



## Research article

# Synthesis of EDTA-cysteine- $\beta$ -cyclodextrin for the removal of organophosphate flame retardants (OPFR) from sediments and soil samples from the Buffalo River Estuary, Eastern Cape of South Africa

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## ARTICLE INFO

## Keywords:

EDTA-Cysteine- $\beta$ -cyclodextrin  
Remediation  
Emerging contaminants  
Pollution

## ABSTRACT

Due to the growing water and environmental pollution worldwide, it is important to develop new effective materials for the remediation of sediments, soil and water contaminated with organic pollutants including flame retardants. In this study, a new soluble and hydrophilic polymer material containing ethylenediaminetetraacetic acid (EDTA), cysteine and beta cyclodextrin ( $\beta$ -CD) depicted as EDTA-Cysteine- $\beta$ -Cyclodextrin was prepared for the removal of organophosphate flame retardants (OPFRs) from simulated sediment and soil samples and those collected from the Buffalo River Estuary in East London, Eastern Cape Province of South Africa. The  $\beta$ -CD was modified using cysteine and EDTA. The EDTA-Cysteine- $\beta$ -Cyclodextrin was characterized by Fourier transform infrared (FTIR), scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDX). The results show that a non-porous spherical and bubble shaped material was synthesized. For the adsorption study, different contaminants' concentrations, solution pH, adsorbent dose and contact time were varied to ascertain the optimum conditions for the removal of OPFRs from soil and sediment. The removal of OPFRs was highly dependent on pH, adsorbent dose, concentration and contact time of the adsorption process. The optimum pH, contact time, OPFRs concentration and adsorbent dose were 3, 120 min, 60 mM and 5 mL, respectively with average adsorption percentage of  $97.13 \pm 14.04$  %. The results proved that this newly developed polymer can decontaminate sediments and soil. The EDTA-Cysteine- $\beta$ -Cyclodextrin gave promising possibilities for practical application for the remediation of OPFRs from sediment and soil samples through adsorption process.

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<https://doi.org/10.1016/j.heliyon.2024.e24951>

Received 2 May 2023; Received in revised form 17 January 2024; Accepted 17 January 2024

Available online 19 January 2024

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## 1. Introduction

Environmental and water pollution are the most serious challenges that humans are facing worldwide [1]. Each year, there is a drastic increase in the number of deaths or health related issues due to water and environmental pollution. Limited knowledge on the effects of toxic substances on the terrestrial and aquatic environment is one of the reasons for this drastic increase in pollution [2]. Industries, human activities and waste production are primary contributors to water and environmental pollution globally [1]. These can badly affect and harm biodiversity and aquatic ecosystems due to the discharge of partially treated pollutants in soil, air, and sediments and/or untreated water containing different pollutants. In South Africa, pollution is mostly influenced by effluents of domestic and industrial sewage. Furthermore, activities such as recreation, timber harvest and grazing have shown high potential on the effect of water and environmental pollution [2]. The long range transportation, condensation, volatilization, evaporation and condensation processes have led to the transfer of these pollutants into aquatic bodies [3].

OPFRs are among the most ubiquitous organic pollutants that appear in unacceptable high concentrations in the environment [4, 5]. Exposure to high level of OPFRs results in neurotoxicity and some show potential risk to cancer [6]. Hence, there is a need to prioritise the development of innovative remediation technologies/materials for these contaminants. Many methods have been previously developed for the removal of these pollutants but not all of them were successful. Cyclodextrin (CDs) are natural and non-toxic oligosaccharides that can form water soluble inclusions with poor lipophilic medicine, and they can be modified using different compounds depending on the physical and chemical properties of the contaminant [7]. The aim of developing these modified CDs was to make them nanosponge and nanoporous materials by using diverse bi-functional linking reagents that can be good in removing organic and inorganic pollutants and these modified CDs should be able to enhance affinity for these pollutants [7]. CDs are obtained easily and quickly in an extensive scale with low production cost and potential to be used in various applications [7,8]. Recently,  $\beta$ -CDs have been widely used since they have shown great potential for the removal and treatment of organic and inorganic pollutants.

Worthy of mention, different techniques have been employed for the removal of OPFRs from water, sediment and soil samples. These techniques include oxidation, adsorption, biological and reduction. Each technique possesses its advantage and disadvantage that have been discussed in the study of [9]. However in this study adsorption was employed since it is the most commendatory and efficient approach for the remediation of OPFRs. In addition, adsorption is a technique that has shown potential for OPFRs removal especially for hydrophobic OPFRs and adsorption helps understand the movement of OPFRs in an aqueous environment [9].

In this study  $\beta$ -cyclodextrin was used for the removal of OPFRs and it was modified using cysteine and EDTA (i.e. ethylenediaminetetraacetic acid). EDTA is a good chelating agent, its four carboxyl groups and two amino groups can be used as the binding sites of metal ions and it can form stable water soluble chelates with most of transition metal ions. Modified CDs have been developed to meet the satisfying results of contaminants removal [7]. The results from the study by Ref. [10] proved that aqueous hydroxypropyl- $\beta$ -cyclodextrin (HPCD) is a useful polymer that can be employed in assessing and removing phenyldecane from soil samples. The process of adsorption can be optimized by using different variables (e.g. pH, temperature, dose of the adsorbent, ionic strength and concentration) [7]. [11] developed a method through adsorption for concurrent analysis of different pollutants in sediments, whereby the results showed stronger adsorption and efficiency in eliminating pollutants from sediments. Another study by Ref. [12] reported the removal of OPFRs and heavy metals using microfiltration or reverse osmosis with 98 % and over 99 % removal efficiencies, respectively.

This study focuses on providing solutions to the water and environmental pollution problem that have become a major concern not only to government but also to the public worldwide, given their attendant health effects to humans and animals. In this work, we developed a new polymer (i.e. EDTA-Cysteine- $\beta$ -CD) composite for the removal of OPFRs (TDCP) in soil and sediments from Buffalo River Estuary, Eastern Cape, South Africa. This polymer is synthesized by the reaction of  $\beta$ -CDs with EDTA and cysteine in the presence of epichlorohydrin and potassium hydroxide. Therefore, to the best of our knowledge, this study will be the first to report on the synthesis of  $\beta$ -CDs modified by cysteine and EDTA for the remediation of OPFRs contaminated sediment and soil samples. In addition, different adsorption parameters including effect of pH, time, adsorbate concentration and adsorbent dose were assessed to determine the optimum conditions required for the removal of these contaminants from sediment and soil. Moreover, the optimum adsorption conditions were employed to six different real sediment and soil samples obtained from Buffalo River Estuary, Eastern Cape, South Africa for the removal of OPFRs.

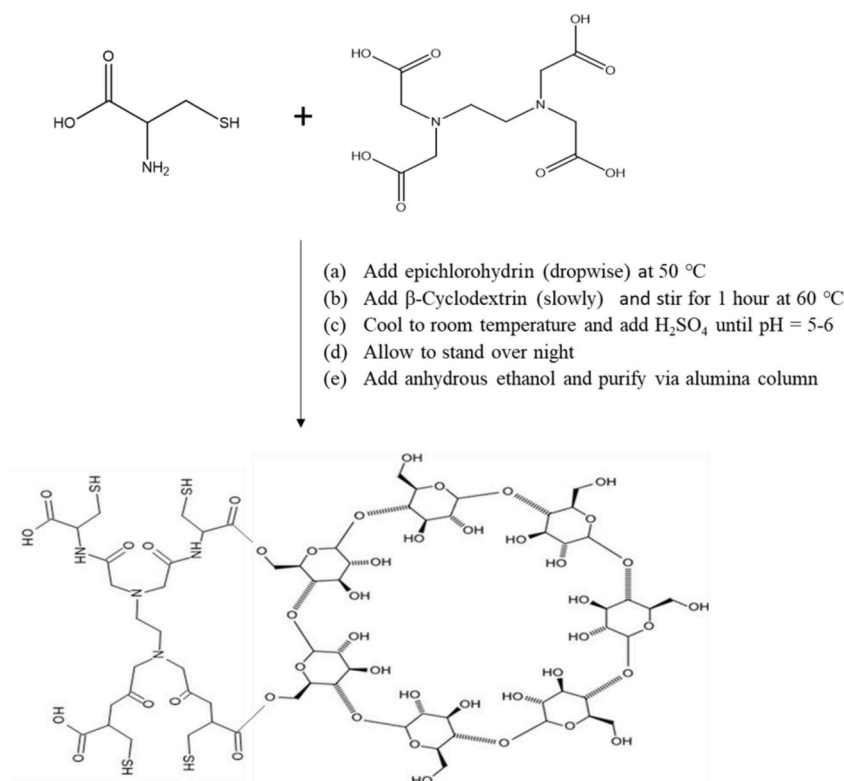
## 2. Experimental

### 2.1. Materials

$\beta$ -CD was procured from Sigma Aldrich (South Africa) with 99 % purity and was used without additional purification. L-Cysteine, ethylenediaminetetraacetic acid (EDTA), potassium hydroxide, pure sand (50–70 mesh particle size) and neutral alumina with 99 % purity were purchased from SAINS AGENCIES (South Africa) with purity of 99 %. Epichlorohydrin ( $d = 1.18 \text{ g/cm}^3$ ), sulfuric acid, ethanol and methanol were HPLC grade and procured from Sigma Aldrich (South Africa). OPFR standard (Tris (1,3-dichloro-2-propyl) phosphate (TDCP)) was purchased from Separations Pty Ltd, South Africa. Throughout the experiment, distilled water was used.

### 2.2. Synthesis of EDTA-Cystein- $\beta$ -cyclodextrin

The synthesis of EDTA-Cysteine- $\beta$ -Cyclodextrin with chemical formula  $\text{C}_{66}\text{H}_{27}\text{N}_4\text{O}_{45}\text{S}_4$  was carried out following the previously



**Fig. 1.** Summary of synthesis of EDTA-Cysteine-β-Cyclodextrin.

published method of [13] with slight modifications. In brief, 8.6 mL of epichlorohydrin was added dropwise to the solution mixture of cysteine (6 g) and EDTA (6 g) prepared in aqueous solution of potassium hydroxide pellets (6.7 g) in 70 mL of distilled water at 50 °C. β-CD (8.1 g) was then added to the solution in small portions while shaking. The mixture was then reacted and stirred for 1 h at 60 °C. After this step, the solution was cooled at room temperature and the pH was adjusted to 5–6 using sulfuric acid and left to stand overnight. The mixture was dehydrated using 150 mL of anhydrous ethanol and was purified through a column packed with glass-wool and neutral alumina. The 60 % v/v ethanol was used as flushing agent and was passed through a column three times. The produced effluent was left to stand for 5 h and the supernatant was discarded. About 100 mL of anhydrous methanol was added to the residue and a slight yellowish EDTA-Cysteine-β-Cyclodextrin precipitate obtained (see Fig. 1) was filtered and dried until further analysis. The structure of EDTA-Cysteine-β-Cyclodextrin, β-CD, EDTA and cysteine were characterised by FTIR, SEM and EDX.

### 2.3. Characterization

The synthesis of EDTA-Cystein-β-Cyclodextrin was confirmed using various characterization techniques such as FTIR, SEM, and EDX. FTIR was used for the confirmation of functional groups present in the structure of EDTA-Cystein-β-Cyclodextrin in comparison with pure β-CD, cysteine and EDTA. Whereas, SEM was used to determine the morphology of the materials and EDX was used to identify the elemental composition of EDTA-Cystein-β-Cyclodextrin.

### 2.4. Preparation of adsorbate solution

For standard preparation, pure TDCP (10 mg) standard powder procured from Separations Pty Ltd, South Africa was used in preparing the adsorbate (standard) solution (i.e. 120 µg/L). The stock solution of TDCP was prepared in Toluene: Acetone (70:30, v/v). TDCP (10 mg) was dissolved in 50 mL volumetric flask of 70:30 v/v of Toluene: Acetone and stored in the dark at –20 °C. The working standard mixtures (i.e. 60, 80, 120, 160, 240, 320, 480, 640, and 960 µg/L) were all then prepared by diluting the stock solution with Toluene: Acetone (70:30, v/v) in different volumes to the required concentrations employed for adsorption studies. The prepared concentrations were then all verified under quality assurance and adsorption studies.

### 2.5. Preparation of co-contaminated sediments and soil

Sediments and soil samples were collected from the Buffalo River Estuary using modified methods of [14,15]. Approximately one kilogram (1 kg) of sediment samples were collected using grab sampler from six selected anthropogenic points of the river water (0–10

cm depth) and were covered with aluminium foil. Whereas, soil samples (1 kg) were collected in a nearby dumpsite (Parkside) using stainless steel shovels and metallic spoon; and were covered with alumina foil. The samples (i.e. soil and sediments) were then placed in an ice chest and transported immediately to the laboratory for further analysis. Sediment and soil samples were kept in a dark room to avoid light exposure and they were air dried at room temperature. Portions of the samples were kept for moisture content analysis. Big stones and obvious debris were removed before drying the samples. When the samples were dry enough, they were crushed, blended, and homogenized using pestle and mortar. The samples were then sieved with 250  $\mu\text{m}$  stainless steel sieve and extracted by ultrasonicator. Samples were collected in duplicates from each sampling site throughout the two seasons for the year 2021 (i.e. winter: August and spring: October) in the Buffalo River Estuary, East London of South Africa. All the vials and glass apparatus were pre-cleaned and dried before use to avoid cross contamination. The OPFR-contaminated soil/sediment was prepared following the study of [16], where 1 g of soil or sediment was polluted with 60 mM of TDCP (OPFR standard) by incubating the sample with a solution containing the pollutant standard dissolved in 50 mL of methanol, then the samples were dried at 40  $^{\circ}\text{C}$  for 3 days.

## 2.6. Adsorption studies

Different parameters (i.e. pH, contact time, adsorbent dose and adsorbate concentration) were evaluated and put into consideration as part of the adsorption experiments of this study. Adsorption experiments were carried out using batch experiments by varying contact time, pH, adsorbent and adsorbent concentration using an orbital shaker with 50 mL brown glass bottles with lid (to avoid effect of light for the degradation of the standard) at 150 rpm. The adsorbent was separated from soil/sediment after each batch adsorption experiment by collecting it for further extraction using ultrasonic extraction method. Effect of pH on the adsorption studies was investigated using pH meter with calibrated glass electrode from pH 2 to 10 by adjusting the initial adsorbate solution to the preferred pH with 0.1 N sodium hydroxide (NaOH) or hydrochloric acid (HCl) solutions. Effect of time was monitored from 5 to 300 min. For the effect of adsorbate concentration, four different concentrations were assessed and three different volumes of the adsorbent were used, to determine which one would best remove the pollutants. To improve reproducibility and precision, each test was evaluated three times ( $n = 3$ ). The adsorption efficiency (% adsorbed) and specific adsorption capacity (mg/gm) were calculated using equations (1) and (2), respectively. In this study two crosslinkers (i.e. epichlorohydrin (EP) and EDTA) were used to improve the adsorption efficiency of the polymers as many published reports have highlighted their improved adsorption efficiencies upon their use.

$$\% \text{ adsorbed} = (C_i - C_{eq}/C_i) \times 100 \quad (1)$$

$$\text{Adsorption capacity (mg/gm)} = [(C_i - C_e)/m] * V \quad (2)$$

Where  $C_i$  is the initial concentration,  $C_{eq}$  denotes the final concentration,  $m$  denotes the mass of the adsorbent and  $V$  is the volume of the adsorbate.

## 2.7. Removal of TDCP from real soil and sediments from the Buffalo River estuary

The removal studies were done following the published study of [16]. In brief, 1 g of polluted sample was stirred with 5 mL aqueous solution of EDTA-Cysteine- $\beta$ -Cyclodextrin adjusted to pH 3 for 120 min at room temperature using orbital shaker, before extraction. After 120 min, the supernatant was separated from the residue and was further extracted using the ultrasonic extraction method as reported in section 2.8 of this study. The real sediments and soil were from selected sites in the Buffalo river estuary that were situated 200 m apart and they are namely: B1 (shallow end), B2 (downstream), B3 (second creek which is an industrial effluent and waste discharge), B4 (first creek and it's under the Steve Biko bridge), B5 (close to upstream under Buffalo bridge), B6 (upstream and is close to the ocean), and Bsoil (dumpsite next to Engine garage).

## 2.8. Sample pre-treatment, extraction and clean-up

The method of [17] was revised and modified after the recovery studies and used subsequently in this work. In brief, 4 g of sediment or soil was accurately weighed and spiked with 20  $\mu\text{L}$  of 16000  $\mu\text{g/L}$  surrogate standard (1-Bromo-2-Nitrobenzene) prepared in appropriate amount of acetone. The samples were extracted using an ultrasonicator for 10 min at 40  $^{\circ}\text{C}$  with 1:1, v/v of Hexane: Acetone. The samples were sequentially extracted three times. After each extraction cycle, the sediment or soil extracts were centrifuged at 3500 rpm for 2 min and the supernatants were collected and transferred into clean glass tubes. The pooled supernatants were evaporated until dryness under a gentle stream of nitrogen using rotary evaporator and re-dissolved into 1 mL of Hexane. The re-dissolved extracts were subjected to SPE cleanup, where cartridges were conditioned with 6 mL of hexane and the extracts were eluted using 8 mL of hexane and 10 mL of ethyl acetate. The extracts were then evaporated until dryness in a rotary evaporator under a gentle stream of nitrogen and reconstituted in 1 mL of iso-octane.

## 2.9. Quality control and quality assurance

All the glass apparatus that were used were cleaned using tap water and soap, afterwards were washed with clean tap and distilled water successively. The glass apparatus were successively dried in an oven, cooled, and cleaned using acetone. Quality assurance was observed by the analysis of the levels of the selected OPFRs congeners/analytes in the laboratory blanks, and matrix spikes. Quality

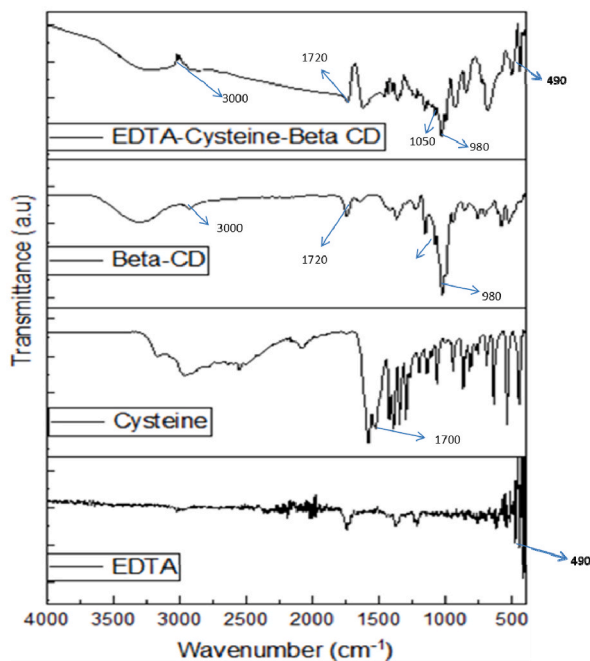


Fig. 2. FTIR spectra of EDTA-cysteine- $\beta$ -CD, EDTA, cysteine and  $\beta$ -CD.

control was accomplished by recovery studies during sample analysis where OPFRs standard mixture (1280  $\mu\text{g/L}$ ) of the target analytes and surrogate standard was spiked into the pure sand procured from Sains Agencies (50–70 mesh particle size) to check for the recovered concentration of the analytes, and blank control samples were run for each batch of samples. The extraction of the spiked sediment/soil was conducted as mentioned under section 2.8. Sample measurements were corrected by subtracting the levels measured in the laboratory blanks [5]. Linear calibration curves were constructed using external standard solutions in the range of 60–1280  $\mu\text{g/L}$  (9 points' curve). Correlation coefficients obtained for the calibration curves of the standards were in the range of 0.988–0.9938. The recoveries obtained for the targeted analytes during QA studies were in the range of 56.57%–90.68%. The LOQ and LOD were calculated by  $10*(\text{Sy/S})$  and  $3.3*(\text{Sy/S})$ , respectively [18], where Sy stands for standard deviation of the instrument's response to the target analytes, and S for slope from the linear regression of each analyte's calibration curve. The GC syringe was pre and post washed 3 times with acetone and n-hexane to avoid cross contamination during instrumental analysis.

### 2.10. Gas chromatograph analysis and condition

The OPFRs were studied using Agilent 7820A gas chromatography coupled with micro electron capture detector (GC- $\mu\text{ECD}$ ), with an Agilent 19091J-413: 1 HP-5 (30 m length x 320  $\mu\text{m}$  diameter x 0.25  $\mu\text{m}$  film) column for separation of analytes. The oven temperature was initially set at 80  $^{\circ}\text{C}$ , then raised to 160  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C}/\text{min}$ , and finally to 265  $^{\circ}\text{C}$  at 3  $^{\circ}\text{C}/\text{min}$ . The maximum temperature was set at 300  $^{\circ}\text{C}$  and the analysis ran for 61 min. Helium was used as a carrier gas with a flow rate of 1.543 mL/min. The injection volume was 1  $\mu\text{L}$  in pulsed splitless mode. Front inlet was used with GC- $\mu\text{ECD}$  at a pressure of 58.82 kPa, flow rate was 1.5 mL/min and the make-up gas (nitrogen) was flowing at 10 mL/min [19].

### 2.11. Data analysis

All data obtained from this study were analyzed using Origin statistical software version 2.0.

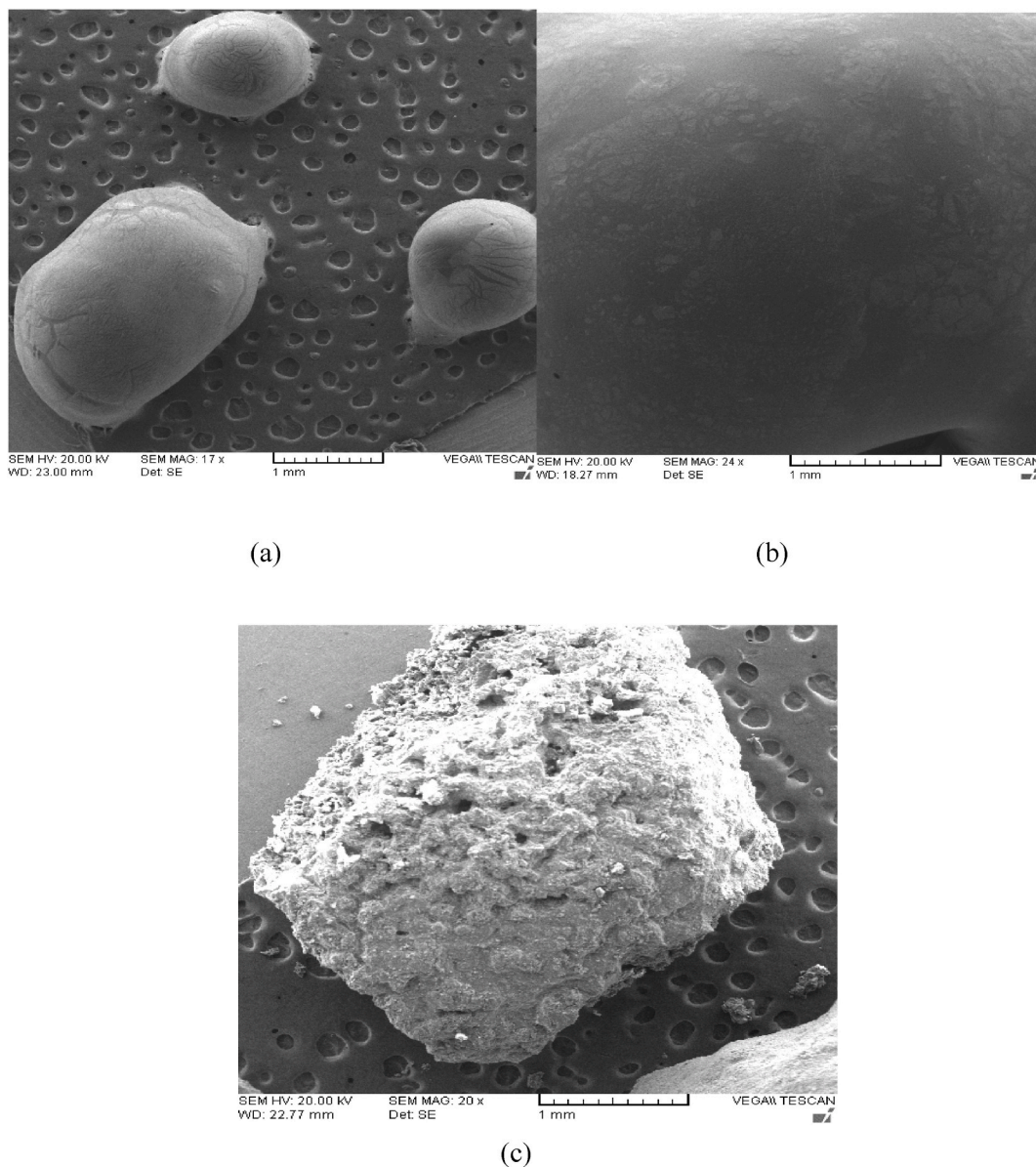
## 3. Results and discussion

### 3.1. Characterization of EDTA-cysteine- $\beta$ -cyclodextrin

#### a) FTIR analysis

The FTIR spectra of pure EDTA, cysteine and  $\beta$ -CD in comparison to EDTA-Cysteine- $\beta$ -Cyclodextrin for the evaluation of the success in the synthesis of the polymer material are shown in Fig. 2. The FTIR spectra of EDTA-Cysteine- $\beta$ -Cyclodextrin resemble some of the peaks from FTIR spectra of the precursor compounds. Most of the characteristic vibrational peaks of  $\beta$ -CD at 700, 980, 1050, 1720 and 3000  $\text{cm}^{-1}$  are also found in the spectra of EDTA-Cysteine- $\beta$ -Cyclodextrin, which is an indication that  $\beta$ -CD was well maintained in the



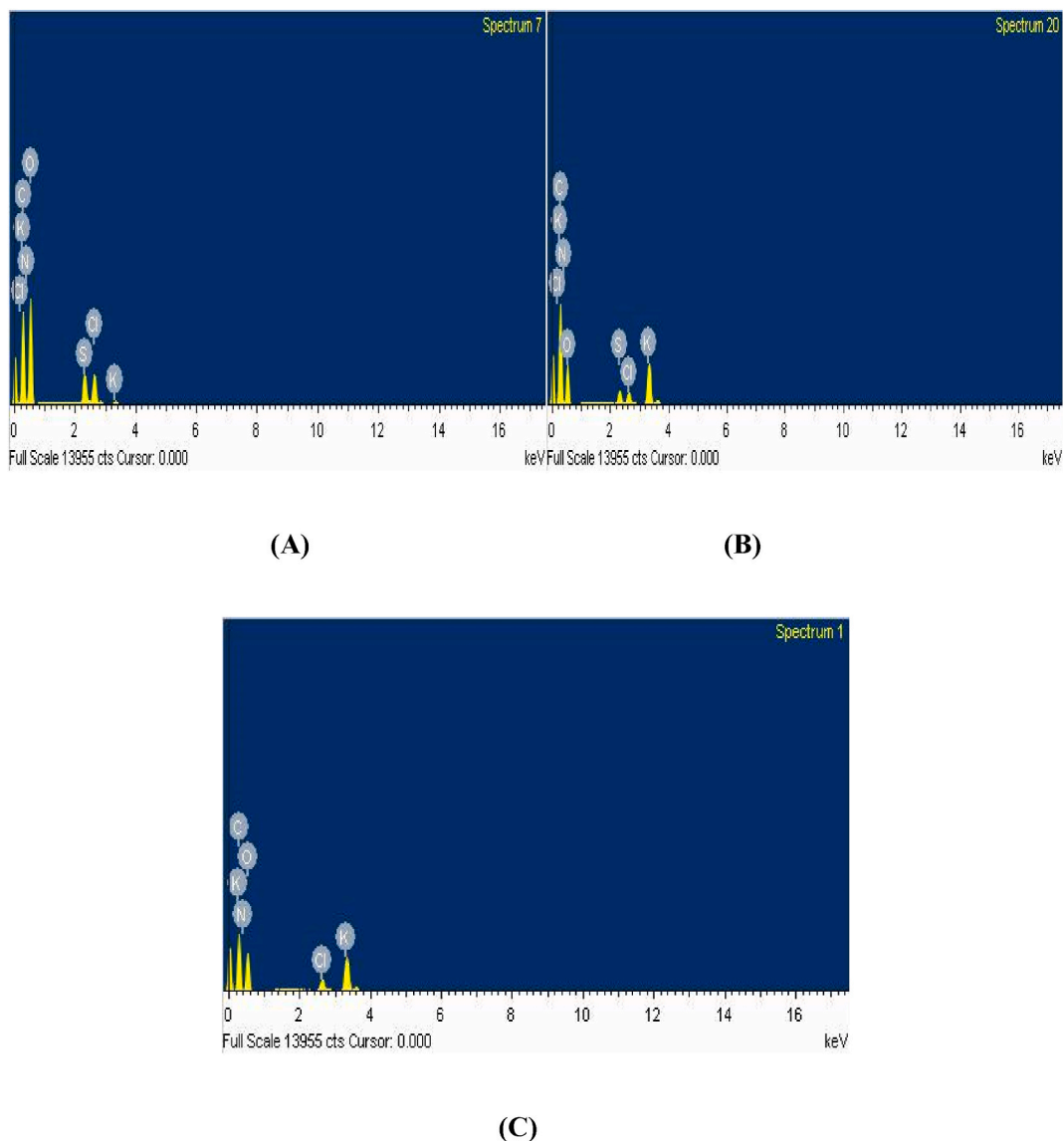


**Fig. 3.** (a–c). SEM images for (a) EDTA- $\beta$ -CD, (b) EDTA-Cysteine- $\beta$ -Cyclodextrin and (c) Cysteine- $\beta$ -CD.

EDTA-Cysteine- $\beta$ -Cyclodextrin molecule [13]. Some adsorption peaks of cysteine and EDTA were also observed at around  $1700$  and  $490$   $\text{cm}^{-1}$ , respectively; explaining that there are traces of these compounds in the EDTA-Cysteine- $\beta$ -Cyclodextrin material. The FTIR spectra for EDTA-Cysteine- $\beta$ -Cyclodextrin shows a sharp peak at  $3000$   $\text{cm}^{-1}$  an indication of the presence of C–H group, also the peak at  $1720$   $\text{cm}^{-1}$  indicates the presence of  $\text{C}=\text{O}$  ascribed to carboxyl group on the material. The peak at  $1600$   $\text{cm}^{-1}$  shows the presence of  $\text{C}=\text{C}$  as well as carbonyl group. The peaks at  $1050$  and  $980$   $\text{cm}^{-1}$  represents alkoxy and epoxy group, respectively. These results are similar to previously published reports on the FTIR spectra of these types of material [13].

#### b) SEM analysis

Fig. 3(a–c) shows the morphology of EDTA-cysteine- $\beta$ -Cyclodextrin, EDTA- $\beta$ -CD and Cysteine- $\beta$ -CD at 1 mm. The morphology of EDTA- $\beta$ -CD show spherical/bubble shapes with lines that are joined together popping on top of a fine, flat surface with holes. The flat surface with holes might indicate the presence of  $\beta$ -CD in the material. The morphology of Cysteine- $\beta$ -CD shows rough and packed crystals. The packed crystals are uneven, which conforms the texture of cysteine that is moderate salt like. EDTA-cysteine- $\beta$ -Cyclodextrin demonstrates the formation of a spherical/bubble shape and a fine surface with uneven shapes. The EDTA-cysteine- $\beta$ -Cyclodextrin demonstrates a non-porous structure, and it is made up of a single crystal with different sizes of separating mapped images on



**Fig. 4.** (A–C). EDX spectrums for (A) Cystein- $\beta$ -CD, (B) EDTA-Cystein- $\beta$ -Cyclodextrin and (C) EDTA-  $\beta$ -CD.

the outside. That might be the representation of mixing different textural materials. EDTA-cysteine- $\beta$ -Cyclodextrin indicates the presence of EDTA and cysteine.

### c) EDX analysis

The EDX images of Cysteine- $\beta$ -CD, EDTA-Cysteine- $\beta$ -CD and EDTA- $\beta$ -CD are shown in Fig. 4 (A-C). All of these different materials were able to show the synthesized composite under EDX spectrum. The spectrum shows the elemental composition of the compounds and confirmed the presence of cysteine and EDTA. The attained peaks for EDTA-Cysteine- $\beta$ -CD corresponded to elements C, N, O, S, Cl and K with atomic percentage of 63.46 %, 5.01 %, 27.26 %, 0.73 %, 0.72 % and 2.73 %, respectively. The peaks for EDTA- $\beta$ -CD corresponded to elements C, N, O, Cl and K with 54.21 %, 5.32 %, 36.22 %, 0.94 % and 3.31 % atomic percentage, respectively. Similarly, the peaks for Cysteine- $\beta$ -CD corresponded to elements C, N, O, S, Cl and K with 53.98 %, 5.58 %, 38.03 %, 1.09 %, 1.21 % and 0.11 %, respectively.

### 3.2. Adsorption studies

The efficiency of the adsorbent for the removal of TDCP (OPFR congener) from sediments and soil was confirmed by conducting batch adsorption experiments where different parameters (i.e. pH, contact time, adsorbate concentration and adsorbent dosage) were

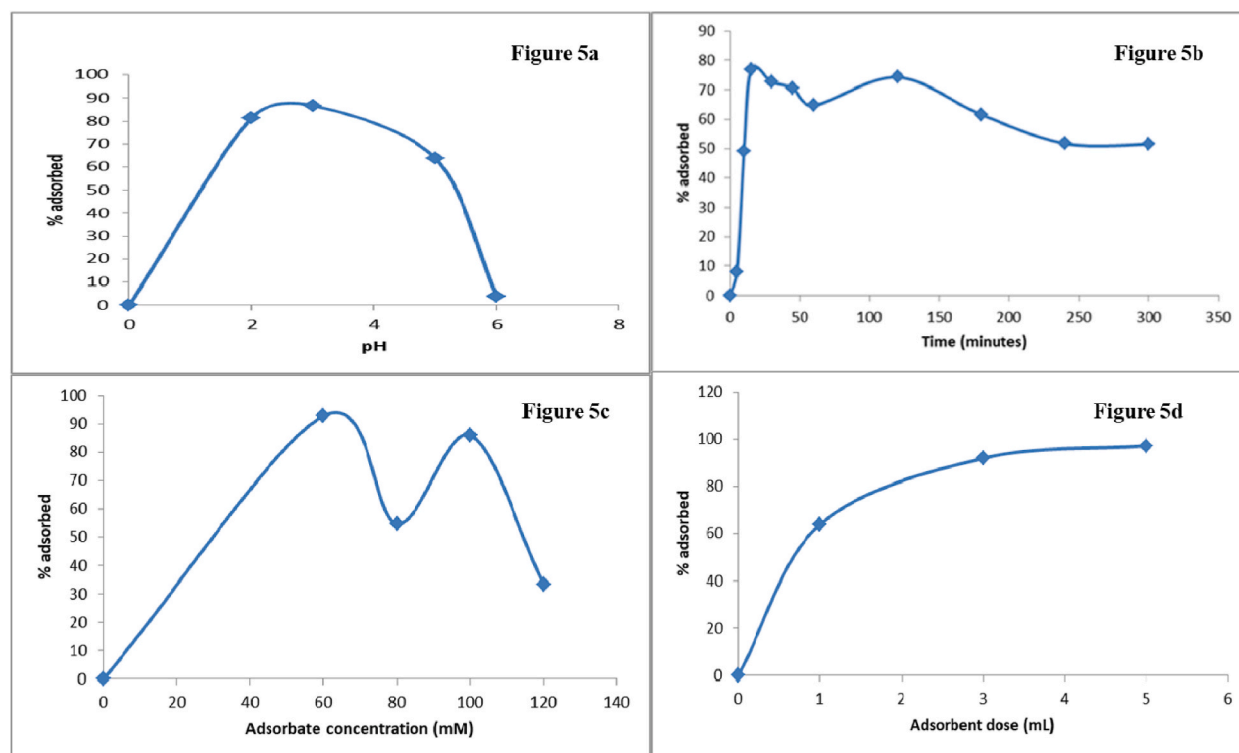


Fig. 5a–d. The removal of TDCP congener from simulated sediment samples.

evaluated in order to obtain the best conditions for the removal of TDCP from sediments and soil as shown in Fig. 5a–d below.

### 3.2.1. Effect of pH

The pH effect was investigated in the adsorption studies of TDCP from the solution at room temperature, 150 rpm and 5 mL of the 10 mM adsorbate concentration from pH 2 to 6 as shown in Fig. 5a. The optimum removal efficiency of TDCP was obtained at low pH. When the pH was increased from pH 7 to 10, the efficiency of removal started decreasing. Optimum pH was obtained at 3 and this pH was used throughout the experiments in this study. This pH was slightly above the point of zero charge to avoid like charge repulsion that might have resulted to pH values below the point of zero charge. The pH is indirectly proportional to removal efficiency, thus implying that at high pH there is more specific surface energy that needs to be reduced in order to increase the removal efficiency and also at high pH, the surface of EDTA-cysteine- $\beta$ -CD became more negatively charged. At low pH the analyte (TDCP) loses  $\text{Cl}^-$  and becomes positive, whereas the adsorbent loses  $\text{H}^+$  to become negative then the negative attacks the  $\text{CH}_2$  to form an ester bond [20]. It is worthy of mention that adsorption capacity of the adsorbent at low pH is positive. This pH trend is supported on the study of [21], where in their study they explained using the zeta potential and they discovered that the zeta potential of the adsorbent decreased with pH increase and at low pH the zeta potential of the adsorbent is positive.

### 3.2.2. Effect of time

Time plays a major role in adsorption studies. In this study, effect of time was monitored at different instances from 5 to 300 min for different samples as shown in Fig. 5b. The removal efficiency was consistent and noticeable in the first 15 min, after which it started decreasing at 30 min and further attained equilibrium until 300 min. The adsorption was at its maximum at 15 min with % adsorption of 76.95 %, for subsequent adsorption experiments, the time used was 120 min since after 15 min there was a decrease in adsorption efficiency, and it is important to be sure that TDCP was completely removed. The highest adsorption capacity was observed at 15 min with 2.36 mg/g, and at 120 min (time used for adsorption studies) it was 2.28 mg/g proving the adsorption efficiency of this polymer.

### 3.2.3. Effect of adsorbate concentration

The effect of adsorbate concentration is shown in Fig. 5c. Concentration was varied from 60 mM to 120 mM, and the optimum value was obtained at the lowest concentration of 60 mM. When the concentration was increased, there was a sharp decrease and then increase in adsorption efficiency and adsorption capacity (4.600–1.652 mg/g) of the material, as adsorption and desorption was noticed to have taken place showing that initial adsorbate concentration has little effect on the removal of this contaminant from sediment samples. The reason for this observation could be ascribed to the absence of more active sites on the surface of the adsorbent for the uptake of this contaminant in solution at 80 mM concentration. Similar results was also reported by Ref. [22]. Hence, 60 mM



**Table 1**Initial and final concentration of TDCP removal from sediments and soil from the Buffalo River Estuary after adsorption with EDTA-cysteine- $\beta$ -CD.

TDCP	B1	B2	B3	B4	B5	B6	BSoil
$C_i$ (mM)	60.60	60	61.08	60	60	60	60
$C_f$ (mM)	ND	18.56	33.06	35.01	ND	ND	25.17
% adsorbed	100 $\pm$ 23.68	69.07 $\pm$ 7.73	45.87 $\pm$ 3.22	49.98 $\pm$ 1.27	100 $\pm$ 16.80	100 $\pm$ 18.00	58.05 $\pm$ 4.54

$C_i$ : Initial concentration and  $C_f$ : Final concentration.

was used throughout the adsorption studies.

### 3.2.4. Effect of adsorbent dosage

The effect of adsorbent dosage is one of the most important parameters to consider for the removal of pollutants from sediments. The removal efficiency increases with increasing amount of the adsorbent as shown in Fig. 5d. That can be explained since during adsorption experiments, there are more sites that are active on the adsorbent and available for adsorption, hence there was an increase in the adsorption efficiency when the dose of the adsorbent was increased.

### 3.3. Adsorption isotherms

The adsorption data of this study were fitted into three different types of isotherms (i.e. Temkin, Freundlich and Langmuir isotherm) as shown in equations (3)–(5) respectively.

$$q_e = B \ln K_T + B \ln c_e \quad (3)$$

$$\log q_e = \log K_F + (1/n) \log c_e \quad (4)$$

$$(1/q_e) = (1/K_L q_{\max}) (1/c_e) + (1/q_{\max}) \quad (5)$$

Where:  $q_e$  (mg/g) is the adsorption capacity,  $q_{\max}$  (mg/g) denotes maximum adsorption capacity,  $K_L$  (L/mg) is Langmuir constant,  $K_F$  [(mg/g)(L/mg) $^{1/n}$ ] is the Freundlich constant and  $n$  is the heterogeneity factor meanwhile  $c_e$  denotes the pollutant's concentration at equilibrium,  $B$  (Jmol $^{-1}$ ) is the Temkin constant and  $K_T$  (Lg $^{-1}$ ). Parameters of Temkin isotherm were determined by plotting a graph of  $q_e$  vs  $\ln c_e$ . The parameters of Freundlich isotherm were determined by plotting linear graph of  $\log q_e$  vs  $\log c_e$  and Langmuir isotherm parameters were determined by plotting a graph of  $1/q_e$  vs  $1/c_e$ . The adsorption isotherms of TDCP were compared, and they proved higher adsorbed amount of TDCP by the polymer. It was observed the adsorbed amounts of TDCP increased with their increasing log  $K_{OW}$ . The Freundlich isotherm  $n$  values ranged from 1.98 to 5.85 proving that all adsorption isotherms are non-linear. The H-bonding and hydrophobic interactions between adsorbent and adsorbate molecules in the adsorption process may be the main reasons for the nonlinearity.

### 3.4. Removal of TDCP from sediments and soil of the Buffalo River estuary using EDTA-Cystein- $\beta$ -CD

The Buffalo River Estuary is a contaminated estuary and it was proven by the previous published studies conducted in this area by Refs. [23–26]. The concentrations of TDCP were significantly higher in the study area, which is an indication that these pollutants were more used and there was more application of materials containing these OPFRs (i.e. soaps, organic compounds and detergents) [27, 28]. This high concentration of TDCP that was recovered and removed in this study could also indicate that there were more amounts of these OPFR congener entering domestic sewage in that river [28]. The high levels of OPFRs obtained in this study confirmed the previous reports about the gross pollution of the study site. The removal experiments in soil and sediments were performed at pH 3, 60 mM concentration using 5 mL of 5 % EDTA-Cystein- $\beta$ -CD solution for 120 min. Table 1 shows the results obtained after the removal experiments with a total average of 92.98  $\pm$  14.04 % adsorption efficiency in the sediments and 58.05  $\pm$  4.54 % in the soil samples. Significant TDCP removal was obtained at 100 % from point B1 (100  $\pm$  23.68 %), B5 (100  $\pm$  16.80 %) and B6 (100  $\pm$  18.00 %) whereas, the lowest adsorption efficiency was obtained at B3 (second creek) and B4 (first creek) with 45.87  $\pm$  3.22 % and 49.98  $\pm$  1.27 %, respectively. The significant removal of TDCP from point B1, B5 and B6 may explain that there was not much of this OPFR congener in these points from soil or sediments and there was probably a dilution of this OPFR pollutant due to high consumption of water in the river [28]. In point B3 and B4 this low removal of TDCP concentration might be linked to the historical contamination of the first creek and second creek. And the results from point B3 and B4 prove extensively high concentrations that were recorded from these points and they indicate primary pollution route from industrial activities and discharge of domestic waste containing these pollutants. Similar routes of contamination from creeks have been reported in previous studies [29]. The degree of pollution always depends on the amount of pollutant input from the surroundings [30]. B2 had a moderate adsorption efficiency of 69.07  $\pm$  7.23 %. The removal is not the same from the entire estuary due to the physical and chemical properties of the sediment found in that area. The results obtained in this study have been compared with other previously published reports on the removal of OPFRs from sediment/soil as shown in Table 2. It can be observed from Table 2 that the material synthesized in this study compared favourably with other materials previously reported for the removal of OPFRs in soil, indicating that this material can serve as alternate new material to the already established materials for the removal of this type of contaminant from soil and sediment.

**Table 2**

Comparison of the result obtained in this study for the removal of TDCP in sediments to other results previously reported in literature.

Location	Matrix	Congener	Range (% adsorbed)	References
South Africa	Sediments and Soil	TDCP	45.87 ± 3.22 % to 100 ± 23.68 % and 58.05 ± 4.54 %	This study
China	Soil	14 OPFRs	57.9 ± 38 % to 63.8 ± 5.6 %	[13]
China	Soil	TCrP	82.28 ± 7.8 %	[31]
		TCEP	48.37 ± 9.52 %	
		TCPP	63.76 ± 10.25 %	

#### 4. Conclusion

In this study EDTA-Cysteine- $\beta$ -CD was successfully synthesized and application for TDCP (OPFR congener) removal from soil and sediments were investigated. The results obtained in this study showed that OPFRs can be removed from sediments and soil by the newly developed soluble and hydrophilic EDTA-cysteine- $\beta$ -CD material. The synthesized polymer was found to be efficient sorbent for TDCP. The characterization of the adsorbent proved that this material was successfully synthesized and it was of high purity as there were no unwanted elements in the EDX spectra. In this study EDTA was chemically grafted into the adsorbent to improve the performance of the adsorbent. Available information on the removal of OPFRs as emerging pollutants is very scarce, but the findings in this study were compared to other studies as tabulated in Table 2. Adsorption experiments that were done considering different parameters proved to be pH dependent and low pH are a promoting factor to this study. This newly developed method is simple, natural and inexpensive. With more development and new testing in all OPFRs congeners, the use of EDTA-cysteine- $\beta$ -CD could be an effective and a non-toxic way of remediating sediments and soil contaminated with OPFRs. This study is the first documented evidence aimed at evaluating organophosphate flame retardants in the Buffalo River Estuary and a nearby dumpsite; as well as synthesizing a compound (EDTA-cysteine- $\beta$ -CD) for its possible remediation. The results of this study are an indication of excellent adsorptive properties of EDTA-cysteine- $\beta$ -CD for the removal of TDCP from soil and sediments. Hence, this chemically modified non-porous polymer will be further explored for its effectiveness in removing other OPFR congeners in future.

#### Funding acquisition

The research was funded by South African Medical Research Council (grant number: UFH/SAMRC/P790).

#### Institutional review board statement

Not applicable.

#### Informed consent statement

Not applicable.

#### Data availability statement

Data will be made available upon request.

#### CRedit authorship contribution statement

**Sinozuko Hope Bika:** Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Formal analysis, Data curation. **Abiodun Olagoke Adeniji:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Mike Onyewehelehi Ojemaye:** Writing – review & editing, Conceptualization. **Elsiddig Ahmed Elmustafa Elsheikh:** Writing – review & editing, Conceptualization. **Brilliance Onyinyechi Anyanwu:** Writing – review & editing, Conceptualization. **Anthony Ifeanyi Okoh:** Writing – review & editing, Funding acquisition, Conceptualization. **Omobola Oluranti Okoh:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization.

#### Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Anthony Ifeanyi Okoh reports financial support was provided by South African Medical Research Council.

#### Acknowledgements

Special thanks to the South African Medical Research Council, National Research Foundation (NRF/RAVAC) of South Africa, and Sasol Trust Fund, South Africa for financial support. We're also grateful to the University of Sharjah for the platform to actualize some

aspects of this study.

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