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EDTA Enhanced Thermal Washing of Contaminated Dredged Marine Sediments for Heavy Metal Removal

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Abstract

Preliminary analysis on dredged marine sediments from Benoi basin in Singapore was carried out showing elevated concentrations of Zn, Cu, Pb, Cd, Cr and Ni. EDTA thermal washing experiments were conducted for heavy metal extraction at temperature 100 °C. Results indicated the significant efficiency of thermal washing to extract Pb, Zn and Ni. However, there was little or no influence in the removal of Cu and Cr, and slightly effect to Cd indicating multiple mechanisms. In addition, agitation was found to have great influence on the removal efficiency of heavy metals as experiments without agitation performed lesser or no extraction due to limited contact of the washing solution and the dredged sediment. Sequencing processes of thermal treatment followed by EDTA washing showed limited performance, likely due to thermal stabilization of the contaminants particularly at low L/S ratio. Furthermore, sequential extraction analysis on the metal speciation was performed before and after thermal washing. It was revealed that metals mainly extracted from fractions bound to carbonates and Fe-Mn oxides, the relative mobile fraction. On the contrary, metals in the residual fraction displayed a considerable stability.

Keywords: Heavy metals removal; thermal washing; EDTA; thermal treatment; sequential extraction analysis.

1. Introduction

Contamination of marine sediments is usually occurred through shipyards, ships and industrial activities near the coast. Marine sediments are often rich in heavy metals due to heavy metals accumulation and resistivity to biodegradation. However, the periodic change of the

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physicochemical properties of seawater conditions could release metals making them available to living organisms (Peng et al. 2009). In addition, heavy metals presence in sediments frequently possesses significant toxic potential to aquatic organisms that can harm human health through food chain via bioaccumulation and biomagnification. It has been estimated that 10% of marine and estuarine sediments in industrialized countries are harmful to the aquatic organisms (Colacicco et al. 2010).

Two approaches are principally adopted for the remediation of contaminated sediments, namely immobilization of the contaminants within the solid matrix and extraction/separation of contaminants from different sediment fractions (Peters 1999). Although immobilization techniques are currently more reliable and generally involve lower remediation costs, extraction/separation methods have the advantage that contaminant concentrations could be reduced to below regulatory limits and the treated material might be suitable for reuse with positive environmental and economic outcomes (Meegoda and Perera 2001). In these methods, contaminants are extracted and transferred from sediments to washing solution. Since water is ineffective washing solution to extract sorbed contaminants from the sediments, other chemical agents (acids, bases, salts, oxidizing or reducing agents, chelating agents, surfactants and solvents) are usually involved to promote the overall extraction efficiency (Giannis et al. 2009; Nowack and VanBriesen, 2005; Polettini et al. 2009; Tsang et al. 2012; Yuan et al., 2010). It is suggested that an ideal chemical agent would interact very weakly with the solid matrix as compared to the target contaminants, and it would increase the solubility and mobility of the target contaminants (Vulava et al. 2000). In this regards, chelating agents such as ethylenediamine tetraacetic acid (EDTA) have been widely studied and exhibited excellent extraction efficiency of metals with less impact (Di Palma and Mecozzi 2007; Shahid et al. 2013). More recently, biodegradable chelating agents such as ethylenediamine disuccinic acid (EDDS) and nitrilotriacetic acid (NTA) have been investigated for their heavy metal extraction efficiency from soil and sediments aiming to more environmental friendly treatments (Harley et al. 2014; Pinto et al. 2013). However, their biodegradable nature was strongly depended on the ambient conditions (Vandevivere et al. 2001a, b). Regarding EDTA, Tiedje (1975) has reported its biodegradability in soil and sediments under aerobic conditions in mixed culture microorganisms.

For the selection of chelating agents as washing solution, multiple factors has to be considered such as cost, efficiency, availability, regulations, and etc.

Thermal process employs the combination of heat and chemical solution to activate reactions through dissolution and desorption (Zhang and Itoh 2006). It implies that solid particles would be eroded and/or destructed under certain temperature, leading to a direct desorption of heavy metals along with other minerals and eventually to chemical reaction with washing solution. The application of the thermal washing process in extraction of heavy metals from sediments has not been widely reported. However, very few studies have been carried out on removal of heavy metals from incinerated fly ash using a thermal process (Bayuseno et al. 2009; Hu et al. 2012; Zhang and Itoh 2006). The effect of thermal washing on heavy metals is yet inconclusive, as heavy metals could either be stabilized due to solidification or chemical fixation (Bayuseno et al. 2009; Jin et al. 2012; Jing et al. 2010; Singer and Berkgaut 1995), or mobilized by the thermal process (Appels et al. 2010). The controversial results could be due to differences in the thermal washing methods that were employed, different nature of the applied wastes, and the addition of various chemicals as well as the method used to determine the stability of heavy metals.

The purpose of this study was to apply a novel thermal washing process in order to extract heavy metals from contaminated sediments. EDTA was selected due to its relatively high thermal resistance (Chen et al. 2006), the high affiliation to extract heavy metals, and the wide application (Leštan et al. 2008). In order to address the issues mentioned above, different conditions on thermal washing processes was applied to identify the impacts on heavy metals removal, and to provide useful reference for practical application of the process in large scale.

2. Materials and Methods

2.1. Sediments sampling and characterization

Dredged marine sediment was originated from the Benoi Basin, a dock located in the industrial zone called the Tuas district (Singapore). The marine sediment was dredged from the sea at a depth of 4 m. Then it was immediately stored at 4 °C until experiments were carried out to prevent potential biodegradation of the organic matter. After homogenization, the

physicochemical properties were measured including particle size distribution, total organic content, pH, heavy metal content and speciation.

Organic matter content was obtained by calculating the difference in weight between dried sediments at 105 °C and combusted sediments at 550 °C for 4 h (ASTM D2974). 30 mL of de-ionized water were added to 15 g of sediments and stirred continuously for 5 minutes. It was then allowed to settle for 15 minutes, and the pH measurements were taken in the supernatant (ASTM D4972). Particle size distribution was determined using a particle size analyser (Malvern Mastersizer 2000, UK). Oven-dried sediment was first crushed before analysis. Metal content was determined according to USEPA3052 method. 8 mL of concentrated nitric acid and 1 mL of hydrogen peroxide were added to 0.1 g of dried sediments in a polymeric microwave digestion tube. The microwave digester was set to 200 °C for 30 min to digest the sediments. After digestion, samples were filtered through 0.45 µm PTFE syringe filters and then topped up with de-ionized water to 50 mL. Heavy metals concentration was determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).

2.2. Sequential extraction analysis

Metal extraction efficiency is highly associated with the metal speciation in the sediment. To determine metal speciation, a five-step sequential extraction procedure modified from Tessier et al. (1979) was carried out. In the extraction procedures, 1 g of the sample was used. The sample was exposed to reagents and agitated. Each fraction was separated from the supernatant by centrifugation at 10,000 rpm for 30 minutes. The supernatant was filtered through a 0.45 µm PTFE syringe filter before further analysis. The solids left behind were used for the following step.

The exchangeable fraction was determined by extraction with 8 mL of 1.0 M sodium acetate (NaOAc) at pH 8.2 for 1 hour under continuous agitation condition. The fraction bound to carbonates was determined by extraction with 8 mL of 1M NaOAc adjusted to pH 5 with acetic acid for 5 hours with continuous agitation. The fraction bound to Fe-Mn oxides was determined by extraction with 20 mL of 0.04 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ dissolved in 25% (v/v) HOAc for 6 hours at

96° C with occasional agitation. The fraction bound to organic matter was determined after extraction with 3 mL of 0.02 M HNO₃ and 5 mL of 30% H₂O₂ adjusted to pH at 2 with HNO₃ for 2 hours at 85 °C with occasional agitation, followed by 3 mL of 30% H₂O₂ adjusted to pH 2 with HNO₃ for 3 hours at 85 °C with intermittent agitation and then 5 mL of 3.2M NH₄OAc in 20% (v/v) HNO₃ diluted to 20 mL for 30 minutes at room temperature with continuous agitation. The residual fraction was determined by microwave assisted acid digestion with 8 mL of concentrated nitric acid and 1 mL of hydrogen peroxide. Triplicate samples were performed. The same procedures were used to perform sequential extractions on selected treated sediments.

2.3. *Washing experiments*

Batch washing experiments were performed using an end-over-end tumbler rotator at 10 rpm for 2, 4 and 8 hours at room temperature. EDTA was used as washing solution at four different concentrations, 0, 0.005, 0.01, and 0.02 M, corresponding to EDTA dosage of 0, 1 mol/mol, 2 mol/mol, and 4 mol/mol (stoichiometric ratio for EDTA/heavy metals content). All experiments were performed in duplicate. After washing, slurries were centrifuged at 6000 rpm for 15 minutes. The supernatant was filtered through a 0.45 µm PTFE filter, and stored for further analysis. The remaining solids were stored at 4 °C for usage in the sequential extraction analysis and scanning electron microscopy (SEM).

2.4. *EDTA Thermal washing experiments*

Considering the results from the washing experiments at room temperature, the subsequent thermal washing experiments were performed for 2 hours at 100 °C using 0.01 M EDTA and L/S ratio 10 mL/g. The thermal experiments were carried out in a 30 mL general-purpose heating vessel (Parr Instrument Company, USA). The vessel was placed in an oven at 100 °C because EDTA decomposition starts at 150 °C (Chen et al. 2006). Agitation was achieved by turning the vessel every half an hour to allow better contact between sediment and EDTA. After thermal washing, the vessel was cooled in room temperature.

2.5. *Thermal treatment followed by EDTA washing (Sequencing process)*

Lastly, the sediment underwent a sequencing process of thermal treatment followed by EDTA washing. The heating vessel was filled with adequate amount of sediment and then placed into

the oven at 100 °C for 2 h. After cooling in room temperature, the solids were mixed with 0.01 M of EDTA at L/S ratio 10 mL/g and rotated to an end-over-end tumbler at 10 rpm for 2 hours. Each test was performed in duplicate. At the end, slurries were centrifuged and heavy metals were measured in the supernatant. All batch experiments were carried out in duplicates.

3. Results and Discussion

3.1. Sediment characterization

Physicochemical characteristics of dredged marine sediment were obtained. The pH was neutral around 7.4 similar to sea water. The sediment had a high organic content of 9.6% (w/w) derived from natural and anthropogenic sources in the dock like sewage or effluents from processing plants. Fig. S1 presents the particle size distribution. According to Unified Soil Classification System (USCS), the sediment was fine-grained and mostly consisted of clay and silt since the large portion of the particles was smaller than 75 µm. The high amount of fine-grained sediment may hinder the effect of sediment washing on heavy metal removal.

Figure 1 shows heavy metal concentration and speciation of metals at different sediment fraction. A wide range of heavy metal concentrations was observed in the sediment. According to Dutch standard (2000), the detected heavy metals (such as Zn and Cu) presented elevated values to the relevant intervention level, while some exceeded the target value. High concentrations was found for Zn and Cu more than 1000 mg/kg, while Pb, Ni and Cr had moderate concentrations around 100-200 mg/kg, and concentration of Cd was relatively low.

(Fig. 1 here)

Regarding to speciation analysis, traces of Zn, Cu, Pb, Cr and Ni were detected in the exchangeable fraction, only Cd had slightly more, indicating that metals were not in readily available form. Peters (1999) found that sediment which having pH higher than 5.6, the amount of exchangeable metals become negligible. There was a considerable amount of Cr and Pb in the residual fraction; hence lower extractions might be expected as well. Besides, Cu and Cr expected to have low extraction efficiency due to their presence in the organic and residual fractions. Particularly, over 90% of Cu was detected in the organic fraction possibly attributed to

(1) high amount of organic matter (9.6%) in the sediment, and (2) high stability constant of organic copper ($10^{11.8}$) compared to other metal species (Hirose et al. 1982). As for Zn, Pb, Cr and Ni, 70-90% were existed in carbonates or Fe-Mn oxides fractions, well agreed with other findings in marine sediments (Di Palma and Mecozzi 2007; Mulligan et al. 2001). Cd presented high mobility potential, since more than 90% existed in the carbonate fraction.

3.2. EDTA washing efficiency

EDTA washing experiments were carried out as baseline. pH values of the washing solution were measured at the end of each test and reported in Table S1. The initial pH of 0.5 M EDTA was 8.6 and dilutions were prepared from this solution for the subsequent experiments. It was found that there was no much pH variation in the washing experiments over different periods, and thus pH role on metal exchange and redistribution could be very limited (Leštan et al. 2008; Nowack et al. 2001).

Metals removal efficiency was estimated after EDTA washing (Fig. 2). As can be seen, the removal of Cu and Cr was minor. The difficulty of Cu extraction could be attributed to the high percentage of organic fraction. Humus organic substances are generally bound strongly with copper in sediments and they form insoluble metal complexes independent on pH change (Barona et al. 2001; Caplat et al. 2005; Di Palma and Mecozzi 2007). The mobility of copper is therefore controlled by redox-associated decomposition of Cu-organic matter complexes (Caplat et al. 2005). Regarding Cr profile, the low removal efficiency could be associated to low affiliation with EDTA solution to form stable metal complexes (Polettini et al 2006). Furthermore, the initial EDTA concentrations in the washing solution may be too low to mobilize Cu and/or Cr (Polettini et al 2006). For Cd, the removal rate was slightly increased with an increase of EDTA concentrations, but in overall the efficiency was comparably lower even without EDTA. The initial low concentration of Cd in the sediments made it less available to the chelating agent, even though it was existed in carbonate fractions. Besides, the presence of competing metals might inhibit chelate formation with EDTA (Tandy et al. 2004).

(Fig. 2 here)

For Pb, Ni, and Zn, the presence of EDTA in the washing solution greatly enhanced the removal efficiency regardless of the washing duration, indicating significant mobilization of sediment constituents by EDTA. Pb presented much higher extraction efficiency compared to Zn because complex stability of Pb^{2+} -EDTA is greater than Zn^{2+} -EDTA under alkaline conditions (Kim et al. 2003). Among three metals, extraction efficiency was increased by increasing EDTA concentrations and washing time.

Changes of metal speciation under sediment washing at 0.01 M EDTA for 2 hours are shown in Fig. 3. After washing, the concentration associated to the mobile fraction (exchangeable) increased for all heavy metals, while a substantial decrease was detected in moderate mobile fractions (bound to carbonates and Fe-Mn oxides) except for Cu. In contrast, there was no metal transition from the residual fraction. This indicates that EDTA was not capable of extracting parts in the less mobile forms (Li et al. 1995). The reactions between EDTA and sediment are described below (Nowack et al. 2001; Zhang et al. 2010).

(Fig. 3 here)

Where Me and Me^* represents different heavy metals and $sediment (P1)$ and $sediment (P2)$ represents the different fractions in the sediment. The increasing metal concentrations in mobile fraction could be due to transformation of metals from Fe-Mn oxides and hydroxides to exchangeable fraction eq. (3), as results of the mobilization by the washing solution (Polettini et al. 2006; Di Palma and Mecozzi 2007). Insufficient washing duration could lead to eq. (1), when the demobilized metals would be loosely attached to sediments particles but not yet release (Zhang et al. 2010). Post-extraction sorption could also take place contributing the exchangeable fraction eq. (2) (Howard and Shu 1996). In addition, competitive earth metals like Ca and Mg could form metal-chelant complexes and influence heavy metal exchange and redistribution during the washing process (Lo et al. 1998; Lo et al. 2011; Tsang et al. 2007; Yip et al. 2009).

3.3. *Effect of EDTA thermal washing*

The pH value in the EDTA solution after thermal washing was 7.8, which was slightly lower than the pH values of EDTA solutions with similar concentrations after sediment washing (8.4, 8.3, and 8.2 for 2, 4 and 8 h of contact time respectively). The slight decrease of pH could be yielded to the enhanced dissolution of sediment via thermal washing, where competitive cations such as Ca and Mg were subjected to complexation with EDTA (Di Palma and Mecozzi 2007; Zhang and Itoh 2006). The extra chelation of cations with EDTA could further reduce pH value.

The removal efficiency of heavy metals after EDTA thermal washing is shown in Fig. 4. The results were compared with sediment washing using 0.01 M EDTA and contact time 2 h. It was found that thermal washing with agitation was much more efficient for metal extraction such as Zn, Ni, and Pb. Especially, the removal efficiency of Zn and Ni was performed better than sediment washing using 0.02 M EDTA for 8 h contact time. This indicates that thermal washing could affect the kinetics of metal extraction (Vuyyuru et al. 2010). Earlier studies on thermal-treated sludge had revealed elevated level of Zn and Ni in their mobile fractions, including exchangeable, diluted-acid-extractable and bound to Fe-Mn oxides (Obrador et al. 2001). Very likely the accelerated dissolution of metals by thermal washing could promote the reaction with chelating agents leading to higher removal efficiencies (Zhang and Itoh 2006). In the case of Pb, the removal by EDTA thermal washing was higher than EDTA washing only for similar contact time (2 hours), but it was less effective than EDTA washing for 4 and 8 hours. Evaluating the influence of agitation in thermal washing, it was found that the absence of agitation could dramatically deteriorate the removal performance. To some extent it could offset EDTA extraction effect indicating the significance of good mixing. Distinct from thermal washing, sequencing process proved to be less efficient in removing more heavy metals compared to EDTA washing alone. Especially for Ni, the initial thermal treatment could inhibit its extraction due to further stabilization in the sediment matrix (Zhang and Itoh 2006).

(Fig. 4 here)

It is noteworthy that during EDTA thermal washing, heavy metal extraction was controlled by EDTA chelation. The enhancement on metal release by thermal washing was important, but not

the dominant pattern. In other words, the application of thermal washing has not altered the release characteristics of metals, which was originally controlled by EDTA chelation. Instead, it acted as an “intensity” step depending on metal thermal sensitivity. In this regards, Cu, Cr and Cd have not responded different among the washing processes (EDTA, thermal, agitation). Other metals like Zn, Pb and Ni could be mobilized by EDTA have demonstrated only differences in the removal rate. To this end, mobilization of Cu, Cd and Cr probably requires more aggressive approaches (other chelating agents, higher concentration, low pH, etc.) (Abumaizar and Smith 1999).

3.4. Sequential extraction analysis

Sequential extraction analysis of sediment after thermal washing was conducted to investigate the distribution of heavy metals among the different fractions (Fig. 5). The effect of EDTA thermal washing and sequencing thermal treatment presented similar metal speciation compared to EDTA washing. It was found that most metals presented an increment in the mobile fraction (exchangeable), and decreased in less mobile fractions (bound to organics and residual) (except for Cr). Interestingly, the increment in the exchangeable fraction appeared to be greater in the EDTA thermal washing, as compared to EDTA washing or sequencing process. The decrease of metals in the less mobile fractions implies that EDTA was capable of extracting the metal with strong binding forces assisted by high temperature in the washing solution. Following paragraphs would explain the influence of different processes for the sake of comparison.

(Fig. 5 here)

3.4.1. EDTA washing vs. EDTA thermal washing

It was interestingly found that the metal content in less mobile fractions, i.e. bound to organics or the residue, was slightly reduced, indicating that thermal washing enhanced metal mobilization. Besides, it is well known that thermal treatment could often lead to stabilization of metals (Hu et al. 2012; Ndiba et al. 2008; Sørensen et al. 2000). However, it has been reported that sorption of certain metals onto sediments is an exothermic reaction and thus extra supply of heat could favor the mobilization (James 1996). In the thermal washing coupled process, a mild temperature 100 °C with high L/S ratio at 10, was applied. This mild temperature could facilitate the interaction

between EDTA and metals due to different mechanisms associated to thermodynamics: 1) creation of more effective surface area by releasing those metal complexes with comparably low thermal stability (James 1996); 2) exposure of hidden metals by dissolution of minerals; and 3) supply with Gibbs energy for thermal complexation reactions with certain metals (Smith and Martell 1987; Vallet et al. 2003; Yong Di and Park 2011). In overall, the availability and accessibility of metals was increased and thus achieved higher removal efficiency. Furthermore, mechanical agitation could inhibit agglomeration of heavy metal complex, involving steps of integration, deposition and stabilization. Different from the consistent performance of metals in other fractions, metals bound to Fe-Mn oxides have an uncertain behaviour. Metal “transformation” may occur from the Fe-Mn oxides either to the immobile residual fraction or to the neighboured mobile fractions, leading to an unclear result.

3.4.2. EDTA washing vs. thermal washing vs. sequencing process

Generally, the efficiency of heavy metal removal was limited in the sequencing process. There was an increment in the residual fraction of Pb and Cr in the sequencing process as compared to the sediments washed with EDTA, suggesting that thermal treatment with limited water content could stabilize certain metals (Hu et al. 2012). Comparing to thermal washing process, sequencing process favoured metal content at fractions bound to carbonate (except for Cr), Fe-Mn oxides and the residue, indicating that thermal treatment might favour the accumulation of heavy metals at these fractions. On the contrary, certain metals (Pb and Cr) presented in the organic fraction were reduced in the sequencing process because of the degradation of organic matter at the higher temperature. This reduced portion was largely made up by the increment in the residual fraction. This was an evidence of metal transformation across fractions, and the lost organic portion appears to be converted to a more stable form bound to residue.

In order to support the extraction efficiency among the experiments, Fig. 6 illustrates the morphological transformation resulted from EDTA washing, thermal washing and the sequencing thermal process. It can be seen that more pores were formed from the dissolution of minerals enhanced by EDTA thermal washing. Agglomerate formation under thermal treatment indicates a change of surface charge as well. Washing the sediment with EDTA has not shown any significant difference on the surfacial properties.

(Fig. 6 here)

4. Conclusion

Heavy metals removal efficiency could be greatly enhanced by EDTA thermal washing. Multiple mechanisms played an important role such as decomposition of low thermal resistant organic complexes, exposure of initial covered metals, and supply of required EDTA complexation energy. However, the enhancement of heavy metal release was observed only for certain metals indicating EDTA chelation with specific metal preference. Sequencing thermal treatment with EDTA chelation had no significant influence for metal extraction. Therefore, experiments should be carefully designed, in consideration to sediment characteristics, heavy metals concentration, and chelate dosage. Interestingly, thermal treatment could adversely stabilize metals by increasing distribution of metals in less mobile fraction.

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Figure caption

Fig. 1 Heavy metal concentrations and the distribution in different fractions of the sediments determined by sequential extraction

Fig. 2 Heavy metal removal under different EDTA concentrations (“No EDTA”: 0 EDTA; “1”: 0.005 M of EDTA; “2”: 0.01 M of EDTA; “4”: 0.02 M of EDTA) and operation periods (at 2, 4 and 8 h, respectively)

Fig. 3 Metal distributions before and after EDTA washing from sequential extraction experiments (recovery rate was calculated based on comparison results of the total metal content achieved and the mass balance of each metal in each fraction done: 1.16 for Zn, 0.99 for Cu, 0.92 for Pb, 0.70 for Cd, 1.40 for Cr and 1.20 for Ni)

Fig. 4 Comparison of heavy metal removal by EDTA washing, thermal washing and sequencing process under different conditions

Fig. 5 Sequential extraction studies of sediment with (a) EDTA washing only, (b) EDTA thermal washing and (c) sequencing process (recovery rates of 1.14 and 0.93 for Zn (b) & (c), 0.73 and 0.59 for Cu (b) & (c), 1.03 and 1.09 for Pb (b) & (c), 0.96 and 0.92 for Cd (b) & (c), 0.93 and 1.01 for Cr (b) & (c), and 1.07 and 0.74 for Ni (b) & (c), respectively)

Fig. 6 SEM Images of (a) untreated sediment, (b) 0.01 M EDTA treated sediment at contact time 2 h, (c) thermal washing with 0.01 M of EDTA 100°C for 2 h, (d) sequencing thermal treatment with water at L/S= 1.88 followed by leaching with 0.01 M of EDTA

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Supplementary table and figure

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Table S1: Final pH of washing solution after EDTA washing.

Treatment methods	pH		
	2 hrs	4 hrs	8 hrs
No EDTA	7.7	7.8	7.6
EDTA (0.005 M)	8.2	8.1	8.0
EDTA (0.01 M)	8.4	8.3	8.2
EDTA (0.02 M)	8.5	8.4	8.3

Figure S1. Particle size distribution of marine sediments of Benoi Basin in Singapore.