). TiO_2 powder (surface area = 4.91 ± 0.71 m^2g^{-1}) was purchased from Sigma-Aldrich (Canada); Fe_2O_3 (surface area = 13.04 ± 0.76 m^2g^{-1}) was purchased from Fischer Scientific. All chemicals were analytical grade or higher. Solutions were prepared in moderately hard synthetic water at the Ecotoxicology Research Facility (ERF) (Jonesboro, AR, USA) according to USEPA guidelines (U.S. Environmental Protection Agency, 2002), and all tests used moderately hard water for the control.

2.2 WET test setup

C. dubia and *P. promelas* (< 24 h) were cultured in-house at the ERF for the 7-d chronic tests according to USEPA guidelines (U.S. Environmental Protection Agency, 2002). A 5-dilution CAT and HQ series for *C. dubia* and *P. promelas* (dilution factor = 0.75 and 0.50, respectively) were used with moderately hard water as diluent (U.S. Environmental

Protection Agency, 2002) (Table 1). The 5-dilution series of CAT and HQ were exposed to 7-d chronic bioassays using *C. dubia* and *P. promelas* prior to and following the addition of 0.1 g.L^{-1} of metal oxides. The tests were performed in triplicate for each pollutant. Stock concentrations and each dilution were analyzed using Thermo Scientific Nicolet™ 8700 Research FTIR Spectrometer (Waltham, MA) equipped with Attenuated Total Reflectance (ATR) accessory to verify nominal concentrations (Abugazleh et al., 2020). The determination of the concentration in the control solution was required to be within 5% of its nominal concentration. Due to the reduction of toxicity following metal oxide treatment, the nominal concentrations increased for both compounds with a highest concentration of 7.50 mg.L^{-1} for CAT, 0.20 mg.L^{-1} for HQ using *C. dubia*, and 60.00 mg.L^{-1} for CAT, and 2.00 mg.L^{-1} for HQ using *P. promelas*, respectively.

A 24-h exposure prior to toxicity test setup between phenolic compounds and metal oxides allowed phenolic adsorption onto the surface of the oxides. After equilibrium, the solution was siphoned to the tested containers while leaving metal oxide particles. Adsorption kinetics, pH, and isotherm studies for CAT and HQ with and without the presence of TiO_2 and Fe_2O_3 have been reported in a previous study (Abugazleh et al., 2020). Briefly, results reported CAT adsorption capacity as 122.8 ± 33.1 mg.g^{-1} and 361.2 ± 0.1 mg.g^{-1} on the surfaces of TiO_2 and Fe_2O_3, respectively. Maximum adsorption capacities calculated from kinetic studies of HQ on Fe_2O_3 was 58.49 mg.g^{-1}, and TiO_2 adsorption was 351.7 mg.g^{-1}. Overall, results indicate that CAT adsorption capacity was greater in Fe_2O_3 than in TiO_2. Results showed that the maximum adsorption occurs at the pH$_{pzc}$ of each oxide, with TiO_2 the preferred adsorbent for HQ and Fe_2O_3 is the preferred adsorbent for CAT, confirming that the nature of adsorbent can influence the adsorption of substrates on their surfaces (Abugazleh et al., 2020).

Table 1

Nominal and measured concentrations (mg.L^{-1}) of CAT and HQ for *C. dubia* and *P. promelas* used in WET test before and after metal oxide absorption.

	Before treatment with metal oxide							
	C. dubia				*P. promelas*			
Concentration (mg.L^{-1})	CAT		HQ		CAT		HQ	
	Nominal	Measured	Nominal	Measured	Nominal	Measured	Nominal	Measured
Control	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	1.58	1.60	0.05	0.04	1.87	1.76	0.03	0.03
	2.10	2.20	0.06	0.06	3.75	3.66	0.05	0.05
	2.81	2.84	0.08	0.08	7.50	7.58	0.10	0.11
	3.75	3.71	0.11	0.11	15.00	15.31	0.20	0.21
100%	5.00	5.02	0.15	0.15	30.00	30.00	0.40	0.40
	After treatment with TiO$_2$							
	C. dubia				*P. promelas*			
Concentration (mg.L^{-1})	CAT		HQ		CAT		HQ	
	Nominal	Measured	Nominal	Measured	Nominal	Measured	Nominal	Measured
Control	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	1.25	1.29	0.06	0.06	3.75	3.77	0.03	0.03
	3.84	3.80	0.08	0.08	7.50	7.58	0.05	0.05
	4.80	4.85	0.11	0.11	15.00	15.74	0.10	0.10
	6.00	6.10	0.15	0.15	30.00	31.70	0.20	0.20
100%	7.50	7.50	0.20	0.20	60.00	60.00	0.40	0.40
	After treatment with Fe$_2$O$_3$							
	C. dubia				*P. promelas*			
Concentration (mg.L^{-1})	CAT		HQ		CAT		HQ	
	Nominal	Measured	Nominal	Measured	Nominal	Measured	Nominal	Measured
Control	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	1.25	1.30	0.06	0.06	3.75	3.69	0.13	0.13
	3.84	3.81	0.08	0.08	7.50	7.42	0.25	0.25
	4.80	4.80	0.11	0.11	15.00	15.06	0.50	0.51
	6.00	6.09	0.15	0.15	30.00	31.39	1.00	1.00
100%	7.50	7.51	0.20	0.20	60.00	60.00	2.00	2.00

2.3 Statistical analysis

WET test results were analyzed using CETIS (Comprehensive Environmental Toxicology Information System™) Software (Tidepool Scientific, LLC). Assumptions of normality were tested using the Shapiro-Wilk test and Bartlett's test for homogeneity of variances, respectively. One-way ANOVA and Post-Hoc tests were used to determine significant differences in survival, reproduction, and growth rates between CAT and HQ concentrations in both experiments. All statistical analyses were conducted at α = 0.05. 7-d chronic endpoints included survival, reproduction (*C. dubia*), and growth (*P. promelas*). Measured concentrations were used to statistically calculate toxic endpoints using the CETIS software program.

3. Results

C. dubia and *P. promelas* were exposed to CAT and HQ before and after TiO_2 and Fe_2O_3 treatments. All USEPA requirements were met during the test periods (U.S.EPA, 2002).

3.1 Ceriodaphnia dubia chronic toxicity responses

Measured toxicity to *C. dubia* confirmed the effectiveness of both oxides in reducing toxicity to CAT and HQ to *C. dubia* (Table 2). Fe_2O_3 has a greater affinity to reduce toxicity in both pollutants than TiO_2. CAT adsorbed by Fe_2O_3 had lower toxicity effects on the tested organisms than CAT adsorbed by TiO_2 or the CAT without treatment with metal oxides (CAT- only). CAT- only to *C. dubia* had a measured 7-d LC_{50} of 3.66 mg.L^{-1}, while for CAT-TiO_2 and CAT- Fe_2O_3 LC_{50} concentrations were 5.89 and 6.57 mg.L^{-1}, respectively.

Table 2

C. dubia and *P. promelas* lethal and sublethal mean endpoints for CAT and HQ in the presence and absence of TiO_2/Fe_2O_3

Organism	Chemical Name	Endpoints	Without Treatment (mg.L^{-1})	Treatment with TiO_2 (mg.L^{-1})	Treatment with Fe_2O_3 (mg.L^{-1})
C. dubia	HQ	LC_{50}	0.07 ± 0.00	0.09 ± 0.01	0.17 ± 0.01
		IC_{25}	0.06 ± 0.01	0.08 ± 0.01	0.16 ± 0.01
	CAT	LC_{50}	3.66 ± 0.75	5.89 ± 0.36	6.57 ± 0.58
		IC_{25}	2.10 ± 0.18	2.52 ± 0.39	5.32 ± 1.97
P. promelas	HQ	LC_{50}	0.05 ± 0.01	0.09 ± 0.02	0.87 ± 0.06
		IC_{25}	0.04 ± 0.00	0.11 ± 0.02	0.98 ± 0.03
	CAT	LC_{50}	12.36 ± 2.80	18.77 ± 2.92	23.99 ± 4.72
		IC_{25}	9.42 ± 1.93	13.35 ± 6.82	14.66 ± 1.16

Sublethal endpoints for *C. dubia* reproduction using CAT included an LOEL of 3.97 mg.L^{-1} for CAT- only expressed a significant change from using CAT-TiO_2 and CAT-Fe_2O_3, which displayed an increased concentration reaching to 7.19 and 7.00 mg.L^{-1}, respectively.

Results indicate that TiO_2 does not improve the sublethal toxicity of CAT to *C. dubia*, as there were no statistical differences in the endpoints (IC_{25}, LOEL, and NOEL were 2.10, 3.10, and 1.60 mg.L^{-1} for CAT- only compared to 2.52, 3.20, and 1.64 mg.L^{-1} respectively for CAT-TiO_2). HQ had more toxic impact than CAT on *C. dubia* as seen in Table 2. Exposure to HQ adsorbed by TiO_2 did not have a significant decrease in mortality (LC_{50} = 0.09 mg.L^{-1}) while HQ adsorbed by Fe_2O_3 lowered the toxicity significantly (LC_{50} = 0.17 mg.L^{-1}). Fe_2O_3 treatment resulted in a greater reduction of toxic endpoints of CAT and HQ than TiO_2 for *C. dubia*.

Fe_2O_3 was more effective in toxicity reduction of CAT and HQ as measured by both test organisms, *C. dubia* and *P. promelas*. The toxicity reductions were calculated by dividing the LC_{50} values obtained for solutions in the presence of metal oxides by the LC_{50} value of the pollutant in the absence of metal oxides for the same organism. TiO_2 and Fe_2O_3 reduced *C. dubia* toxicity of CAT by 1.60- and 1.80-fold and the toxicity reduction for HQ by 1.27- and 2.43-fold, respectively.

3.2 *Pimephales promelas* chronic toxicity responses

Results of *P. promelas* exposure to CAT and HQ before and after TiO_2 and Fe_2O_3 treatments are shown in Table 2. LC_{50} value for CAT-only was 12.36 mg.L^{-1} whereas LC_{50} value for HQ-only was 0.051 mg.L^{-1}. No significant differences in CAT and HQ LC_{50} values were measured between test repetitions. An overview of TiO_2 and Fe_2O_3 effectiveness in reducing the toxicity of CAT and HQ are presented in Table 2. For *P. promelas*, using TiO_2 and Fe_2O_3 reduced the toxicity of the CAT by 1.51 and 1.94 times compared to using the pollutant without adding the oxide, while the reduction of HQ using TiO_2 and Fe_2O_3 was 1.79 and 16.94, respectively.

Overall, the results indicate that the exposure of *P. promelas* to CAT adsorbed by TiO_2 or Fe_2O_3 has less toxicity than exposure to CAT-only (Fig. 2).

Chronic *P. promelas* bioassays to CAT, using TiO_2 and Fe_2O_3 reduced the measured toxicity as the LC_{50} was increased (LC_{50} were 20.45 and 26.71 mg.L^{-1} respectively, compared to 13.97 mg.L^{-1} for CAT-only). These bioassays using HQ adsorbed by the metal oxides resulted in clear reduction of toxicity as the LC_{50} was 0.09 and 0.87 mg.L^{-1} for TiO_2 and Fe_2O_3, respectively, compared to 0.051 mg.L^{-1} for HQ-only, while Fe_2O_3 significantly reduced the toxicity of HQ compared to TiO_2 (Figure 2). Metal oxide treatments increased the mean dry weight of *P. promelas* indicating a reduction in sublethal effects to the test organism. Bioassay results indicate Fe_2O_3 was more efficient in reducing sublethal toxicity in CAT and HQ as measured by increased mean dry weight of surviving fish.

4. Discussion

The USEPA reports that the sensitivity of freshwater organisms to chemicals can provide important clues about the nature of the toxicity (U.S. Environmental Protection Agency, 1999). Phenolic compounds are chemicals of significant concern due to their toxicity to aquatic organisms at the ppm level (Duan et al., 2018). In this study, we measured a pronounced toxicity of HQ to aquatic organisms, *P. promelas* and *C. dubia*, and CAT was considerably less toxic than HQ to both organisms. A previous study reported that HQ is 100X more toxic than CAT to *Photobacterium phosphoreum* bacteria (Enguita and Leitão, 2013) which coincides with this present study for *P. promelas* and *C. dubia.* Guerra (2001) concluded that HQ is the most toxic compound in dihydric phenols through acute tests on freshwater organisms. DeGraeve et al. (1980) reported the 96-hr LC_{50} for HQ to *P. promelas* was < 0.1 mg.L^{-1}, while Russom et al. (1997) reported the 96-hr LC_{50} value for CAT was 9.22 mg.L^{-1}. These 96-h results are similar to the 7-d values reported in this present study for *P. promelas*.

In additional aquatic studies, CAT was exposed to *Oncorhynchus mykiss* (rainbow trout) with resulting 24-h LC_{50} = 2.3 $mg.L^{-1}$ and 14-d chronic EC_{50} = 0.55 $mg.L^{-1}$ (Calamari et al., 1983). According to an assessment by the Canadian Environment and Health Ministry, the acute LC_{50} values for fish (*Leuciscus idus*) exposed to HQ are as low as 0.044 $mg.L^{-1}$ (Canadian Ministry of the Environment and of Health, 2008a). For CAT, acute LC_{50} values varies between 3.5–10 mg/L for the same fish, while for invertebrates (shrimp) the LC_{50} exceeded 40 $mg.L^{-1}$ (Canadian Ministry of the Environment and of Health, 2008b). Toxicity endpoints for *P. promelas* were verified through in silico toxicity models using QSARS to predict aquatic toxicity of endocrine disruptors; predictions include a 96-h LC_{50} of CAT and HQ = 33.19 and 0.01 $mg.L^{-1}$, respectively (Bohlen et al., 2019).

This study measured that HQ is very toxic compared to CAT and *C. dubia* is more sensitive to CAT than *P. promelas* (*C. dubia* HQ LC_{50} = 0.07 $mg.L^{-1}$; *P. promelas* HQ LC_{50} = 0.05; *C. dubia* CAT LC_{50} = 3.66 $mg.L^{-1}$; *P. promelas* CAT LC_{50} = 12.36 $mg.L^{-1}$). These results support previous studies (Bährs et al., 2013; National Toxicology Program, 1989; United Nations Environment Programme, 2012) which report that HQ is the most toxic compound of the tested phenolic chemicals, and CAT and HQ toxic endpoints for *P. promelas* are comparable to previous research (Canadian Ministry of the Environment and of Health, 2008b; DeGraeve et al., 1980; U.S. Food and Drug Administration, 2009). Although Guerra (2001) suggested that *C. dubia* is a more sensitive species than *P. promelas* to the acute toxicity of CAT and HQ, in our chronic 7-d study, we measured comparable sensitivity of both organisms to HQ, but greater sensitivity to CAT. Although these species normally demonstrate similar sensitivities to most toxicants (Mount et al., 1993), Dwyer et al. (2004) reported *C. dubia* were often more sensitive than *P. promelas* to effluents from domestic or industrial facilities, which differs from this study. The difference could be due to the presence of mixtures of other contaminants present in effluents.

Metal oxides, especially Fe_2O_3, reduce phenolic toxicity in domestic or industrial effluents through adsorption onto the surface of the metal oxides. The adsorption capacity can be influenced by surface functional groups (Mojoudi et al., 2019). The protonation of hydroxyl groups allows water to become the leaving group. This creates a large number of active sites for the adsorption of CAT and HQ. Large surface area and structural nature also contribute to effective removal through adsorption of pollutants. Results indicates that the toxicities of CAT and HQ are influenced by their chemical structure, solubility, and the characteristics of the metal oxide. This study examined TiO_2 and Fe_2O_3 treatments to reduce the aquatic toxicity of CAT and HQ. Due to their small particle size and large specific surface area, Fe_2O_3 particles have a strong adsorption capacity for CAT and HQ. Fe_2O_3 treatment resulted in greater reduction of *C. dubia* toxicity of HQ (2.43X reduction) compare to CAT (1.79X reduction) during the 7-d exposures. In *P. promelas*, treatment with Fe_2O_3 reduced toxic effects of HQ (toxicity reduction = 16.94) to CAT (toxicity reduction = 1.94). Although not as effective as Fe_2O_3, TiO_2 reduced the toxic effects of CAT to *C. dubia and P. promelas*, (toxicity reduction = 1.61X and 1.52X, respectively).

The less effective metal oxide detoxification by TiO_2 might be due to its structure, and the high sensitivity of *C. dubia* to TiO_2. Pakrashi et al. (2013) reported the toxicity of TiO_2 on *C. dubia* under light and dark conditions and reported this light-sensitive oxide had greater toxicity in lighted conditions (LC_{50} = 8 $mg.mL^{-1}$/ 32 $mg.mL^{-1}$; light/dark, respectively). Residual TiO_2 following treatment could possibly have lessened the benefits of this metal oxide in reducing the toxic effects of CAT and HQ.

One mechanism that reduces pollutant bioavailability following treatment is molecular binding (Ayangbenro and Babalola, 2017). The different chemical structures of CAT and HQ control the binding position on the surface of oxides. Redfern et al. (2003) reported, in theoretical calculations that CAT molecules adsorb onto TiO_2 surfaces in a bidentate

bridging structure, in which both oxygen atoms bond to the same titanium atom. For HQ, the para position makes it capable of adsorbing onto the oxide surface through one hydroxyl group only. Each type of binding influences the adsorption type and capacity. The observed reduction of toxicity following treatment with Fe_2O_3 or TiO_2 may result from the interactions between each chemical that ultimately impacts the mechanisms of action at different biological organization levels.

5. Conclusion

Results presented in this study report that the presence of TiO_2 and Fe_2O_3 in water containing CAT or HQ can reduce toxicity to *C. dubia* and *P. promelas*. HQ exhibited greater toxicity than CAT to both organisms with the 7-d LC_{50} values of 0.07 and 0.05 mg.L^{-1} for *C. dubia* and *P. promelas*, respectively, compared to 3.66 and 12.36 mg.L^{-1}, respectively, for CAT. Following metal oxide treatment, both oxides reduced the toxicity of tested pollutants; however, Fe_2O_3 was more efficient for CAT and HQ toxicity reduction than TiO_2.

These results confirm the importance of metal oxides as adsorbents and detoxicants preceding industrial discharge to water bodies and water treatment facilities. Fe_2O_3 is an effective detoxifier of catechol and hydroquinone and may apply to the investigation of other toxic agents. Further work could include metal oxides in the treatment of additional phenolic compounds to reduce toxicity prior to discharge into receiving streams or municipal water treatment facilities.

Declarations

Conflict of interest

The authors declare no competing interests.

Author contributions

Mohd K. Abugazleh: Acquisition of data, data curation, visualization, investigation, formal analysis, writing - original draft, **Hashim M. Ali**: Funding acquisition, supervision, project administration, review & editing; **Jae A. Chester**: Participated in the data acquisition; **Jennifer L. Bouldin**: Formal analysis, funding acquisition, investigation, methodology, project administration, resources, software, supervision, validation, and editing.

Compliance with ethical standards

Conflict of interest

The authors declare no competing interests.

References

1. Abugazleh, M.K., Rougeau, B., Ali, H., 2020. Adsorption of catechol and hydroquinone on titanium oxide and iron (III) oxide. J. Environ. Chem. Eng. 8. https://doi.org/10.1016/j.jece.2020.104180

2. Alias, N., Rosli, S.A., Sazalli, N.A.H., Hamid, H.A., Arivalakan, S., Umar, S.N.H., Khim, B.K., Taib, B.N., Keat, Y.K., Razak, K.A., Yee, Y.F., Hussain, Z., Bakar, E.A., Kamaruddin, N.F., Manaf, A.A., Uchiyama, N., Kian, T.W., Matsuda, A., Kawamura, G., Sawada, K., Matsumoto, A., Lockman, Z., 2020. Metal oxide for heavy metal detection and removal, in: Metal Oxide Powder Technologies. Elsevier, pp. 299–332. https://doi.org/10.1016/B978-0-12-817505-7.00015-4

3. Amin, M.T., Alazba, A.A., Manzoor, U., 2014. A review of removal of pollutants from water/wastewater using different types of nanomaterials. Adv. Mater. Sci. Eng. 2014. https://doi.org/10.1155/2014/825910

4. Ankley, G.T., Villeneuve, D.L., 2006. The fathead minnow in aquatic toxicology: Past, present and future. Aquat. Toxicol. 78, 91–102. https://doi.org/10.1016/j.aquatox.2006.01.018

5. Anku, W.W., Mamo, M.A., Govender, P.P., 2017. Phenolic compounds in water: Sources, reactivity, toxicity and treatment methods, in: Phenolic Compounds - Natural Sources, Importance and Applications. https://doi.org/10.5772/66927

6. Ayangbenro, A.S., Babalola, O.O., 2017. A new strategy for heavy metal polluted environments: A review of microbial biosorbents. Int. J. Environ. Res. Public Health 14, 94. https://doi.org/10.3390/ijerph14010094

7. Babich, H., Borenfreund, E., 1987. Fathead minnow FHM cells for use in in vitro cytotoxicity assays of aquatic pollutants. Ecotoxicol. Environ. Saf. 14, 78–87. https://doi.org/10.1016/0147-6513(87)90086-8

8. Bahri, S., Jonsson, C.M., Jonsson, C.L., Azzolini, D., Sverjensky, D.A., Hazen, R.M., 2011. Adsorption and surface complexation study of L-DOPA on rutile (α-TiO2) in NaCl solutions. Environ. Sci. Technol. 45, 3959–3966. https://doi.org/10.1021/es1042832

9. Bährs, H., Putschew, A., Steinberg, C.E.W., 2013. Toxicity of hydroquinone to different freshwater phototrophs is influenced by time of exposure and pH. Environ. Sci. Pollut. Res. 20, 146–154. https://doi.org/10.1007/s11356-012-1132-5

10. Blaise, C., Férard, J.F., 2005. Small-scale freshwater toxicity investigations, Toxicity Test Methods. https://doi.org/10.1007/1-4020-3120-3

11. Bohlen, M.-L., Jeon, H.P., Kim, Y.J., Sung, B., 2019. In silico modeling method for computational aquatic toxicology of endocrine disruptors: A software-based approach using QSAR toolbox. J. Vis. Exp. 150. https://doi.org/10.3791/60054

12. Brayner, R., Ferrari-Iliou, R., Brivois, N., Djediat, S., Benedetti, M.F., Fiévet, F., 2006. Toxicological impact studies based on Escherichia coli bacteria in ultrafine ZnO nanoparticles colloidal medium. Nano Lett. 6, 866–870. https://doi.org/10.1021/nl052326h

13. Calamari, D., Galassi, S., Setti, F., Vighi, M., 1983. Toxicity of selected chlorobenzenes to aquatic organisms. Chemosphere 12, 253–262. https://doi.org/10.1016/0045-6535(83)90168-6

14. Canadian Ministry of the Environment and of Health, 2008a. Screening assessment for 1,4-Benzenediol (hydroquinone)(123-31-9). Canadian Council of Ministers of the Environmen.

15. Canadian Ministry of the Environment and of Health, 2008b. Screening assessment for 1,2-Benzenediol (catechol) (120-80-9).

16. Dave, P.N., Chopda, L. V., 2014. Application of iron oxide nanomaterials for the removal of heavy metals. J. Nanotechnol. 2014. https://doi.org/10.1155/2014/398569

17. DeCaprio, A.P., 1999. The toxicology of hydroquinone - Relevance to occupational and environmental exposure. Crit. Rev. Toxicol. 29, 283–330. https://doi.org/10.1080/10408449991349221

18. DeGraeve, G.M., Geiger, D.L., Meyer, J.S., Bergman, H.L., 1980. Acute and embryo-larval toxicity of phenolic compounds to aquatic biota. Arch. Environ. Contam. Toxicol. 9, 557–568. https://doi.org/10.1007/BF01056935

19. Deisinger, P.J., Hill, T.S., English, J.C., 1996. Human exposure to naturally occurring hydroquinone. J. Toxicol. Environ. Heal. - Part A 47, 31–46. https://doi.org/10.1080/009841096161915

20. Duan, W., Meng, F., Cui, H., Lin, Y., Wang, G., Wu, J., 2018. Ecotoxicity of phenol and cresols to aquatic organisms: A review. Ecotoxicol. Environ. Saf. 157, 441–456. https://doi.org/10.1016/j.ecoenv.2018.03.089

21. Dwyer, F.J., Hardesty, D.K., Henke, C.E., Ingersoll, C.G., Whites, D.W., Augspurger, T., Canfield, T.J., Mount, D.R., Mayer, F.L., 2004. Assessing contaminant sensitivity of endangered and threatened aquatic species: Part III. effluent toxicity tests. Arch. Environ. Contam. Toxicol. 48, 174–183. https://doi.org/10.1007/s00244-004-0104-2

22. El Morabet, R., 2018. Effects of outdoor air pollution on human health, in: Reference Module in Earth Systems and Environmental Sciences. Elsevier. https://doi.org/10.1016/B978-0-12-409548-9.11012-7

23. Elmenaouar, K., Benbrik, R., Aamouche, A., 2017. Influence of C6H4(OH)2 isomers on water disinfection by photocatalysis: A computational study. Condens. Matter Phys. 20. https://doi.org/10.5488/CMP.20.23302

24. Enguita, F.J., Leitão, A.L., 2013. Hydroquinone: Environmental pollution, toxicity, and microbial answers. Biomed Res. Int. 2013, 1–14. https://doi.org/10.1155/2013/542168

25. García-Araya, J.F., Beltrán, F.J., Álvarez, P, Masa, F.J., 2003. Activated carbon adsorption of some phenolic compounds present in agroindustrial wastewater. Adsorption 9, 107–115. https://doi.org/10.1023/A:1024228708675

26. Geiger, D.L., Poirier, S.H., Brooke, L.T., Call, D.J., 1986. Acute toxicities of organic chemicals to fathead minnows (Pimephales promelas): Volume III. University of Wisconsin-Superior, Center for Lake Superior Environmental Studies.

27. Guerra, R., 2001. Ecotoxicological and chemical evaluation of phenolic compounds in industrial effluents. Chemosphere 44, 1737–1747. https://doi.org/10.1016/S0045-6535(00)00562-2

28. Karpińska, J., Kotowska, U., 2019. Removal of organic pollution in the water environment. Water 11, 2017. https://doi.org/10.3390/w11102017

29. Kodavanti, P.R.S., Royland, J.E., Sambasiva Rao, K.R.S., 2014. Toxicology of persistent organic pollutants, in: Reference Module in Biomedical Sciences. https://doi.org/10.1016/b978-0-12-801238-3.00211-7

30. Lewandowski, C.M., Co-investigator, N., Lewandowski, C.M., 2015. Powder metal technologies and applications, in: ASM International: Materials Park, OH.

31. MacHala, L., Tuček, J., Zbořil, R., 2011. Polymorphous transformations of nanometric iron(III) oxide: A review. Chem. Mater. 23, 3255–3272. https://doi.org/10.1021/cm200397g

32. Milligan, P.W., Häggblom, M.M., 1998. Biodegradation of resorcinol and catechol by denitrifying enrichment cultures. Environ. Toxicol. Chem. 17, 1456–1461. https://doi.org/10.1002/etc.5620170804

33. Mojoudi, N., Mirghaffari, N., Soleimani, M., Shariatmadari, H., Belver, C., Bedia, J., 2019. Phenol adsorption on high microporous activated carbons prepared from oily sludge: Equilibrium, kinetic and thermodynamic studies. Sci. Rep. 9, 19352. https://doi.org/10.1038/s41598-019-55794-4

34. Mount, D.R., Gulley, D.D., Evans, J.M., 1993. Salinity/toxicity relationships to predict the acute toxicity of produced waters to freshwater organisms, in: All Days. SPE, San Antonio, Texas, p. SPE-26007-MS. https://doi.org/10.2118/26007-MS

35. Nagpal, M., Kakkar, R., 2019. Use of metal oxides for the adsorptive removal of toxic organic pollutants. Sep. Purif. Technol. 211, 522–539. https://doi.org/10.1016/j.seppur.2018.10.016

36. National Toxicology Program, 1989. Toxicology and carcinogenesis studies of hydroquinone (CAS No. 123-31-9) in F344/N Rats and B6C3F1 Mice (Gavage Studies). Natl. Toxicol. Program Tech. Rep. Ser. 366, 1–248.

37. Neilson, A.H., Allard, A., Hynning, P., Remberger, M., 1991. Distribution, fate and persistence of organochlorine compounds formed during production of bleached pulp. Toxicol. Environ. Chem. 30, 3–41. https://doi.org/10.1080/02772249109357638

38. Odumosu, P.O., Ekwe, T.O., 2010. Identification and spectrophometric determination of hydroquinone levels in some cosmetic creams. African J. Pharm. Pharmacol. 4, 231–234.

39. Pakrashi, S., Dalai, S., Humayun, A., Chakravarty, S., Chandrasekaran, N., Mukherjee, A., 2013. Ceriodaphnia dubia as a potential bio-indicator for assessing acute aluminum oxide nanoparticle toxicity in fresh water environment. PLoS One 8, e74003. https://doi.org/10.1371/journal.pone.0074003

40. Rasalingam, S., Peng, R., Koodali, R.T., 2014. Removal of hazardous pollutants from wastewaters: Applications of TiO2-SiO2 mixed oxide materials. J. Nanomater. 2014, ID 617405. https://doi.org/10.1155/2014/617405

41. Redfern, P.C., Zapol, P., Curtiss, L.A., Rajh, T., Thurnauer, M.C., 2003. Computational studies of catechol and water interactions with titanium oxide nanoparticles. J. Phys. Chem. B. 107, 11419–11427. https://doi.org/10.1021/jp0303669

42. Russom, C.L., Bradbury, S.P., Broderius, S.J., Hammermeister, D.E., Drummond, R.A., 1997. Predicting modes of toxic action from chemical structure: Acute toxicity in the fathead minnow (Pimephales promelas). Environ. Toxicol. Chem. 16, 948–967. https://doi.org/10.1002/etc.5620160514

43. Saha, N.C., Bhunia, F., Kaviraj, A., 1999. Toxicity of phenol to fish and aquatic ecosystems. Bull. Environ. Contam. Toxicol. 63, 195–202. https://doi.org/10.1007/s001289900966

44. Schweigert, N., Hunziker, R.W., Escher, B.I., Eggen, R.I.L., 2001a. Acute toxicity of (chloro-)catechols and (chloro-)catechol–copper combinations in escherichia coli corresponds to their membrane toxicity in vitro. Environ. Toxicol. Chem. 20, 47–239. https://doi.org/https://doi.org/10.1002/etc.5620200203

45. Schweigert, N., Zehnder, A.J.B., Eggen, R.I.L., 2001b. Chemical properties of catechols and their molecular modes of toxic action in cells, from microorganisms to mammals. Environ. Microbiol. 3, 81–91. https://doi.org/10.1046/j.1462-2920.2001.00176.x

46. Shadnia, H., Wright, J.S., 2008. Understanding the toxicity of phenols: Using quantitative structure-activity relationship and enthalpy changes to discriminate between possible mechanisms. Chem. Res. Toxicol. 21, 1197–1204. https://doi.org/10.1021/tx800058r

47. Sophia, C., Lima, E.C., 2018. Removal of emerging contaminants from the environment by adsorption. Ecotoxicol. Environ. Saf. 150, 1–17. https://doi.org/10.1016/j.ecoenv.2017.12.026

48. Subramanyam, R., Mishra, I.M., 2013. Critical review of anaerobic biodegradation of benzenediols: Catechol, resorcinol, and hydroquinone. J. Hazardous, Toxic, Radioact. Waste 17. https://doi.org/10.1061/(asce)hz.2153-5515.0000178

49. U.S. Department of Health and Human Services, 2008. Toxicological profile for phenol.

50. U.S. Environmental Protection Agency, 2002. Short-term methods for estimating the chronic toxicity of effluents and receiving waters to freshwater organisms.

51. U.S. Environmental Protection Agency, 1999. Toxicity reduction evaluation guidance for municipal wastewater treatment plants.

52. U.S. Food and Drug Administration, 2009. Hydroquinone supporting information for toxicological evaluation.

53. United Nations Environment Programme, 2012. SIDS initial assessment report (SIAR): Hydroquinone, in: UNEP Publications. United States of America.

54. Vasudevan, D., Stone, A.T., 1996. Adsorption of catechols, 2-aminophenols, and 1,2-phenylenediamines at the metal (hydr)oxide/water interface: Effect of ring substituants on the adsorption onto TiO2. Environ. Sci. Technol. 30, 1604–1613. https://doi.org/10.1021/es950615+

55. Versteeg, D.J., Stalmans, M., Dyer, S.D., Janssen, C., 1997. Ceriodaphnia and daphnia: A comparison of their sensitivity to xenobiotics and utility as a test species. Chemosphere 34, 869–892. https://doi.org/10.1016/S0045-6535(97)00014-3

56. Warnecke, D., Duis, K., Knacker, T., Schüürmann, G., Kühne, R., 2014. Review and enhancement of new risk assessment concepts under REACH. Federal Environment Agency (Germany).

57. Watanabe, K.H., Jensen, K.M., Orlando, E.F., Ankley, G.T., 2007. What is normal? A characterization of the values and variability in reproductive endpoints of the fathead minnow, Pimephales promelas. Comp. Biochem. Physiol. Part C Toxicol. Pharmacol. 146, 348–356. https://doi.org/10.1016/j.cbpc.2007.04.015

58. Wu, Y., Zhu, P., Reddy, M. V., Chowdari, B.V.R., Ramakrishna, S., 2014. Maghemite nanoparticles on electrospun CNFs template as prospective lithium-ion battery anode. ACS Appl. Mater. Interfaces 6, 1951–1958. https://doi.org/10.1021/am404939q

59. Yang, K., Jiang, Y., Yang, J., Lin, D., 2018. Correlations and adsorption mechanisms of aromatic compounds on biochars produced from various biomass at 700°C. Environ. Pollut. 223, 64–70. https://doi.org/10.1016/j.envpol.2017.10.035

60. Zheng, C., Zhao, L., Zhou, X., Fu, Z., Li, A., 2013. Treatment technologies for organic wastewater, in: Water Treatment. InTech. https://doi.org/10.5772/52665
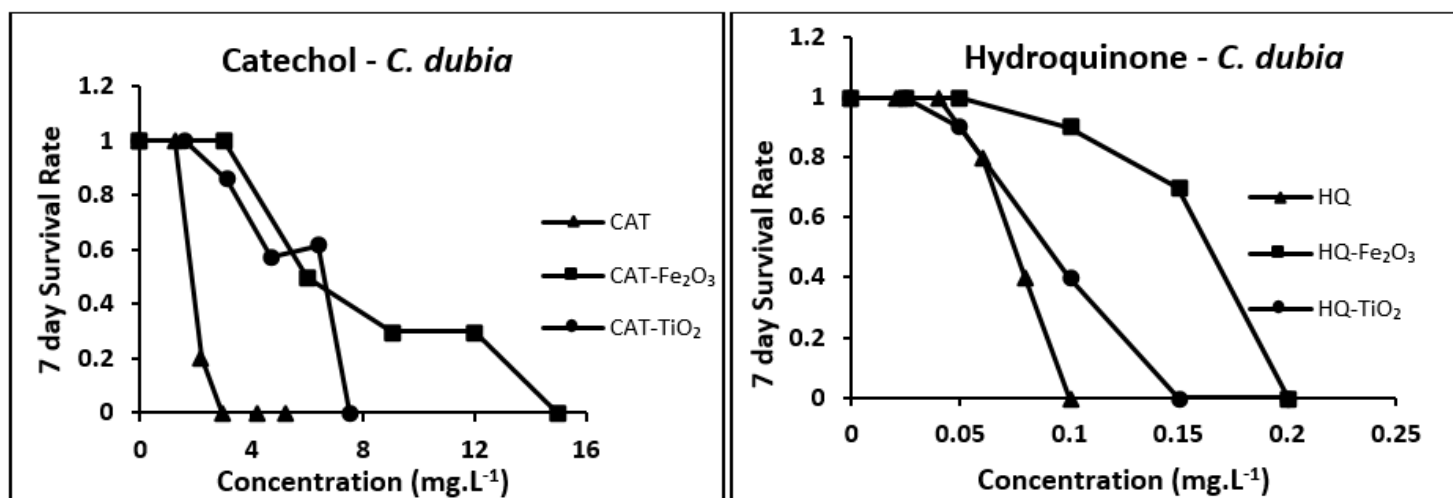
Figures

Figure 1

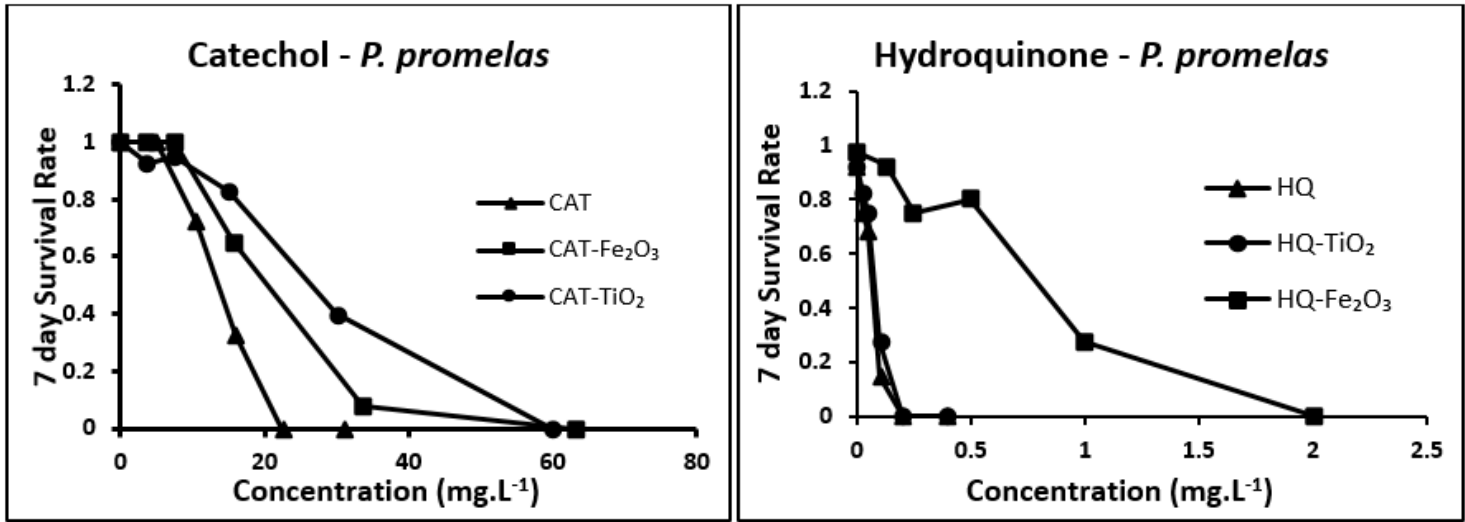Proportion survival of *Ceriodaphnia dubia* after exposure to CAT and HQ

Figure 2

Proportion survival of *P. promelas* after exposure to CAT and HQ