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Heavy Metal Biosorption Efficiencies of Expanded Bed Biofilm Reactor and Sequencing Batch Biofilm Reactor

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Conventional physico-chemical processes for removing heavy metals from industrial effluents are high in chemical usage and produce large amounts of chemical sludges, which in turn needs secure disposal. Biological processes to overcome these problems have been developed for treatment of wastewaters containing heavy metals. Heavy metal biosorption efficiencies of an expanded bed biofilm reactor and a sequencing batch biofilm reactor were studied, using zinc and copper containing wastewaters. Without adding any precipitant, the processes could achieve Zn removal of 60-95 and 50-80 %, respectively for expanded bed biofilm reactor and sequencing batch biofilm reactor and Cu removal of 50-70 % by using sequencing batch biofilm reactor. Metal biorecovery carried out in this study achieved 84.5 and 82.0 % metal recovery for Cu and Zn, respectively. This shows a promising potential for bio-recovery *via* this low cost anaerobic process, which becomes also a means of reducing sludge volume and weight. This bio-recovery prevents discharge of metals to the environment and conserves these nonrenewable resources. The processes used were operated in continuous mode (expanded bed biofilm reactor) and sequencing mode (sequencing batch biofilm reactor). Thus the Monod growth model could be used, with biomass measured during aeration stage for the sequencing batch biofilm reactor. The kinetic parameters obtained for the processes for μ_H, K_H, d_H and Y_H are 0.230 d^{-1}, 482.998 mgL^{-1}, 0.038 day^{-1} and 0.076 mg/mg for the expanded bed biofilm reactor and for sequencing batch biofilm reactor system: 0.235 d^{-1}, 73.190 mgL^{-1}, 0.008 d^{-1} and 0.020 mg/mg for Zn removal and 0.092 d^{-1}, 284.590 mg L^{-1}, 0.003 d^{-1} and 0.312 mg/mg for Cu removal. Compared to a conventional physico-chemical process, treatment of a cubic meter of wastewater with Zn would require about 1390 mg of chemical and would generate 1736 mg of chemical sludge. No chemical is required here and no chemical sludge is generated instead 545 mg of metal is recovered.

Key Words: Biofilm, Zinc, Copper, Biosorption, Bio-recovery.

INTRODUCTION

Heavy metals released into the environment have been increasing continuously as a result of industrial activities and technological development, posing a significant threat to environment and public health because of their toxicity, accumulation in the food chain and persistence in nature[1]. Increasing awareness of accumulation of heavy metals in the environment has led to a quest for new and improved "clean" technologies. The contamination of the environment by heavy metals is of growing concern because of the numerous health risks to animals and humans following exposure[2]. Common sources of metal polluted wastewaters include metal finishing operations, such as electroplating plants, as well as many mining, nuclear and electronics industries. All of these contribute to anomalously high concentrations of metals in the environments relative to the normal background levels[3], leading to their accumulation in the food chain. Heavy metal ions are accumulated by microorganisms and this may instead be employed as a means of removing and recovering metals from waste streams[4]. Physico-chemical methods, such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange and membrane technologies have been widely used to remove heavy metal ions from industrial wastewater. These processes may be ineffective or expensive, especially when the heavy metal ions are in solutions containing in the order of 1-100 mg dissolved heavy metal ions/L^5. Biological methods such as biosorption/bioaccumulation for the removal of heavy metal ions may provide an attractive alternative to physico-chemical methods[6]. Wastewater treatment plants are expected to control the discharge of heavy metals to the environment. However, with new stricter regulations aimed at protecting the environment, wastewater treatment authorities are faced with problems

of disposal of toxic heavy metal laden sludges[7]. Toxicity of heavy metals is well documented[8]. As metals are non-renewable resources, metals should be recovered instead of disposed. Numerous processes exist for removing heavy metal ions from liquid solutions including chemical precipitation, chemical oxidation or reduction, ion exchange, membrane filtration and carbon adsorption[1]. However, these processes have significant disadvantages such as incomplete metal removal, high reagent or energy requirements, generation of toxic sludge or other waste products and are generally very expensive when the contaminant concentration is in the range (10-100) mg/L. Biological processes have shown potential for heavy metal removal[9-11]. In a biofilm processes, dissolved organic materials and nutrients are directly absorbed from bulk phase to the biofilm by means of concentration gradient, where dissolved heavy metals are adsorbed onto and into biofilm as a result of interactions between metal ions and the negatively charged microbial surfaces, gradually reducing the aqueous metal concentration[12]. Microbial metal accumulation has received much attention in recent years, due to the potential use of microorganisms for treatment of metal polluted water or wastewater streams[13]. The potential for metal bio-recovery is studied here The use of bacteria for biosorption is a fast growing field in metal remediation because of their ubiquity, ability to grow under controlled conditions and small size. The bacterium used in this work, *Arthrobacterviscosus*, is a good exopolysaccharide producer, which by itself allows foreseeing good qualities for support adhesion and for metal ions entrapment[14].

Biological growth kinetics: Kinetic parameters for biomass growth in expanded bed biofilm processesare to be obtained here. Using the simplest of kinetic models, the Monod model applying to biomass, the balances give kinetic parameters μ_H, K_H, d_H and Y_H. To obtain these parameters, the Monod equation for the electron acceptor can be expressed as,

$$\mu = \frac{\mu_H S}{K_H + S} \quad (1)$$

$$\mu = \frac{1}{\theta_x} + d_H \quad (2)$$

where μ: specific growth rate (day^{-1}); K_H: half saturation coefficient (mg/L); d_H: death coefficient (day^{-1}); S: substrate concentration (mg/L).

Substituting for μ in the above equation for biomass growth and rearranging,

$$\frac{K_H}{S\mu_H} + \frac{1}{\mu_H} = \frac{\theta_x}{1 + \theta_x d_H} \quad (3)$$

Values for biomass growth kinetic parameters K_H and μ_H values can be obtained by plotting $\frac{\theta_x}{1+\theta_x d_H}$ *versus* $\frac{1}{S}$. At steady state, $\frac{dS}{dt} = 0$, therefore the mass balance for biomass gives,

$$\mu = \frac{Q_i Y_H (S_i - S_e)}{VX} \quad (4)$$

where Q: flowrate (L/s); Y_H: growth coefficient (mg/mg); V: reactor volume (L); X: biomass concentration (mg/L).

Substituting $\mu = \frac{1}{Q_x} + d_H$ in the above equation and rearranging gives,

$$\frac{1}{Y_H \theta_x} + \frac{d_H}{Y_H} = \frac{Q_i (S_i - S_e)}{VX} \quad (5)$$

Values for d_H and Y_H can be obtained by plotting $\frac{Q_i (S_i - S_e)}{VX}$ *versus* $\frac{1}{\theta_x}$.

EXPERIMENTAL

Metal solutions and wastewater: Zinc and copper were chosen for study as they are commonly used in industries, such as electroplating as plating metals, rubber products as initiators, *etc*. Stock solutions (1000 mg L^{-1}) were prepared in distilled water by using $ZnCl_2$ (Merck) and $CuSO_4$ (Merck). All working solutions were prepared by diluting these stock solutions with distilled water. To ensure wastewater composition consistency, simulated wastewater feed with glucose as carbon source and salt medium (Table-1) was used. Bicarbonate buffer of pH 7 maintained the system at pH at 7 to 8. Analytical grade reagents were used in all cases.

TABLE-1
SIMULATED WASTEWATER SALT, BUFFER AND NUTRIENTS

	Content	Concentration (mg/L)
Carbon source	Glucose	Varies
Salt solution	NH_4NO_3	360
–	$MgCl_2 \cdot 6H_2O$	103
–	$CaCl_2 \cdot 2H_2O$	7.72
–	$FeCl_3 \cdot 6H_2O$	0.51
–	$MnCl_2 \cdot 4H_2O$	0.51
Buffer	$NaHCO_3$	630

Expanded bed biofilm reactor (EBBR): The expanded bed bioreactor column of 7 L volume was made of Plexi-glass (1 m height, 10 cm internal diameter) (Fig. 1). This reactor was packed with granular activated carbon (GAC) of 0.25-2.00 mm particle size, with mean diameter of 1.30 mm and particle density of 1200 kg m^{-3}. At start up, the reactor was seeded with a mixed culture acclimatized to simple and complex organics. The reactor was continuously fed in the up flow mode by a variable speed peristaltic pump, at an inlet flow rate, Q of 21 L/day. Initially, hydraulic retention time (HRT) was maintained at 8 h. The feed had glucose as carbon source at chemical oxygen demand (COD) = 3000 mg/L and initially, Zn as the heavy metal at 200 mg/L. An aerator maintained dissolved oxygen (DO) at 2.0-2.5 mg/L and a recycle pump provided hydrodynamic and expansion conditions so as to maintain 30 % bed expansion, where bed clogging is avoided.

Sequencing batch biofilm reactor (SBBR): SBBR reactor of volume 2 L were operated to compare the system efficiency with the EBBR. At start up, the reactor were also seeded with a mixed culture acclimatized to simple and complex organics. The reactor was fed with a simulated wastewater

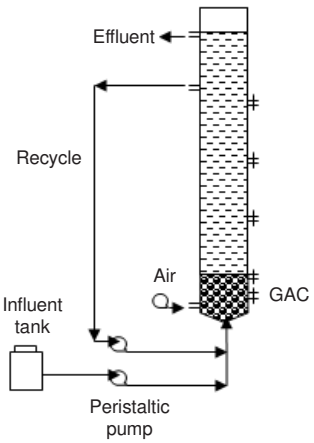


Fig. 1. Expanded bed biofilm reactor (EBBR) set up

with COD = 500 mg/L and metal (Zn or Cu) at 10 mg/L at start up. The HRT was maintained at 2 days.

Metal recovery bio-fermentation: A 2 L conical flask was employed as a sequencing batch bio-recovery reactor operated at HRT of 5 days. It was fed with the sludge obtained from EBBR or SBBR and stirred without any aeration. The dissolved oxygen would drop to zero and precipitates a white precipitation for ZnS and green precipitation for CuS would form which settled at the bottom of the flask. This was decanted to remove the biomass and concentrate the metal salts. Metal contents in the sludge after and before anaerobic digestiontreatment were measured using acid digestion method. The sludg ewas digested in an anaerobic digestion reactor for metal recovery followed by acid treatment for metal dissolution and separation from organic materials.

Sample analysis: Sampled effluent from each of the stated reactors was filtered through a 0.45 µm pore membrane filter (Whatman) and the filtrate was analyzed for COD and heavy metals. Metal concentration was analyzed using 5100PC atomic absorption spectroscopy (AAS- Perkin Elmer, USA) while, COD was spectrophotometrically analyzed using DR 2010 spectrophotometer (HACH) following methods as in the HACH Spectrophotometric Instrument manual.

RESULTS AND DISCUSSION

Aquatic organisms are adversely affected by heavy metals in the environment. The toxicity is largely a function of the water chemistry and sediment composition in the surface water system. Many organisms are able to regulate the metal concentrations in their tissues. Fish and crustacea can excrete essential metals, such as Cu, Zn and Fe that are present in excess. Some can also excrete non-essential metals, such as mercury and cadmium, although this is usually met with less success[15]. Research has shown that aquatic plants and bivalves are not able to successfully regulate metal uptake[15]. Thus, bivalves tend to suffer from metal accumulation in polluted environments. In estuarine systems, bivalves often serve as biomonitor organisms in areas of suspected pollution.

Metal biosorption study: In the EBBR, the interaction between biofilm and heavy metals resulted in the adsorption of heavy metals onto biofilm, which gradually reduced the aqueous metal concentrations (Fig. 2a). Presence of Zn at high concentration of 200 mg/L did not seem to diminish COD

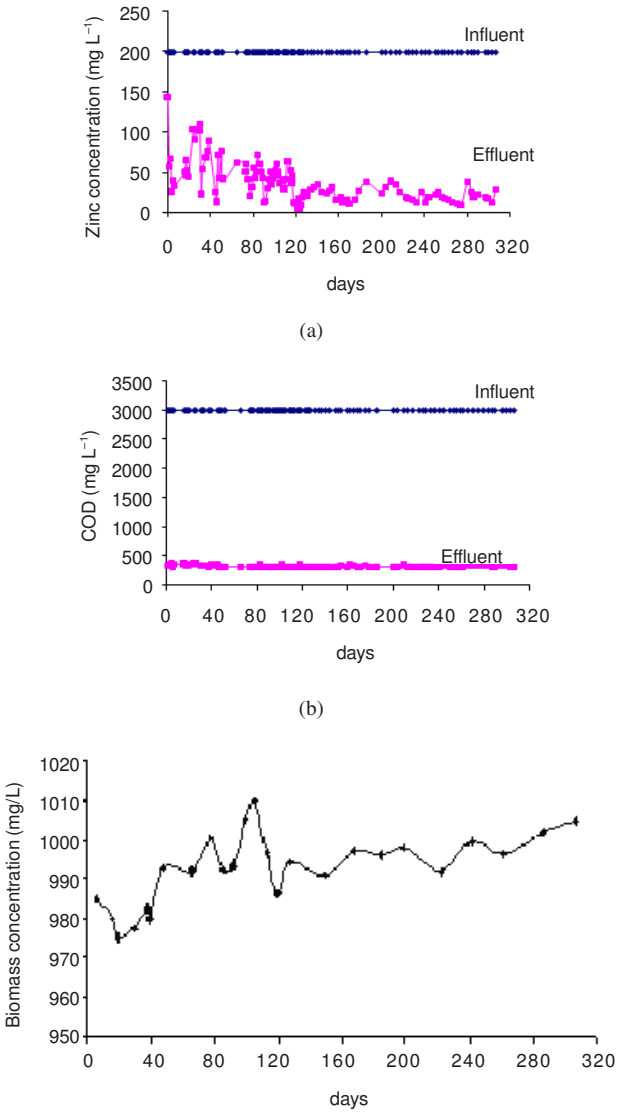


Fig. 2. Zinc removal study using EBBR reactor

removal and biomass growth. The removal range for Zn was *ca.* 60-95 % (Fig. 2a) and COD removal was about 87-90 % (Fig. 2b)[16] studied Zn removal from wastewater using fluidized bed reactor and obtained *ca.* 92-95 % removal of Zn. The effects of biomass concentrations on removal performance were also shown in this study. Simultaneous reaction of sorption and precipitation of metals were found to occur in the sequencing batch reactors. In the SBBR reactor, high biomass concentration was reached after 40th day, giving good removal of Zn and COD, which were more than 70 % (Fig. 3). This study shows that the biomass concentration in the reactor has to be kept at relatively high levels, *ca.* 10,000 and 3500 mg/L in EBBR and SBBR, respectively to achieve high removal of COD and metal Zn. Such high biomass concentrations are possible using biofilm processes, but not suspended biomass systems without adversely affecting effluent quality. Studies on Cu removal using SBBR showed good removal of *ca.* 50-70 and 40-70 %, respectively for Cu and COD (Fig. 4), also at biomass concentrations of *ca.* 3500 mg/L. This bio-removal of Cu does not require chemical addition and results in a biological sludge whose volume and weight can be further reduced, such as through anaerobic digestion.

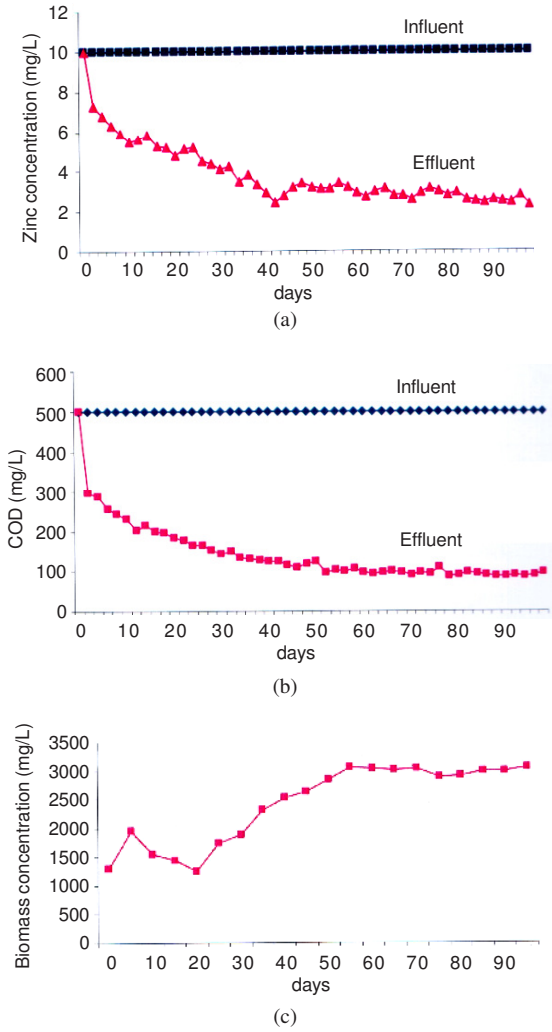
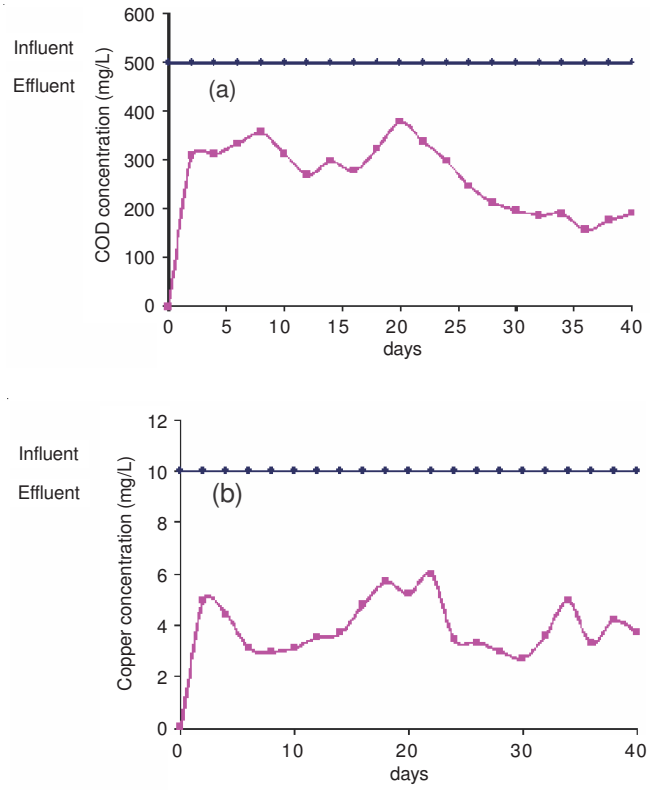


Fig. 3. Zinc removal study using SBBR reactor



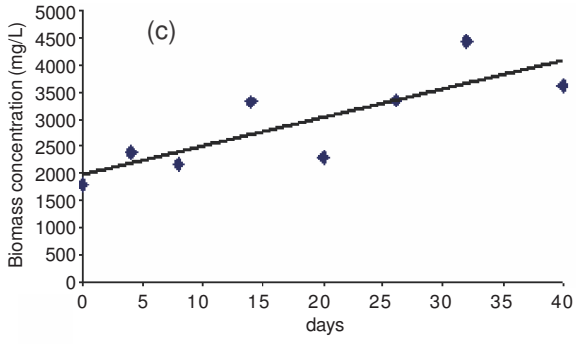


Fig. 4. Copper removal study using SBBR reactor

Metal bio-recovery: The bio-recovery of metal carried out in this study achieved *ca.* 84.5 and 82.0 % metal recovery for Cu and Zn, respectively. This shows a promising potential for bio-recovery *via* this low cost anaerobic process, which becomes also a means of reducing sludge volume and weight. This bio-recovery prevents discharge of metals to the environment and conserves non-renewable resources.

Biological growth kinetics: The Monod growth kinetic parameters were graphically calculated using the data obtained from the studies. The values of the parameters, specific growth rate (μ) and half saturation coefficient (K_H) are dependent on the concentration of the limiting nutrient, which can be the carbon source, the electron donor, the electron acceptor, nitrogen or any other factor needed by the organisms for growth[17].

Readily biodegradable substrates are characterized by high values of mand low values of K, whereas slowly biodegradable substrates have low mand high K values. By plotting the graphs as shown in Figs. 4-6, the growth kinetics parameters were obtained for the expanded bed reactor and sequencing batch reactor.

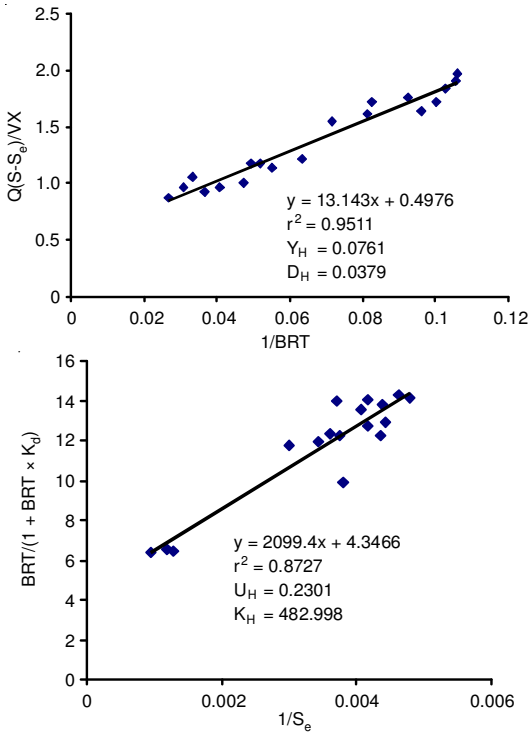


Fig. 5. Plots to obtain growth kinetic parameters for zinc removal study using EBBR reactor

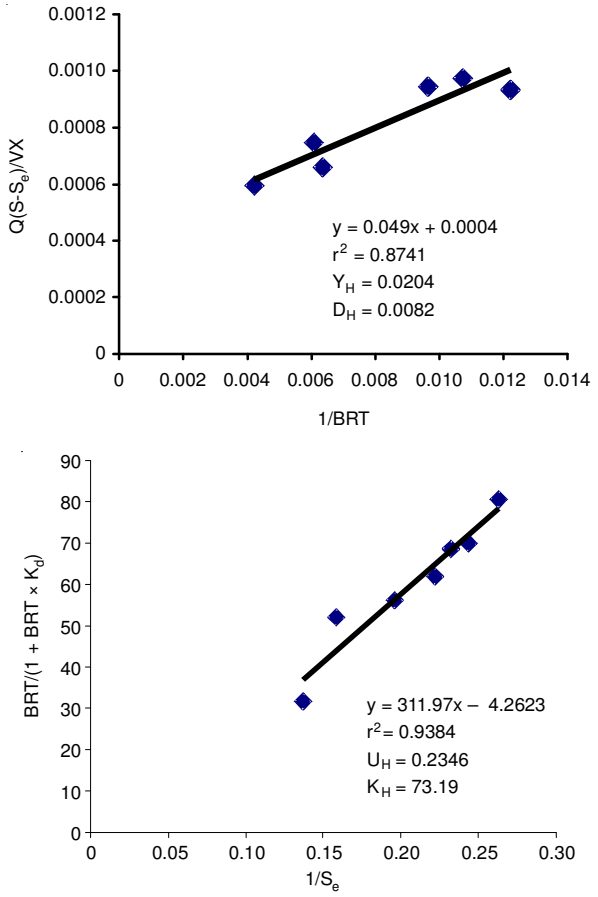


Fig. 6. Plots to obtain growth kinetic parameters for zinc removal study using SBBR reactor

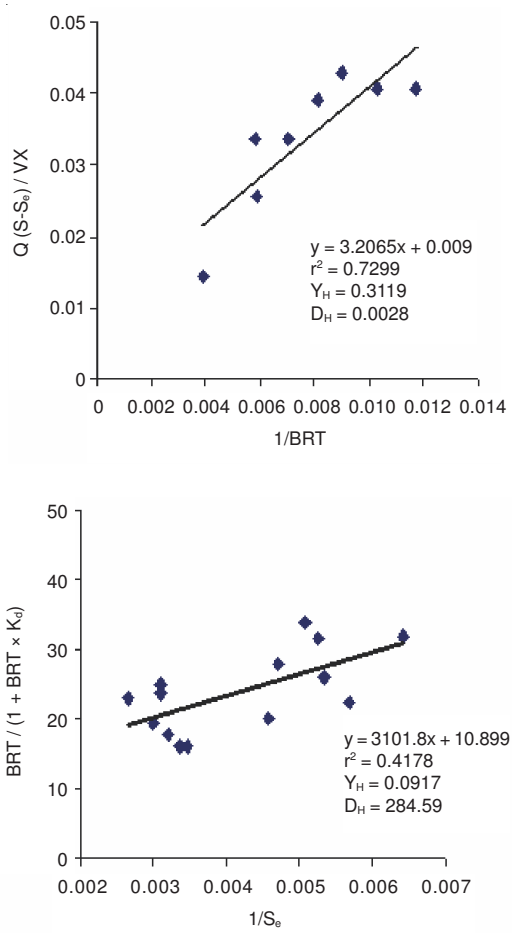


Fig. 7. Plots to obtain growth kinetic parameters for copper removal study using SBBR reactor

The kinetic parameters obtained from this study and others are shown in Table-2 for comparison. A point that stands out from the data is that the system for Zn has higher growth rate than that for Cu. These kinetic parameters are needed for scale up purposes, which willbe applied to the next stage of this study, the pilot plant stage (Fig. 7).

TABLE-2
COMPARISON OF MONOD GROWTH KINETIC PARAMETERS

Growth kinetic parameters				References
D_H (day^{-1})	K_H (mg L^{-1})	Y_H (mg/mg)	μ_H (day^{-1})	
0.140	25	0.490	2.900	[19]
–	–	0.490	0.301	[15]
0.110	–	–	–	[18]
–	4558	0.390	1.128	[19]
0.0028	284.59	0.3119	0.0917	SBBR copper (this study)
0.0082	73.19	0.0204	0.2346	SBBR zinc (this study)
0.0379	483.0	0.0761	0.2301	EBBR zinc (this study)

Conclusion

This study has shown that the biofilm processes employed can be used to substantially remove both organics and heavy metal from wastewaters and has potential to be further developed into a low cost, environmentally friendlier process for treating wastewaters containing organics and heavy metals. This technology is based on the biosorption of heavy metals onto biomass surface in an expanded bed bioreactor and sequencing batch bioreactor, is viable for removing heavy metals from industrial wastewaters. The study also shows that the metals can also be substantially recovered biologically. This bio-removal/biorecovery system form affordable technologies as no chemical was employed and no chemical sludge was produced; instead cleaner water and metal salts were produced.

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