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## Biosorption for carbon capture on acclimated sludge-Process kinetics and microbial community



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#### ABSTRACT

This study investigated the biosorption process kinetics and the associated microbial community. Seed sludge from the aeration tank of a wastewater treatment plant in Singapore was acclimated with synthetic wastewater formulated to contain colloidal (ca. 40%) and dissolved COD (Chemical Oxygen Demand). The COD removal kinetics and the individual mechanisms involved were determined by subjecting the acclimated sludge to increasing organic loadings (0.1, 0.5, 1.0, and 2.5 g COD per g suspended solid) of synthetic wastewater. Under pH 7, sorption capacity of the acclimated sludge increased with organic loading. Comparison between live and azide-inactivated sludge revealed that under organic loading of 1.0 g COD/g SS, a level similar to a typical contact tank for carbon capture, at least 74% of the biosorption capacity was contributed by carbon storage. Kinetics data suggested that carbon storage was the predominant mechanism in the first 20-30 min of the carbon capture biosorption process. The removal kinetics of dissolved COD can be represented by a pseudo-second-order model and intraparticle diffusion model. These suggested the rate-limiting steps could include chemisorption and intraparticle diffusion. On the other hand, colloid COD removal can be described as a first order process with respect to initial organic loading. Taxa capable of carbon-storage which include Chloroflexi, Thiobacillus sp., Xanthobacter sp., Mycobacterium sp., and Nakamurella sp., were uniquely detected in the acclimated sludge.

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#### 1. Introduction

Conventional activated sludge-based technologies used in wastewater treatment rely on bio-oxidation through aeration for pollutant removal, and are thus energy intensive. Lately, there has been a paradigm shift on the role of wastewater treatment plants (WWTPs), from pollutants removal to resource recovery. Moreover, global warming concerns call for WWTPs which are more environmentally sustainable. Due to such concerns, the AB-process has been received considerable attention. The AB-process is a two-stage approach with pre-treatment in an extremely high loaded biosorption stage (A-stage) for carbon capture, followed with a treatment

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solved organics and ammonia. The organic carbon captured is then recovered as energy from the solids train containing A- and Bstage sludge through biogas generation in anaerobic digesters [1]. Through this approach, energy can therefore be recovered from the wastewater influent to improve the energy self-sufficiency of treatment plants. Researchers had attempted to demonstrate the feasibility of

in a low loaded biological stage (B-stage) ensuring removal of dis-

carbon capture (energy) from raw municipal wastewater using biomass, i.e. activated sludge, anaerobic sludge or acclimated sludge [2-8]. Earlier studies had concluded the process involved solely physical-chemical processes [2,3], which is consistent with the common definition of a metabolically-passive "biosorption" process [9]. Xiao et al. had, however, reported active sludge tended to give better biosorption than inactive sludge. It was then concluded biosorption is a combination of metabolically-mediated biological and physical-chemical processes [10]. Lim et al. [5] reported the biological component involved in carbon capture by activated sludge can be attributed mainly to carbon storage. Carbon storage can occur in the form of poly-hydroxyalkanoates

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Nomenclature

Ap	Intraparticle diffusion constant
ATP	Adenosine triphosphate
ATU	Allylthourea
CCB	Carbon capture biosorption
С	Dissolved COD at t contact time (mg COD/L)
Се	Dissolved COD at equilibrium (mg COD/L)
Со	Initial dissolved COD, mg COD/L
Cor	Organic loading
COD	Chemical oxygen demand
COD	Colloidal COD fraction
COD	Dissolved COD fraction
CODT	Total COD fraction
DGGE	Denatured gradient gel electrophoresis
DO	Dissolved oxygen
EPS	Extracellular polymeric substance
EPSp/EP	Ss Ratio of protein to polysaccharide fraction in EPS
F/M rati	o Food-to-Microorganisms ratio
$k_1$	Rate constant of pseudo-first-order process $(min^{-1})$
$k_2$	Rate constant of pseudo-second-order process
2	(g/mg min)
$k_{c\alpha}$	Rate constant of colloidal COD removal with respect
cu	to organic loading (mg COD/g COD L min)
<i>k</i> <sub>f</sub>	Rate constant of film mass transfer $(min^{-1})$
$k_n$	Rate constant of intraparticle diffusion $(g/g min^{0.5})$
MLSS	Mixed liquor suspended solids
OTP	Operational taxonomic unit
PCR	Polymerase chain reaction
PHA	Polyhydroxyalkanoate
Q <sub>C.t</sub>	Amount of colloidal COD sorbed at t min contact
	time per unit weight of sorbent (mg/g)
Qse	Amount of dissolved COD sorbed at equilibrium per
	unit weight of sorbent (mg/g)
Qst	Amount of dissolved COD sorbed at t min contact
-0,0	time per unit weight of sorbent (mg/g)
Q <sub>T.t</sub>	Overall capacity, amount of total COD sorbed at t
	min contact time per unit weight of sorbent $(mg/g)$
$R_{C}$	Specific colloidal COD removal rate
Rs	Specific dissolved COD removal rate
$R_T$	Specific total COD removal rate
SBR	Sequencing batch reactor
SRT	Sludge retention time
SS	Suspended solids
t	Contact time t, min
TAG	Triacylglycerols
TSS	Total suspended solids
WWTP	Wastewater treatment plant
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(PHA) [11] and triacylglycerols (TAG) [12]. In addition, bacteria in activated sludge can also form other storage products such as glycogen [13]. Therefore, insofar as carbon capture is concerned, usage of the term "biosorption" alone can cause confusion as the phenomenon can go beyond physical-chemical process(es). To better describe, without ambiguity, the phenomenon where biomass capture, concentrate and retain carbon within the sludge flocs, Lim et al. [5] had proposed the term "carbon capture biosorption" (hereafter abbreviated as "CCB"). CCB could involve (i) surface sorption: metabolically-passive uptake of organics; (ii) carbon storage: metabolically-mediated uptake of organics and accumulated within the cell; and (iii) carbon entrapment: entrapment of larger particles in the open structure of the sludge floc, facilitated by extracellular polymeric substances (EPS) [5].

It has been reported removal of the colloidal fraction reaches equilibrium in about 10-20 min, whereas removal of the dissolved fraction reaches equilibrium in 40–45 min [2,3,5,6]. However, there have been few reports on the predominant mechanism(s) and possible limiting steps involved, if any, throughout the CCB process. To the authors' knowledge, despite various adsorption kinetic models having been used to describe the adsorption of metal ions, few such attempts have been reported for CCB [7]. Guellil [2] reported CCB of total COD obeyed the first order kinetic model. Whereas a more recent study conducted by Modin et al. [7] reported that the sorption of TSS and dissolved TOC occurred by a near-instantaneous sorption event followed by a slower process that obeyed first order kinetics. Wei and Hong [14] demonstrated the overall biosorption process for organic pollutants was well described by the pseudosecond-order model, although the kinetic data were for specific pollutants and the organic loading applied was not reported. There are obviously gaps in the understanding of CCB capacity and removal kinetics of COD components at loadings higher than 0.4 g COD/g SS. Typical organic loadings observed in the contact tank of the AB-process was 0.18-0.63 g COD/g SS [1], but previous studies on CCB had been conducted at organic loadings of 0.1-0.33 g COD/g SS [2,3,5,6]. There is also still a relative lack of information on the microbial communities involved in CCB except for the earlier attempt by Lim et al. [5] using DGGE.

In this study, the CCB capacity of seed sludge was enhanced through feast-famine cycle acclimation, under low Food-to-Microorganisms (F/M) ratio. The investigation had attempted to elucidate the predominant mechanism(s) involved in CCB under increasing organic loadings. The COD removal kinetics and the individual mechanisms involved were determined by subjecting the acclimated sludge to increasing organic loadings (0.1, 0.5, 1.0, and 2.5 g COD/g SS) of synthetic wastewater. Dynamics of the removal of COD fractions during CCB were analysed using pseudo-first-order and pseudo-second-order kinetic models. Microbial community analyses, with next-generation sequencing technique, were also attempted to identify the groups associated with higher CCB capacity.

#### 2. Materials and methods

#### 2.1. Sludge acclimation

Seed sludge was obtained from the aeration tank of a local WWTP in Singapore. Sludge acclimation was carried out at 30°C, pH 6.8-7.3, in a Sequencing Batch Reactor (SBR) with a cycle time of 6 h comprising 6 stages: (i) filling, 5 min; (ii) contact, 10 min; (iii) sludge discharge, 2 min; (iv) aeration, 290 min, (v) settling, 38 min; and (vi) decantation, 15 min. Working volume was 61. The mixed liquor suspended solids (MLSS) of the seed sludge inoculated was about 3 g/L. The reactor was operated under F/M 0.1, volumetric exchange ratio of 50%, DO 2.0-2.2 ppm, and 13 days SRT (sludge retention time). The synthetic wastewater (SW1) was formulated to simulate effluent from the Primary Settling Tank which had 42% dissolved COD, 54% colloidal COD and 4% particulates COD. The SW1 was formulated with sucrose, 50 mg/L; sodium acetate trihydrate, 179 mg/L; starch (cooked), 150 mg/L; urea, 62.5 mg/L; yeast extract, 1 mg/L; bacto peptone, 1 mg/L; ammonium chloride, 180 mg/L; and monopotassium phosphate, 23.5 mg/L. The SW1 was prepared using tap water and cooked before use. The total COD of cooked SW1 was then 300 mg COD/L with about 40% in colloidal form and the balance dissolved. The mixture was supplemented with a trace elements solution [15]. ATU was added to inhibit nitrification. The sludge acclimated with SW1 is hereafter designated as "Sludge A1".

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