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Enhanced carbon capture biosorption through process manipulation

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ABSTRACT

The feasibility of manipulating operating parameters, i.e. Food-to-microorganisms (F/M) ratio, SRT, and residual DO, to enhance biosorption performance was investigated. It was observed that lower F/M and longer SRT resulted in sludges which captured carbon mainly through carbon storage. Surface sorption, however, was the dominant mechanism for sludges grown under the higher DO condition. Generally, biosorption was optimal at pH 7. Sorption kinetic studies revealed that sludge cultivated under the low F/M ratio of 0.15 (Sludge S1) showed the best overall biosorption performance. Determination of calorific value revealed that Sludge S1 was able to capture energy as much as 0.9 kJ/g SS within 15 min contact time. About 66.3% of the overall biosorption capacity was attributed to carbon storage. Sludge S1 was able to accumulate organic substrate and stored this as polyhydroxyalkanoates (PHA). Culture-independent microbial community analysis through DGGE revealed the presence of strains capable of PHA-accumulation, e.g. *Rhodobacter* sp., and *Thauera* sp. While different dominating mechanisms resulted from different cultivation conditions, the best biosorption performance was significantly contributed by carbon storage activity.

1. Introduction

Current activated sludge-based operations in conventional wastewater treatment systems are considered economically and environmentally unsustainable due to the energy consumed [1]. The increasing concern over carbon footprints and global warming has led to more interest in energy reduction in wastewater treatment. The potential energy contained in raw municipal wastewater was reported to possibly exceed the energy requirements at a wastewater treatment facility [2].

Owing to its low cost and high efficiency, the usage of various types of biosorbent for the removal of toxic pollutants or for the recovery of valuable resources from wastewaters has been gaining momentum. Using sludge biomass as the sorbent, biosorption has been studied by numerous researchers but mainly focused on heavy metal and dye sorption [3,4]. Biosorption is generally accepted as a passive process [5], which is affected by factors which include pH, biosorbent (floc) size, biosorbent dosage, initial pollutant concentration, ionic strength, and temperature [4]. The mechanisms involved in adsorptions of metal ions by biosorbent, as reviewed by Tsezos et al. [6], are passive and non-metabolic. As a generalization, the two possible major mechanisms involved are (i) ion exchange: cation-binding with ionizable functional; and (ii) complexation: complex formation of metal ions with organic molecules involving ligand centers in the organic species. Complexation may be electrostatic or covalent [6].

In the context of energy recovery from wastewater influent, biosorption is described as the phenomenon where biomasses concentrate carbon substrates from the wastewater in a rapid manner [7,8]. This phenomenon is hereafter denoted as "carbon capture biosorption" (CCB). Only a few researchers have studied the CCB performance of activated sludge in terms of energy recovery. Both Guellil et al. [7] and Yu et al. [8] concluded that CCB in activated sludge involves only passive uptake (surface sorption). Whereas later study by Xiao et al. [9] reported that CCB consisted of metabolically-mediated biological and physical-chemical components. This conclusion indicated surface sorption could be the first step but not necessarily the last step involved in CCB. Review of the literature would suggest possibility of enhancement of CCB performance by manipulating operating parameters, e.g. Food-to-microorganisms (F/M) ratio, Dissolved Oxygen (DO) level and Sludge Retention Time (SRT), as well as the consequent dominant mechanisms involved has yet to be investigated and reported.

Li et al. [10] reported that, while low F/M ratio favors the growth of smaller granules, larger size granules appear in the system when

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Nomenclature

ATP	adenosine triphosphate
ATU	allylthiourea
SBR	sequencing batch reactor
CCB	carbon capture biosorption
CFB	*Cytophaga–Flexibacter–Bacteroides*
COD	chemical oxygen demand
DGGE	denaturing gradient gel electrophoresis
DO	dissolved oxygen
EPS	extracellular polymeric substances
F/M ratio	food-to-microorganisms ratio
HRT	hydraulic retention time
NAD^+	nicotinamide adenine dinucleotide (oxidized form)
NADH	nicotinamide adenine dinucleotide (reduced form)
PHA	polyhydroxyalkanoate
SRT	sludge retention time
SS	total suspended solid
VSS	volatile suspended solid

high F/M ratio was applied during later stage of sludge granulation. It is envisaged that under low F/M ratio, a smaller floc size would facilitate uptake in low substrate environment. DO levels could also affect the growth pattern of the sludge [11]. Low DO environment leads to growth of filamentous bacteria, whereas high DO condition increases risk of fungi growth which would then compete with the bacterial species for the organic carbon [12]. Difference in the floc size and microbial community structure would result in different surface areas and this can have crucial effect on CCB. With more available surface area, biomass tended to have better CCB capacity [13]. Longer SRT leads to a denser and more compact floc structure, while in contrast, shorter SRT usually results in dispersed growth and fine flocs [14]. On the other hand, Wang et al. [15] suggested that SRT could affect the biomass's extracellular polymeric substances (EPS) production. More EPS is produced at longer SRTs to improve floc aggregation. EPS acts like a glue-gel, entrapping particles. Ionic strength of the biomass, e.g. surface charge, could also affect CCB to certain extent. The electron attraction or repulsion force between the sorbate (e.g. metal ion or negatively-charged colloids) and the biomass affects the CCB performance. In addition, Wilén et al. [16] pointed out that the ionized group from the EPS of biomass could change the surface charge of the biomass.

The surface charge of microbial cells, EPS and sludge flocs originates from dissociation or protonation of carboxyl, phosphate and amino groups, and consequently depends on pH. Flocs and EPS of all activated sludge carry a net negative charge, mostly within the range of zeta potential −20 to −30 mV [17], due to the protonation of the anionic functional groups, such as carboxylic and phosphate. Zeta potential, which represents the potential drop in the diffuse double layer on the surface, is measured based on the electrophoretic mobility in an electric field. However, since sludge surface are inherently heterogeneous, whereas measurement of the electrophoretic mobility only yields an average value of the surface charge, local differences can be expected [18]. Positively charged domains containing lysyl, histidyl and arginyl side chains, would result in localized positive charge on the cell surface [6].

Polyhydroxyalkanoates (PHAs) is one of the most common carbon storage polymers among prokaryotic organisms, including species of both Bacteria and Archaea. PHAs are synthesized classically under unfavorable growth conditions due to imbalanced nutrient supply [19]. Such conditions result from an excess of carbon and energy-source coupled with a depletion of growth-essential substrates like nitrogen, phosphate, or dissolved oxygen [20]. When conditions warrant PHAs are then broken down for biosynthesis or ATP production [19]. Studies on carbon substrate uptake by PHA-accumulators, using acetate as the model substrate, showed that acetate uptake involved metabolically-mediated transport of acetate by the enzyme acetate permease, a symporter than transfer acetate together with proton. The efficiency of the enzyme relies on the membrane potential. Membrane potential is the difference in electric potential between the interior and the exterior of a cell [21].

In this study, "carbon capture biosorption" (CCB) is defined as the phenomenon of carbon capture and concentration within the sludge floc. The CCB process could involve (i) surface sorption: passive uptake of organics through physical-chemical interactions; (ii) carbon storage: metabolically-mediated transport and accumulation of sorbed material or dissolved organic compounds within the cell; (iii) carbon entrapment: entrapment of larger particles in the open structure of the sludge floc, likely to be facilitated by the production of extracellular polymeric substances. The application of CCB in the wastewater, and the possible ways to enhance CCB performance were investigated. The objectives of this study include (i) investigation on the effect of operation parameters, e.g. F/M ratio, DO level and SRT, on enhancing CCB performance; (ii) investigation on the effect of pH on biosorption performance; and (iii) elucidation of the mechanisms involved in CCB.

2. Materials and methods

2.1. Sludge acclimation

Seed sludge was collected from a local water reclamation plant. Sludge acclimations were carried out through feast-famine cycle by employing a modified SBR with 6 stages: (i) 3 min fill (feast); (ii) 10 min contact (biosorption); (iii) 5 h react (famine); (iv) 40 min settling; (v) 6 min discharge; and (vi) 1 min idle. The total cycle time was 6 h, with a working volume of 3L, and a HRT of 12 h. Table 1 shows the six conditions for acclimating sludge. Conditions S1 and S2 were meant to investigate the effect of food-to-microorganisms (F/M) ratio; conditions D1 and D2 to look into the effect of different dissolved oxygen (DO) level; whereas condition R1 and R2 look into the effect of different sludge retention time (SRT). The reactors were operated within the pH range of pH 6 to pH 8.

The bioreactors were fed with synthetic wastewater comprising 200 mg/l glucose, 358 mg/l Na-accetate·$3H_2O$, 200 mg/l starch (soluble), 125 mg/l urea, 100 mg/l NH_4Cl, 23.5 mg/l KH_2PO_4, resulting in a total COD of 600 mg/l. The mixture was supplemented with a trace elements solution [22]. Allylthiourea (ATU) was also added at 10 mg/l to inhibit nitrification. Bioreactor performance was monitored based on the residual COD over a SBR cycle and the final discharge quality. When the reactors reached pseudo steady state, sorption capacity of the sludge was determined as described in the following section.

2.2. Determination of carbon capture biosorption capacity

Mixed liquor (100 ml) was collected from the bioreactor at the end of the aerobic phase and allowed to settle for 30 min to achieve liquid–solids separation. 50 ml supernatant would then be decanted, and the remaining 50 ml mixed liquor transferred to a 100 ml Erlenmeyer flask. Synthetic wastewater (50 ml) was then quickly added into the flask to initiate the experiment (batch test). The duration of batch tests was 15 min as preliminary experiments revealed that carbon removal would reach steady-state within such period. Mixed liquor samples (3 ml each) would be withdrawn from the flask at the following time intervals: 10 s, 2 min, 4 min, 6 min, 8 min, 10 min and 15 min. The samples were centrifuged at 10,000 rpm to separate the solids from the liquid. Residual COD in