

## Efficiency of conventional drinking water treatment process in the removal of endosulfan, ethylenethiourea, and 1,2,4-triazole

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### ABSTRACT

The aim of this work was to study the removal of three pesticides using conventional drinking water treatment (DWT) processes. These methods are the most used in Brazil, and include coagulation–flocculation of water. The pesticides/metabolites evaluated were: endosulfan, ethylenethiourea (ETU), and 1,2,4-triazole. The laboratory tests were carried out in triplicate using the jar test. Synthetic water samples prepared with kaolin, simulating the dry and rainy periods, were contaminated with different concentrations of pesticides. Results showed that conventional DWT methods are not suitable for the removal of the pesticides/metabolites evaluated. No significant difference ( $p < 0.05$ ) was observed for the dry and rainy seasons. However, the removal was observed to decrease with higher initial concentrations of the contaminants. With regard to the removal of contaminants, ETU and 1,2,4-triazole resulted in the lowest removal percentages (ETU: median  $\leq 11\%$  in decanted water and 1,2,4-triazole  $\leq 18\%$  in decanted water) compared to endosulfan (median  $\leq 54\%$  in decanted water). This fact can be justified by the low solubility of endosulfan in water at 20 °C and high  $K_{oc}$ ,  $\log K_{ow}$  and molar mass, in relation to the other two pesticides.

**Key words** | coagulation–flocculation, conventional drinking water treatment, organic micropollutants, pesticide

### INTRODUCTION

Trace organic contaminants in potable water have become an increasing cause of concern for governments and water authorities around the world, because the impact of prolonged low-level exposure on human health is not clearly understood as yet. Therefore, it is vital that effective water treatment processes be employed to remove trace organic contaminants, thus ensuring that any potential human health risks are mitigated prior to consumption (Alexander *et al.* 2012).

Half-life, sorption, and solubility are the properties that most significantly affect the presence of pesticides in water. Highly sorbable and persistent pesticides remain sorbed in the soil and can contaminate surface waters;

persistent but weakly adsorbed pesticides (low  $K_{oc}$  and high half-life) are leached from the soil, contaminating groundwater. Non-persistent and weakly sorbed compounds (low  $K_{oc}$  and half-life) can contaminate both surface waters and groundwater (Cerejeira *et al.* 2003; Bortoluzzi *et al.* 2006; Claver *et al.* 2006; Soares *et al.* 2010, 2013; Vanzela *et al.* 2010). Thus, the assessment of treatment processes for the removal of pesticides is timely and the topic has been studied increasingly in recent years (Stackelberg *et al.* 2007; Ormad *et al.* 2008; Thuy *et al.* 2008).

However, fewer studies have documented the occurrence of these organic compounds in drinking water supplies (Stackelberg *et al.* 2007). Most of the available publications

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refer to pharmaceuticals (Heberer 2002; Boyd *et al.* 2003; Schwab *et al.* 2005; Gibs *et al.* 2007; Kim *et al.* 2007) and endocrine disruptors (Boyd *et al.* 2003; Rodriguez-Mozaz *et al.* 2004; Chen *et al.* 2007; Kim *et al.* 2007).

Conventional processes have been shown to be largely ineffective for emerging micropollutants; while various advanced treatment technologies, such as ozonation, advanced oxidation processes (AOPs), activated carbon adsorption, reverse osmosis, and nanofiltration have been shown to be effective.

Coagulation–flocculation is typically used in conventional drinking water treatment (DWT) plants for the removal of suspended solids, preceding rapid filtration, and has been shown to be especially ineffective in removing polar micropollutants. However, removal may occur if the compounds partition onto particulates or onto precipitated flocs through hydrophobic interactions. Compounds with a high hydrophobicity, as indicated by a high octanol-water partitioning coefficient ( $\log K_{ow}$ ) value, tend to partition onto the solids phase. In addition, water solubility is inversely related to the hydrophobic property of a chemical (Jin & Peldszus 2012).

Despite the limitations of conventional DWT for the public supply, such techniques are unfortunately the most used in Brazil. Also in Brazil, in many cases, there is an aggravating exposure of surface waters, especially in agricultural areas.

Soares *et al.* (2012) studied the risk of contamination of water sources by pesticides used on coffee crops. They took into account the number of pesticides marketed in an agricultural area in Brazil, between 2007 and 2010. Among the pesticides that present a risk of water contamination, three were selected for this study: endosulfan, mancozeb, and epoxiconazole.

Endosulfan is one of the most used pesticides on coffee crops in Brazil to control the coffee berry borer (*Hypothenemus hampei*). Endosulfan is a toxic compound, with great potential for bioaccumulation, and is one of the persistent pollutants banned worldwide by the Stockholm Convention. In Brazil, the marketing of products based in ‘endosulfan’ will be discontinued beginning in August 2013.

Endosulfan is one of the most abundant organochloride pesticides in the global atmosphere and is capable of undergoing long-range transport to remote locations, such as the Arctic. Degradation of isomers,  $\alpha$ - and  $\beta$ -endosulfan,

occurs in temperate/tropical soil and aquatic systems, by both abiotic and biotic processes, although this is highly dependent on prevailing environmental conditions (Weber *et al.* 2010). Removal of up to 95% of endosulfan and its metabolites is achieved by adsorption on natural organic substances (El Bakouri *et al.* 2008), sal wood charcoal (Mishra & Patel 2008), and zeolites (Yonli *et al.* 2012); also by electro dialysis membranes (Banasiak *et al.* 2011), nanofiltration (De Munari *et al.* 2013), and reductive transformation using bimetallic systems (Thangadurai & Suresh 2013). Aslan & Turkman (2006) reported 95% removal of  $\alpha$ - and  $\beta$ -endosulfan in a biodegradation reactor followed by a sand filter. However, this system did not meet the requirements for drinking water. Adsorption on activated carbon was needed, and removal of endosulfan reached 100%. Adsorption by activated carbon was found to be the most promising method for removing pesticides; however, this process is not cost-effective, particularly in developing countries (Mishra & Patel 2008).

Mancozeb, widely used on Brazilian coffee crops, is converted photochemically into various metabolites, among them ethylenethiourea (ETU), classified as carcinogenic by the International Union of Pure and Applied Chemistry (IUPAC 2012). ETU is predicted to be susceptible to leaching due to its high solubility and mobility.

Epoxiconazole, a fungicide of the triazole group, is also widely used on coffee crops and has great transport potential when dissolved in water and associated with the sediment in suspension. Its environmental degradation leads to the formation of 1,2,4-triazole, a metabolite stable in water, and considered relevant in environmental risk analyses (IUPAC 2012).

The degradation of derivatives of triazolidine and triazole is achieved by photocatalytic processes, with  $TiO_2$  and UV or visible light (Zaza *et al.* 2001; Guillard *et al.* 2002; Lhomme *et al.* 2007). Pesticide removal using zero-valent iron (ZVI) has been explored and reported in recent papers. Ghauch (2008) reported the complete removal of flutriafol, a persistent triazole pesticide in water, after 20 min of contact with ZVI. Amorim *et al.* (2013) reported 75% removal of ETU and 1,2,4-triazole by adsorption in commercial activated carbon.

Therefore, the aim of this study was to evaluate the removal of three compounds, which present great potential

for contamination of surface water, by conventional DWT processes.

## METHODS

Before carrying out experiments to evaluate the efficiency of conventional water treatment on the removal of selected compounds, preliminary tests were conducted to assess the behavior of the substances used to prepare synthetic water (kaolin and sodium bicarbonate) and to determine jar test conditions that would simulate the operation of a treatment plant of water for human consumption.

The synthetic water was prepared with the following characteristics: turbidity between  $10 \pm 1$  uT (dry season) and  $100 \pm 5$  uT (rainy season), and alkalinity of  $15 \pm 3$  mg  $\text{CaCO}_3 \text{ L}^{-1}$ . Turbidity was obtained by adding kaolin suspension according to the methodology proposed by Silva (2008), and alkalinity was obtained by adding sodium bicarbonate ( $25.2 \text{ mg NaHCO}_3 \text{ L}^{-1}$ ).

The decision to use synthetic water, with turbidity and color added by kaolin, allowed assessment of the removal of pesticides through the destabilization of the colloids by coagulation–flocculation, minimizing the influence of pesticide sorption onto the natural (organic and inorganic) matter. Adsorption of the contaminants by kaolin was investigated prior to coagulation–flocculation tests. Table 1 shows the characteristics of the pesticides and metabolites studied.

### Preliminary tests

In order to analyze the feasibility of using kaolin to add turbidity and apparent color to the study water, the material was characterized according to its BET (Brunauer–Emmett–Teller) surface area and porosity.

The adsorption of contaminants (ETU, 1,2,4-triazole, and endosulfan) and change in alkalinity were also investigated. A sample of synthetic water was prepared using  $100 \pm 5$  uT; the alkalinity was monitored every 15 min for  $3\frac{1}{2}$  hours, and then at the end of 36 hours.

To investigate the adsorption of contaminants, tests were carried out with different ratios/proportions between the masses of the adsorbent and the adsorbates, as shown in Table 2.

The adsorption tests with ETU and 1,2,4-triazole were conducted using a benchtop shaker (QUIMIS<sup>®</sup>, model Q816M20, 220 V), at room temperature, with 100 mL of sample in Erlenmeyer flasks (200 mL) sealed with Parafilm<sup>®</sup>. The experiments with endosulfan were conducted using the jar test (Nova Ética<sup>®</sup>, 218/LDB06 model), with 2 L of sample, because the analytical technique for endosulfan demands more volume.

### Determining optimum operating conditions for the jar test

Synthetic turbid waters were prepared with turbidity values of  $10 \pm 1$  and  $100 \pm 5$  uT (dry and rainy seasons, respectively), and alkalinity of  $15 \pm 3$  mg  $\text{CaCO}_3 \text{ L}^{-1}$ . The tests were done using jar test equipment, with pH of the raw water adjusted to between 8.0 and 12.0 by adding a saturated solution of  $\text{Ca(OH)}_2$  at  $0.87 \text{ g L}^{-1}$ . The tests started with a coagulant concentration ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) of  $30 \text{ mg L}^{-1}$ , the optimum scanning area of the theoretical diagram developed by Amirtharajah & Mills (1982), which was used as the reference. The effective removal, in this case, was due to the effects of sweep coagulation in the water samples.

Aluminum sulfate and alkalinity were added using prepared solutions at 1%. One hundred and fifty-six tests were carried out, and the optimum conditions were identified

Table 1 | Compound characteristics

Compound	CAS	Chemical formula	Molecular mass ( $\text{g mol}^{-1}$ )	Solubility in water at 20 °C ( $\text{mg L}^{-1}$ )	$K_{oc}^a$ ( $\text{mL g}^{-1}$ )	$\text{Log } K_{ow}^a$ pH7 at 20 °C
ETU	96-45-7	$\text{C}_3\text{H}_6\text{N}_2\text{S}$	102.16	20,000	142	−0.85
1,2,4-triazole	288-88-0	$\text{C}_2\text{H}_3\text{N}_3$	69.03	730,000	120	−1.0
Endosulfan	115-29-7	$\text{C}_9\text{H}_6\text{Cl}_6\text{O}_5\text{S}$	406.93	0.32	11,500	4.75

<sup>a</sup> $K_{oc}$ : Soil organic carbon-water partition coefficient;  $K_{ow}$ : octanol-water partition coefficient.

Source: IUPAC (2012).

**Table 2** | Variables of the adsorption tests and analytical techniques used

Contaminant	Kaolin mass (mg)	Contaminant mass (mg)	Test time (h)	Analytical technique
ETU	0.10	2–5–25–50	72	TOC, spectrophotometry UV-Visible
1,2,4-triazole	0.10	2–5–25–50	72	TOC
Endosulfan	1.0–10.0	0.020	48	GC/MS-MS

TOC: total organic carbon; GC/MS-MS: gas chromatography/tandem mass spectrometry.

using response surface methodology. Based on the analysis of the results, coagulation diagrams were constructed to establish the best coagulant concentration and pH for water treatment.

### Jar test and filtration

Bench tests were carried out in triplicate, using the jar test method, to reproduce the conventional water treatment systems that are used to produce drinking water: coagulation–flocculation and sedimentation, followed by filtration. The ETU and 1,2,4-triazole pesticides (both with 98% purity) were added to the study water in two different concentrations, 25 and 50 mg L<sup>-1</sup>, and their removal was verified by analysis of total organic carbon (TOC). The removal of ETU was followed by UV/Vis spectrophotometry ( $\lambda = 232$  nm), at initial concentrations of 2, 5, 25, and 50 mg L<sup>-1</sup>, and by high performance liquid chromatography with UV detector (HPLC/UV), with an initial concentration of 100  $\mu$ g L<sup>-1</sup> ETU. For the removal of endosulfan (95% purity), initial concentrations of 0.5 and 20.0  $\mu$ g L<sup>-1</sup> of the contaminant were tested. The removal was evaluated by gas chromatography coupled with tandem mass spectrometry (GC-MS/MS).

The jar test equipment used was from Nova Ética, 218/LDB06 model, fitted with 2 L glass beakers (tall form). The decanted water samples were collected using glass volumetric pipettes with cut-off tips to allow the suspended material to enter. These adaptations were used to minimize possible adsorption of contaminants by the jars and by the equipment used in the original collection system of samples, which are made of acrylic and rubber, respectively.

The jar test trials were performed according to the Brazilian standard NBR 12.216:1992, in order to better represent the operation of water treatment plants, as follows:

1. rapid mixture: dispersion of aluminum sulfate carried out using a speed gradient of 800 s<sup>-1</sup>, with a mixing time of 5 s;
2. mechanized flocculation: total time of 35 min, with a gradual reduction of speed from 70 s<sup>-1</sup> (initial) to 10 s<sup>-1</sup> (final);
3. decantation: sedimentation rate of 1.74 cm min<sup>-1</sup> (treatment plant with capacity up to 1,000 m<sup>3</sup> day<sup>-1</sup>).

A 1% aluminum sulfate solution (Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·18 H<sub>2</sub>O p.a. Merck<sup>®</sup>), prepared just before it was used, and a saturated Isofar<sup>®</sup> solution (0.87 g L<sup>-1</sup>) of Ca(OH)<sub>2</sub> p.a. were used to coagulate the water. A 37 mL volume of Ca(OH)<sub>2</sub> was added to each jar of raw water prepared with kaolin; this value was determined in the previous step. To obtain the sedimentation rate according to ABNT (Brazilian Technical Standards Association), equal to 1.74 cm min<sup>-1</sup>, the decanted samples were collected simultaneously in all beakers, 4 min after flocculation, at a depth of 7 cm from the water surface.

Filtration of the samples was done by gravity, using 125 mm diameter Whatman<sup>®</sup> grade 40 filters, according to Di Bernardo & Dantas (2005).

The glassware used in the experiments was previously washed using Merck's Extran<sup>®</sup> neutral detergent and rinsed with clean tap water. After this step, the glassware was washed using ultrasound (three washes of 15 min each), acclimatized in deionized water, and dried in an oven (150 °C for 2 hours). The bottles used to store the samples to be analyzed by chromatography were also acclimatized using n-hexane (Merck) and labeled.

The liquid effluents generated in the laboratory were properly collected and packed in canisters, previously labeled, and forwarded to the Department of Environmental Management of UFMG.

### Analytical techniques

The apparatus used for measuring pH, color, and turbidity in the tests were the Quimis<sup>®</sup> pH meter, HACH<sup>®</sup> DR2800

spectrophotometer, and HACH® 2100AN turbidimeter, respectively. Alkalinity was measured by titration (2320-B-Titration Method), according to *Standard Methods for the Examination of Water and Wastewater* (APHA 2005). The determination of ETU was carried out spectrophotometrically by measuring absorbance at 232 nm, using the Perkin Elmer® Lambda XLS, UV-VIS benchtop spectrophotometer.

The analyses of total organic carbon were conducted using a Shimadzu TOC-VCPN analyzer. ETU analysis by liquid chromatography was carried out in accordance with Hogendoorn et al. (1991) using Perkin Elmer® Series 200 equipment; and samples were analyzed using the direct-injection method, without extraction. The quantification limit (QL) of ETU was  $50 \mu\text{g L}^{-1}$ , according to the lower concentration of the analytical curve (Guidance on Validation of Analytical Methods used in Brazil: DOQ-CGCRE-008). Endosulfan analyses for GC-MS/MS with liquid-liquid extraction, according to APHA (2005), were undertaken in the Pesticide Laboratory of the Ezequiel Dias Foundation (FUNED). The detection limit (DL) for endosulfan was  $0.005 \mu\text{g L}^{-1}$  and the QL was  $0.010 \mu\text{g L}^{-1}$ .

### Data processing

The Minitab® 16 software, at the 5% significance level, was used for the statistical analysis of the results obtained in the adsorption tests. In this case, the non-parametric Kruskal-Wallis test, for comparing two or more independent sample groups (populations) regarding the central tendency of the data, was used. Thus, all concentrations obtained at the different sampling times, including the zero-hour time, were compared to each other.

The statistical analyses for the water treatment tests (jar test and filtration) were performed with removal percentage data obtained for each water (dry and rainy seasons), contaminant concentrations and by different analytical techniques.

The Mann-Whitney test, applied to each contaminant and concentration, was used for the analysis of seasonality: i.e., to check whether there is a difference between the percentage removal of the contaminant in  $10.0 \pm 1.0$  uT turbid water (dry season) and  $100.0 \pm 5.0$  uT turbid water (rainy season).

To assess if the initial concentration of the tests influences the percentage of contaminant removed, the data for both types of water were grouped together and treated as a single sample for each concentration of the different contaminants. However, in cases where the *p*-values were less than 5%, the data could not be grouped.

The Mann-Whitney test was also used to check differences in the percentages of endosulfan removal, in relation to the initial concentrations, since there were only two possible values of initial concentration. The Kruskal-Wallis test was applied to other contaminants and analytical methods, where there were more than two possible values of initial concentrations.

## RESULTS AND DISCUSSION

### Preliminary tests

The results obtained in the characterization of kaolin powder, used to prepare turbid water for this study, indicated that the material surface BET area is equal to  $5.30 \text{ m}^2 \text{ g}^{-1}$  and is not porous.

There was no change in alkalinity with  $2.5 \text{ mg L}^{-1}$   $\text{CaCO}_3$ , during monitoring, even after 36 hours of evaluation. These results show that the kaolin used in the preparation of synthetic turbid water should not interfere with the alkalinity of the water during the tests.

When comparisons of different concentrations of ETU and 1,2,4-triazole were performed over time, including the zero hour time, the tests showed *p*-values greater than 5%. This indicates that there is no difference in the results of the medians in relation to sample collection times. In the case of endosulfan ( $\alpha$  and  $\beta$ ), contaminant retention by kaolin was less than 3%.

Under these conditions, kaolin should not retain the contaminants and, therefore, can be used to simulate turbidity and color in the water in the bench scale tests.

### Determination of optimum conditions for the jar test

The coagulant concentration of  $40 \text{ mg L}^{-1}$ , at pH of coagulation in the range of 6.5 to 8.0 for the two waters, was chosen based on the analysis of coagulation diagrams

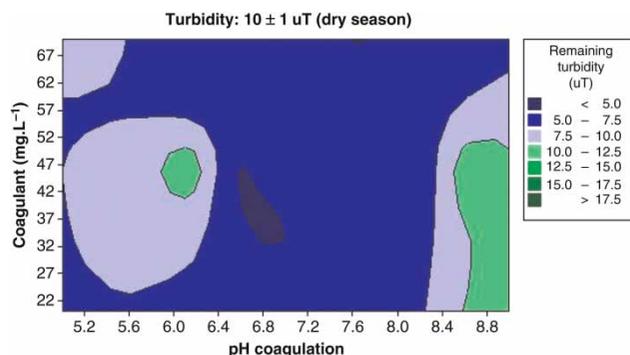


Figure 1 | Coagulation diagram (10 uT).

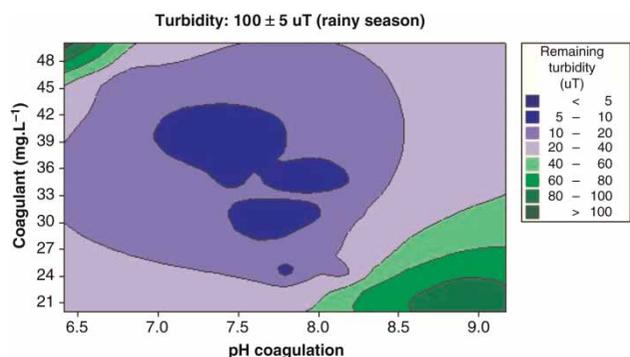


Figure 2 | Coagulation diagram (100 uT).

constructed and presented in Figures 1 and 2. Diagrams were constructed using response surface methodology (RSM), exploring the relation between the explanatory variables (coagulant dose and pH) and the response variable (turbidity). The main purpose of RSM is to use a sequence of experiments designed to obtain an optimal response. The concentration of coagulant corresponding to the lower values of turbidity (sweep area) remaining in the treated water was selected.

### Jar test and filtration

Table 3 shows the results for turbidity and apparent color removal obtained in the optimization trials. All results considered in this study met the standards for turbidity and apparent color, set forth in Brazilian legislation for the Ministry of Health for drinking water standards, in force at the time of the tests.

The results also found the turbidity standard in current Brazilian legislation (Ordinance of the Ministry of Health

Table 3 | Results for turbidity and apparent color removal

Sample	Collection point	Turbidity removal	Apparent color removal
Water – dry season	After decantation	>91%	>93%
	After filtration	>95%	>99%
Water – rainy season	After decantation	>66%	>71%
	After filtration	>97%	>98%

No. 2.914/2011) after the filtration step, thereby demonstrating that the treatment was effective in the removal of solids that confer color and turbidity to the waters.

### Analysis of removal of contaminants in the bench tests

Tables 4 and 5 present the medians and corresponding coefficients of variation of the percentage removal of contaminants obtained in the bench studies.

The higher values of CV presented in Tables 4 and 5 are due to the less accurate (TOC) analytical technique.

The highest removal efficiency of endosulfan, in relation to ETU and 1,2,4-triazole, can be attributed to the lower water solubility, higher  $K_{oc}$  and  $K_{ow}$  presented by the substance. More hydrophobic compounds showed higher removal in the coagulation–flocculation treatment, indicating that hydrophobicity is an important factor to be considered in pesticide removal from water.

Although hydrophobicity can explain the high removal of certain compounds, such as endosulfan, Alexander et al. (2012) reported that there was no discernible correlation between  $\text{Log } K_{ow}$  and trace organic contaminant removal, using the coagulation–flocculation process. This suggests that hydrophobicity is not the sole factor governing removal by coagulation, even for significantly hydrophobic compounds. It further implies that the usual method of coagulant selection, based on turbidity (suspended solids) removal, may not always be effective. Pre-coagulation has been found to enhance trace organic contaminant removal of advanced treatment processes, such as ozonation, active carbon adsorption, and nanofiltration (Alexander et al. 2012). This research focused largely on traditional coagulants, such as ferric and aluminum, which were not designed for the purpose of removing trace organic

**Table 4** | Median percentage removals of ETU in bench studies and their coefficients of variation (CV)

Water	Decanted						Filtered					
	Initial concentration (mg L <sup>-1</sup> ) <sup>a</sup>	0.1*	2	5	25	25**	50**	50	0.1*	2	5	25
Removal (%)	1–3	11	8	10	6	2	4	3–4	15	11	13	8
CV (%)	58–65	25	22	30	68	63	59	55–60	27	28	20	43

<sup>a</sup>Concentration measured by absorption at 232 nm, except \* (HPLC/UV-Vis) and \*\* (TOC, results in mgC L<sup>-1</sup>).

**Table 5** | Median percentage removals of endosulfan and 1,2,4-triazole in bench studies and their coefficients of variation (CV)

Contaminant sample	1,2,4-triazole <sup>a</sup>		Endosulfan (ES) <sup>b</sup>			
	Decanted water		Decanted water		Filtered water	
Initial concentration (mg L <sup>-1</sup> )	25	50	0.0005	0.002	0.0005	0.002
Removal (%)	18	8	54	11	68	46
CV (%)	42	68	40	28	16	17

<sup>a</sup>Measured by TOC, as mgC L<sup>-1</sup>.

<sup>b</sup>Measured by GC/MS-MS, mgES L<sup>-1</sup>.

contaminants. Therefore, the authors concluded that there is a potential to investigate the efficiency of new generation, high-performance coagulants for removing trace organic contaminants.

According to Table 1, endosulfan has low solubility, high molecular mass, high hydrophobicity (log  $K_{ow}$ ) and  $K_{oc}$ . ETU and 1,2,4-triazole, with lower  $K_{oc}$  values, showed maximum removal of 11 and 18%, respectively, in the decanted water.

Research developed by Thuy *et al.* (2008) evaluated the removal of four pesticides (aldrin, dieldrin, atrazine, and bentazone) from water, using coagulation–flocculation processes with different concentrations of aluminum sulfate (0–300 mg L<sup>-1</sup>) and contaminants (0.1–100 µg L<sup>-1</sup>) from distilled water and water from the River Dijle, in Belgium. The studies indicated removal of less than 50% for all compounds, under all conditions evaluated, and demonstrated that increased concentrations of coagulant had low or negligible effect. The studies carried out by Thuy *et al.* (2008) also showed lower efficiency for the experiments conducted with distilled water. The study indicated that removal of micro-pollutants using such treatments occurs due more to sorption in organic matter of the river water than due to the destabilization of the colloids, provided by the

coagulation–flocculation process. This conclusion regarding coagulants was confirmed by Ormad *et al.* (2008).

Studies conducted by Ormad *et al.* (2008) under conditions similar to this research, using conventional treatment, coagulant concentration of 40 mgAl L<sup>-1</sup>, initial concentration of 0.5 µg L<sup>-1</sup> endosulfan  $\alpha$ , liquid–liquid extraction, and analysis by GC/MS, showed 35% removal for this contaminant from decanted water.

Considering that conventional DWT is efficient in removing turbidity from water, and that this parameter is associated with suspended particulate material, this treatment technique helps to remove contaminants that have lower solubility in water and higher  $K_{oc}$ ,  $K_{ow}$ , and molar mass.

### Analysis of seasonal variation (type of water) in pesticide removal

In general, there was no evidence of difference in the percentage of contaminant removal in relation to the type of synthetic water. This fact is justified by the low adsorption of contaminants by kaolin.

A difference in the percentage of contaminant removal was only observed in relation to water turbidity ( $p < 0.05$ ),

in the case of the percentage of ETU removal in the decanted sample, analyzed by HPLC/UV-Visible.

### Analysis of influence of the initial concentration on the percentage of removal of the contaminants

For ETU, analyzed by HPLC/UV-Visible, there was a difference in the percentage of contaminant removal in relation to the type of water in the decanted sample. Therefore, the analysis to verify the difference, compared to the initial concentration, was carried out separately for each type of water. In the other cases (ETU analyzed spectrophotometrically; endosulfan analyzed by GC/MS-MS), the analysis was performed using the results obtained for the two types of water.

Table 6 shows statistical test results. It can be observed that the results obtained for the *p*-values were less than 5%, indicating that the percentage removal of contaminants (ETU and endosulfan) are different, in at least one initial concentration value. Therefore, the initial concentration of the tests interferes with the percentage removal of the contaminant from the sample. The percentage of pesticide removal was found to decrease corresponding to the increase of the initial concentration of pesticides. This finding agrees with that presented by Thuy *et al.* (2012).

As there were not enough data regarding the influence of seasonality for samples contaminated with ETU (25 mg L<sup>-1</sup>) and analyzed for TOC, only the low turbidity water (10 uT) was analyzed. The *p*-values obtained by the Kruskal–Wallis test, of the initial concentration of the contaminant for samples decanted and analyzed for TOC, were 0.0656 (1, 2, 4-triazole) and 0.0933 (ETU). Thus, the results obtained for the *p*-values in both cases were greater than 0.05, indicating

that the removal percentages of the contaminant are not different in relation to the initial concentration of 1,2,4-triazole and ETU in the samples, when analyzed for TOC, which is a less accurate analytical technique.

### CONCLUSIONS

The results obtained indicate that pesticide removal using the conventional DWT method, with aluminum sulfate as the coagulant, is not suitable and is being used with decreasing frequency in developed countries. The bench test results showed efficiency in removing suspended solids, according to the standards set forth in Brazilian legislation regarding drinking water and by the World Health Organization. However, the removal of the pesticides analyzed was not equal to the removal of solids that characterize turbidity and apparent color. Given the uncertainty surrounding the potential impacts of prolonged ingestion of trace organic contaminants on human health, it is vital that effective and sustainable treatment methods be utilized.

Therefore, it is essential that effective water treatment processes be employed to remove trace organic contaminants, thus ensuring that any potential risks to human health are mitigated prior to consumption. Consequently, until more suitable methods for water treatment are implanted, developing countries such as Brazil should restrict the use of soil in watersheds in which surface water is used for the public supply. These restrictions should include the prohibition of certain activities, such as agriculture, which require the intensive use of pesticides. In these watersheds, there should be greater conservation

**Table 6** | Mann–Whitney and Kruskal–Wallis test results for the analysis of interference of the initial concentration of the tests in the percentage removal of the contaminant

Contaminant	Test	Analysis	Sample collection	<i>p</i> -value
ETU	Kruskal–Wallis	Spectrophotometry/UV-Visible	Decanted	0.0060
			Filtered	0.0050
		Spectrophotometry/UV-Visible and HPLC/UV-Vis	Decanted <sup>a</sup>	0.0000
			Decanted <sup>b</sup>	0.0000
Endosulfan	Mann–Whitney	GC/MS-MS	Filtered	0.0122
			Decanted	0.0122

<sup>a</sup>With only 10 uT water for chromatography.

<sup>b</sup>With only 100 uT water for chromatography.

of riparian forests surrounding bodies of water, along with other conservation areas (hilltops, steep areas, etc.), established by legislation.

No significant influence ( $p < 0.05$ ) was observed using synthetic water prepared with kaolin for the rainy and dry season waters. However, the removal of pesticides decreases with higher initial concentrations of the contaminants.

Regarding the removal of contaminants, ETU and 1,2,4-triazole resulted in the lowest removal percentages (ETU: median  $\leq 11\%$  in decanted water and 1,2,4-triazole  $\leq 18\%$  in decanted water), as compared to endosulfan (median  $\leq 54\%$  in decanted water). This fact can be justified by the low solubility of endosulfan in water at 20 °C, with high  $K_{oc}$ ,  $K_{ow}$ , and molar mass, as compared to the other two pesticides. Therefore, the physico-chemical properties and hydrophobicity of the compounds are important factors to be considered regarding pesticide removal from water. However, it is necessary to make clear that hydrophobicity is not the sole factor governing the removal of trace organic contaminants by coagulation. This implies that the usual method of coagulant selection, based on turbidity (suspended solids) removal, may not always be effective for removing pesticides. Thus, there is potential to investigate the efficiency of new generation, high-performance coagulants for the removal of trace organic contaminants.

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