Performance of cathode catalysts for bio-electricity from paper recycling, wastewater-fed, microbial fuel cells

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This work deals with the performance of a microbial fuel cell, focusing on the electrocatalytic activity of selected cathodes constructed by coating nanocomposites over graphite felt under neutral pH in a double-chamber configuration using paper-recycled waste water as a typical electrolyte. Among all cathodes, iron phthalocyanine (FePc) combined multiwalled carbon nanotubes (MWCNT) shows the highest power density (9.34 W/m^2) compared to other two catalysts, FePc/Ketjan black (4.68 W/m^2) and MWCNT (2.9 W/m^2) under similar conditions of using a reference platinum/carbon (Pt/C) loading of 0.5 mg/cm^2. The morphology of these catalyst coated electrodes was characterized by scanning electron microscopy. Their electrocatalytic activities were examined using cyclic voltammetry. This work provides an appropriate alternative for cathode catalysts in treatment as well as in electricity production as demonstrated by the high power density of the above catalysts compared to that using precious Pt metal catalyst in microbial fuel cells.

Keywords: Iron phthalocyanine, microbial fuel cell, multiwalled carbon nanotubes, oxygen reduction rate, paper recycling wastewater.

THE economic growth of a country significantly depends on the extensive availability of energy sources. Energy demand has been mainly balanced by fossil fuels and other resources such as coal, oil, gas and nuclear energy[1]. Energy from fossil fuel is not adequate to meet future demands. Microbial fuel cell (MFC) is an advanced method for treatment of wastewater and production of electricity to avoid over-exploitation of natural resources and reduce the demand for water[2]. Bacteria in MFC grow under anoxic condition which can benefit cellulose fermentation and degradation of paper recycling effluent with the added benefit of electricity generation rather than power consumption[3]. Wastewater contains a lot of easily degradable organic matter which is metabolized by active bacteria present in wastewater itself producing electricity during the process[4]. Different types of wastewater have been successfully treated by MFC[5]. The sludge organic matter is oxidized in a double chambered salt bridge MFC with a simple compound in the anode

chamber[6]. The fuel cell performance is based on fuel transport to microbes, metabolic activity and the effectiveness of MFC using membrane electrode assembly (MEA)[7]. Besides, in a single chambered microbial fuel cell (SCMFC), material upgradation of anode is an important parameter[8]. Power generation can be increased by increasing the solution conductivity using concentrated phosphate buffer solution (PBS) which also improves the treatment efficiency in paper recycling wastewater[3].

The performance of SCMFC on Nafion®117 and sulphonated polystyrene–ethylene–butylene–polystyrene (SPSEBS) polymer membranes is compared using platinum (Pt) catalyst[9]. MFCs produce electrons and protons due to oxidation of organic matter present in the anode chamber. The fundamental purpose of proton exchange membrane (PEM) is to transport only the protons from anode to cathode and in turn prevent the transfer of oxygen and substrate to the next chamber[10]. Electrons transferred from anode to cathode chamber through an electrical circuit are accepted by an electron acceptor. Several studies have used oxygen as an effective electron acceptor[11]. However, oxygen reduction reaction (ORR) requires an efficient cathode catalyst for overcoming the high overpotential of electrode[12]. Despite the possibility of using Pt as a cathode catalyst, it is impractical to scale-up the reactor. Identification of best cathode catalyst with efficient ORR and cost effectiveness are the biggest challenges for the past few years. Several studies reported that non-Pt cathode catalysts enhanced electrocatalytic activity more or less equal to Pt catalyst[13]. Manganese oxide (MnO_2) with activated carbon has been widely used as a cathode catalyst in place of Pt[14,15]. The potential of manganese–polypropelene–carbon nanotube (Mn–PPY–CNT) has been demonstrated to replace Pt which may facilitate desirable ORR process[16]. Ammonia-treated activated carbon in presence of peat, increases the nitrogen functional groups and improves ORR activity[17]. Poly-anilene–iron–carbon (PANI–Fe–C) has specific surface area (228.3 m^2/g) less than Pt (733.9 m^2/g), but power generation is high due to its chemical structure[18]. Composite cathode catalysts have higher potential in ORR compared to Pt catalyst. Hence, a majority of studies were aimed at developing a new non-noble metal composite catalyst to replace Pt catalyst in MFC[19–22]. Recently, iron-based catalyst, viz. iron pthalocyanine (FePc) has gained attention owing to its good oxygen reduction property[23]. FePc supported carbon nanotube (CNT) electrode reportedly enhanced electrocatalytic activity, since CNTs can easily integrate with other functional groups, which significantly improve ORR activity[24].

In the present study, it was proposed to utilize multiwalled carbon nanotubes (MWCNT) supported FePc as a cathode catalyst for improving ORR activity in double chambered microbial fuel cell (DCMFC). The performance of MWCNT/FePc was compared with FePc/Ketjen Black (KB) and MWCNT catalyst in DCMFC. The

electrocatalytic activities of catalyst-coated electrodes were compared using voltammograms.

Electrodes for electrochemical studies were prepared using graphite felt (GF) which was procured from Synergy fuel cell store, India. Three different cathode catalysts, viz. MWCNT, FePc/KB and MWCNT/FePc composite catalyst were used in DCMFC. MWCNT and FePc were procured from Nano Shell, USA and Sigma-Aldrich respectively. MWCNT (>80% purity) had a surface area of 90–350 m^2/g with a diameter of 20–30 nm and length of 5–10 µm. FePc had carbon and nitrogen content of 67.3% and 19.5% respectively and was in the size of 657 nm as specified by the manufacturer. Catalytic ink was prepared by dispersing the catalyst in isopropyl alcohol followed by mixing 10% Nafion (5% wt Nafion from Sigma-Aldrich) solution for the total weight of catalyst for binding with the electrode. Catalytic ink was sprayed over the electrode and dried at 70°C to evaporate the solvent. FePc/KB, MWCNT and FePc/MWCNT catalyst coated electrodes were produced by the overhead process. In the present study, the efficacy of 0.8% wt FePc with KB, 0.8% wt FePc with MWCNT and MWCNT at the loading rate of 1 mg/cm^2 has been compared[25]. A bare carbon cloth was used as an anode.

A DCMFC was constructed as reported by Limson et al.[26]. Anodic and cathodic chambers were separated by proton exchange membrane (PEM) (Nafion[®]117) which was procured from Dupant & Co, USA. The MFC consisted of two cylindrical chambers made of borosilicate, each with volume of 250 ml. Proton exchange membrane was held by a clamp between two flattened chambers, interspaced with an air tight gasket. Spacing between anode and cathode was maintained as 12 cm. Carbon cloth was used as an anode and GF was used as a cathode, and both electrodes were of size 3 cm × 3 cm. The electrodes were connected by a copper wire with an external resistor 66 Ω to a multimeter. Anolite of paper recycling wastewater with inoculum and catholite of PBS with potassium permanganate were used[27]. The pH was maintained at 6.9 by adding NaOH or HCl. The raw paper recycling wastewater was collected from a paper recycling industry in Tamil Nadu and stored below 4°C until further use. The collected wastewater was characterized as per standard methods and pH, chemical oxygen demand (COD), total dissolved solids (TDS), total suspended solids (TSS) and biochemical oxygen demand (BOD) values were found to be 7.12, 1792 mg/l, 615 mg/l, 1428 mg/l and 158 mg/l respectively. A mixture of sludge and soil collected from the paper recycling mill was used as inoculum. Whenever the voltage dropped below 50 mV, the reactor solution required replacement and some quantity had to be left in the reactor for inoculating the next cycle of treatment. Anode and cathode chambers were maintained in anaerobic and aerobic conditions respectively. The cathode chamber was aerated using fish tank aerator. The total setup was operated at room temperature in fed batch mode. Before starting the experiment, both compartments were sterilized by autoclave for 20 min. The Nafion[®]117 membrane was pretreated with hydrogen peroxide solution followed by distilled water, each for one hour. Also, the electrodes were pretreated by soaking in 1N HCl for 24 h followed by 1N NaOH for another 24 h before catalyst coating.

The present study compares the electrocatalytic activity of different electrodes, viz. FePc/KB, FePc/MWCNT, MWCNT and bare GF in 100 mM PBS with 5 mM potassium permanganate electrolite under an oxygen saturated condition. Cyclic voltammetry was done in the potential window –0.6 V and 1.2 V at a scan rate of 10 mV/s, using 3 electrode setup. A Pt wire and Ag/AgCl electrodes were used as counter and reference electrodes respectively. The catalyst coated GF electrodes were used as working electrodes. Voltage across the external resistor was monitored at intervals of 10 h using a multimeter. Morphology of catalyst coated electrodes was investigated by scanning electron microscopy (SEM) with a Zeiss instrument. Power density and substrate degradation were considered as two main parameters to estimate the performance of fuel cells. Columbic efficiency (CE), current density (CD) and power density (PD) values were calculated using eqs (1)–(3) respectively

$$CE = \frac{M.\int_0^t I \, dt}{FbV\Delta COD},$$ (1)

$$CD = I_{max}/A,$$ (2)

$$PD = P_{max}/A,$$ (3)

where F is the Faraday constant, I the harvested current, V the volume of anode, b the number of electrons exchanged per mole of oxygen and M is the molecular weight of oxygen; A is the surface area of the electrode; CD is the ratio of the maximum current to the surface area of the electrode and PD is the ratio of maximum power to the surface area of the electrode. COD, TDS, TS and BOD were measured for wastewater by standard methods (APHA)[28].

Different types of bacterial attachments were observed, which acted as biocatalysts and assisted the transfer of electrons from anolite to electrodes. SEM images for bare carbon cloth and microbial attached carbon cloth (anode) electrodes are shown in Figures 1 and 2 respectively.

SEM images of bare GF, MWCNT, FePc/KB and FePc/MWCNT are shown in Figures 3–6 respectively. The bare GF structure can be seen in Figure 3. In Figure 4, dense layer of MWCNTs attached over GF can be noticed. Increase in surface area enhances power generation retaining the same material characteistics[29]. Figure 5 shows the typical particle morphology of phthalocyanine

compounds[2]. Figure 6 shows the SEM image of FePc dispersed over MWCNT at the external pores of coatings. It can also be noted that FePc/MWCNT coated electrodes have rough surface which can provide a higher specific surface area and improve current production, resulting in an increase in power density compared to other electrodes. It is reported that MWCNT/FePc composite catalyst adsorbed to the surface of GF electrode can improve the oxygen reduction rate. In addition, surface chemistry changes affect power generation[30].
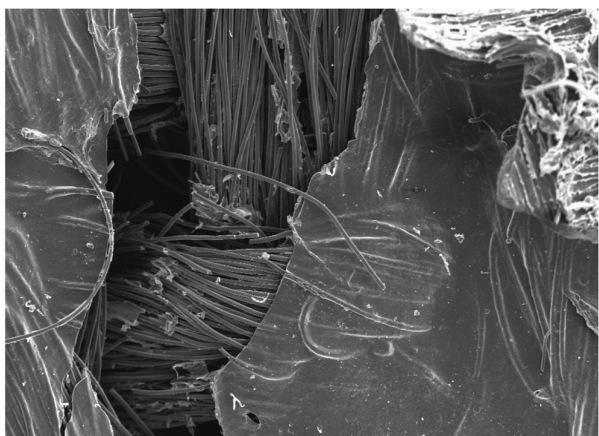

Figure 1. SEM image of bare carbon cloth.

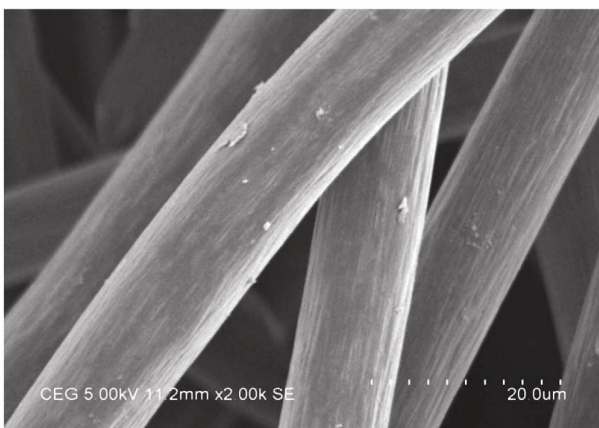**Figure 2.** SEM image of bacterial attachment.

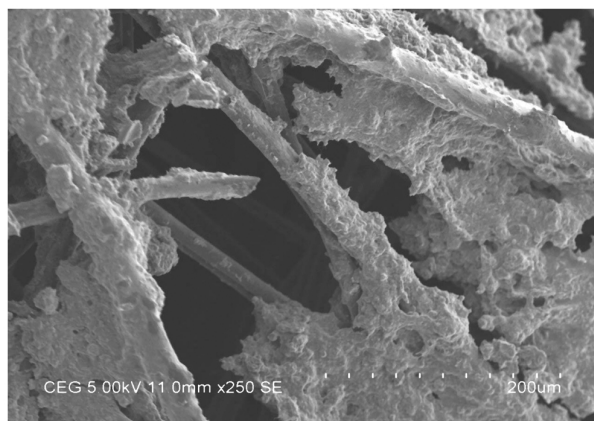**Figure 3.** SEM image of bare graphite felt.
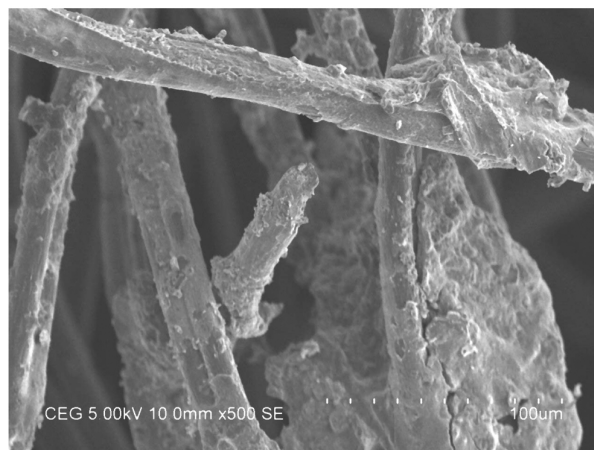

Figure 4. SEM image of MWCNT.

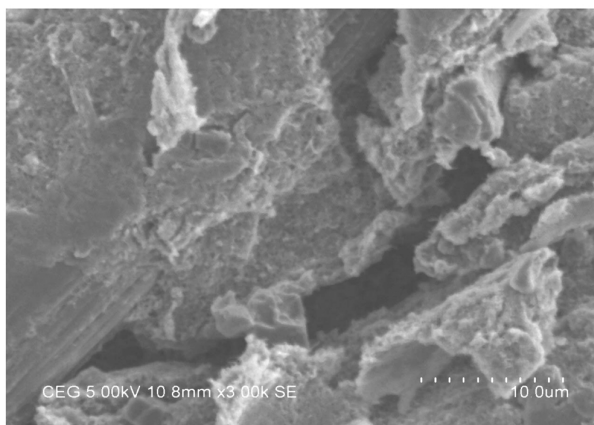**Figure 5.** SEM image of FePc/KB.

Figure 6. SEM image of FePc/MWCNT.

The cyclic voltammogram (CV) of different composite electrodes is shown in Figure 7. Voltammogram results did not indicate any Faradic current for bare GF electrode and GF/MWCNT coated electrode. But the real surface area of electrode was increased by MWCNT[31]. MWCNT enhanced the promising ORR activity. However, the oxygen reduction potential was further improved by introducing MWCNT with FePc[32]. Among the four electrodes, FePc/MWCNT produced the maximum peak on CV, at +0.19 V. This peak may be due to the effect of FePc[12]. Nitrogen-doped MWCNTs coated electrodes have better stability and negligible loss than single walled carbon nanotube (SWCNT)/FePc electrodes[33]. A previous study revealed that the peak was at +0.12 V for CNT on Pt which was greater than CNT alone[33]. Electrochemical

activity of electrodes is greatly enhanced by associating nitrogen groups in CNT[31]. Oxygen reduction is an H^{+} ion consuming process. Amino group composite catalysts (FePc/MWCNT) have more positive charge, which helps the kinetic and electrocatalytic reactions by delivering H^{+} ions[34]. FePc with CNT therefore enhanced heterogeneous electron transfer mechanism at high rate and since the electrocatalytic activity of FePc/CNT is greater than FePc/Carbon (C), every carbon atom of MWCNTs donates one electron to establish p–p electrostatic interactions between the molecules. The overlapped orbitals of C atoms contributed to Vander Waals interaction with some p-conjugated molecules, which, upon adsorption onto CNTs, enhanced the catalytic activity of FePc[35].

The performance of DCMFC was evaluated by assessing the power density. A plot of power density versus
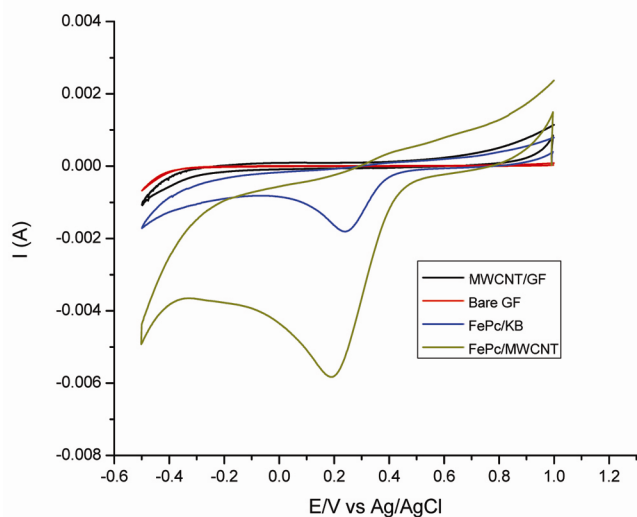

Figure 7. CV characterization of MWCNT, FePc/KB, FePc/MWCNT and bare graphite felt.
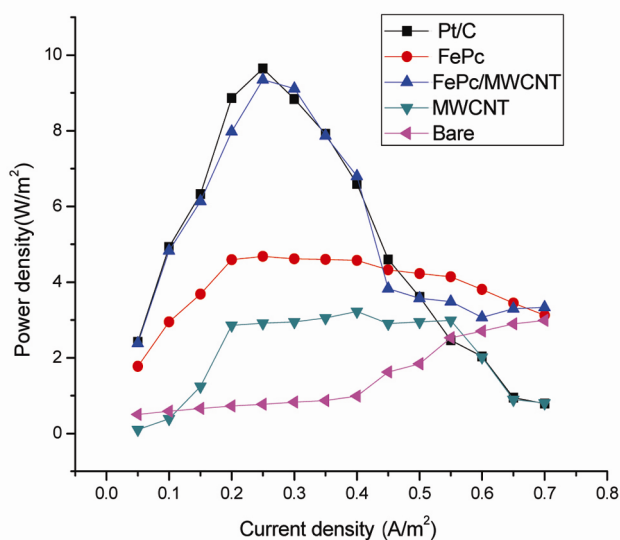

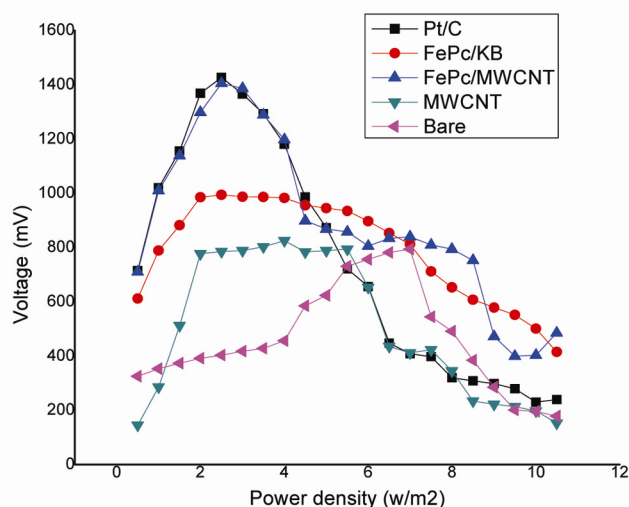**Figure 9.** Effect of power density with current in different electrodes.

Figure 8. Effect of power density with voltage in different electrodes.
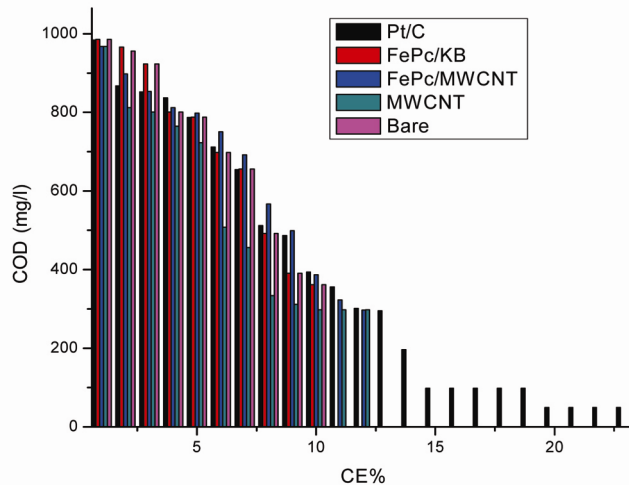

Figure 10. COD removal with CE% for various electrodes.

voltage is presented in Figure 8. The power density values for MWCNT, FePc/KB and bare GF electrodes were 0.768, 2.91 and 4.67 W/m^2 respectively. Among the three electrodes, FePc catalyst coated electrode produced higher values than MWCNT and bare GF. In a controlled experiment, Pt/C was used as a catalyst coated electrode and power density was measured as 9.64 W/m^2. Power density was further improved by introducing FePc with MWCNT as cathode catalyst over GF, which was 9.34 W/m^2. The power density of FePc/MWCNT was almost equal to the Pt/C cathode catalyst and nearly 12 times of bare GF. Power density versus current density is shown in Figure 9. This revealed MWCNT/FePc catalyst as an excellent alternative to Pt in MFCs. Power density of FePc/KB was higher than FePc/vulcan-XC and also slightly higher than Pt[23]. Power density obtained for FePc/MWCNT was higher than FePc/KB due to four electron pathway[12]. This also shows that MWCNT is a good supporting material compared to KB.

Figure 10 shows the analysis of effectiveness of the catalyst in bio-electricity production by using paper recycling wastewater. The COD removal efficiency for MWCNT, FePc/KB and MWCNT/FePc coated electrodes was 69%, 71% and 73% respectively. The CE for MWCNT, FePc/KB and MWCNT/FePc coated electrodes was 10.64%, 7.44% and 8.37% respectively. The electrochemical activity was enhanced by the hybrid bacterial attachment over the electrode[36]. COD removal efficiency increased with increase in initial concentration[37]. It can also be observed that COD removal too was higher for FePc/MWCNT than other electrodes.

Bio-electricity was successfully produced using DCMFC with different cathode catalysts and paper recycling wastewater as an anolite. In this study, MWCNTs-supported FePc cathode catalyst in a DCMFC was found to be efficient for ORR. The power density produced by MWCNT/FePc composite catalyst (9.34 W/m^2) was slightly less than Pt/C (9.64 W/m^2). In addition to this, the COD removal efficiency of 73% and CE of 8.4% were achieved using FePc/MWCNT deposited electrode. The results clearly revealed that the iron phthalocyanine deposited MWCNT/FePc composite electrode could yield higher power density and acheive higher COD removal. Hence, MWCNT/FePc could be considered as a promising and economically viable catalyst for producing bio-electricity using DCMFC.

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Phosphorus accumulation associated with intense diagenetic metal-oxide cycling in sediments along the eastern continental margin of India

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Sequential phosphorus extractions were carried out to understand phosphorus cycling and enrichment in surface sediments along the eastern continental margin of India. Phosphorus associated with authigenic (P_{aut}) and biogenic (P_{bio}) phases is high by a factor of 2–10 in the continental shelf sediments compared to slope and deep-sea sediments. Phosphorus associated with Fe oxides (P_{Fe}) is enriched by a factor of 2–5 in the continental slope and rise sediments (500–3000 m water depth) compared to shelf sediments. Fe–Mn oxy(hydroxides) formed during early diagenesis adsorb phosphate from the water column or pore waters, thereby enriching the P_{Fe} fraction in the continental slope sediments. These results are in contrast with those from the Arabian Sea, where wide and intense mid-depth oxygen minimum zone (150–1200 m water depth) releases P_{Fe} to pore waters and enhances P_{aut} accumulation in the continental slope sediments.

PHOSPHORUS (P), an essential nutrient for life in the terrestrial and aquatic environment, is thought to control marine productivity on geological timescales[1]. Continental weathering is the most significant source of P to the oceans and is transported mainly by rivers in particulate and dissolved forms[2,3]. The dissolved phosphorus forms are utilized by phytoplankton and subsequently released to the water column during organic matter regeneration. A part of the dissolved phosphate transforms to particulate form during biogeochemical processes in the oceanic environment. The particulate P also occurs in apatite and other minerals, and is generally not involved in biogeochemical processes. However, clay particles with coatings of Fe–Mn oxy(hydroxides) have high capacity to adsorb phosphate from freshwater. It has been shown that phosphate desorption from clay minerals is nearly 2–5 times high due to buffering when compared to dissolved phosphate load entering into the ocean via rivers[4].

Sediments are the main sink for authigenic P which occurs mainly as a mineral, carbonate flourapatite (CFA). CFA formation is predominant in sediments from shallow water depths and continental slope sediments experiencing coastal upwelling[5–9]. In oceanic sediments P is associated

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