

Revised manuscript for *Bioresource Technology*

Date: 2014-08-14

**Effect of granular activated carbon addition on the effluent
properties and fouling potentials of membrane-coupled expanded
granular sludge bed process**

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ABSTRACT:

To mitigate membrane fouling of membrane-coupled anaerobic process, granular activated carbon (GAC: 50 g/L) was added into an expanded granular sludge bed (EGSB). A short-term ultrafiltration test was investigated for analyzing membrane fouling potential and underlying fouling mechanisms. The results showed that adding GAC into the EGSB not only improved the COD removal efficiency, but also alleviated membrane fouling efficiently because GAC could help to reduce soluble microbial products, polysaccharides and proteins by 26.8%, 27.8% and 24.7%, respectively, compared with the control system. Furthermore, excitation emission matrix (EEM) fluorescence spectroscopy analysis revealed that GAC addition mainly reduced tryptophan protein-like, aromatic protein-like and fulvic-like substances. In addition, the resistance distribution analysis demonstrated that adding GAC primarily decreased the cake layer resistance by 53.5%. The classic filtration mode analysis showed that cake filtration was the major fouling mechanism for membrane-coupled EGSB process regardless of the GAC addition.

Keywords: Membrane-coupled anaerobic process; membrane fouling; granular activated carbon; membrane resistance; soluble microbial products.

1. Introduction

Due to the importance of energy recovery and resources recycling, anaerobic membrane bioreactor (AnMBR) and membrane coupled anaerobic processes have become more and more promising technologies for wastewater treatment in recent years (Stuckey, 2012). Although AnMBR has advantages such as high removal efficiency of organic matters and small footprint etc., there are still some challenging issues. Particularly, membrane fouling is the key challenge for the widespread applications of AnMBR (Guo et al., 2012; Meng et al., 2009).

It is reported that soluble microbial products (SMP) or loosely bound extracellular polymeric substances (EPS), which are produced from cell metabolism and lysis, play an important role in membrane fouling (Lin et al., 2009; Wang et al., 2014). Barker and Stuckey (1999) have reviewed the advanced treatments such as activated carbon, synthetic resin adsorption, ozonation, oxidation, coagulation and breakpoint chlorination for reducing SMP. Among all the options, granular activated carbon (GAC) is the most effective method for the removal of SMP.

As GAC has high removal efficiency of SMP than others (powdered active carbon, synthetic resin etc.) (Barker & Stuckey, 1999), several researchers investigated the GAC addition in the membrane bioreactor (MBR) system to alleviate membrane fouling. Johir et al. have reported that the addition GAC as a suspended medium in a submerged membrane bioreactor (SMBR) achieved high organic removal (95%) as well as reduced transmembrane pressure (TMP) development by 58%, as GAC addition eliminated the organic molecules in SMP with molecular weight of

1200-150 Dalton (Da) (Johir et al., 2013; Johir et al., 2011) . Kim et al. (2010) have also found that GAC addition into an anaerobic fluidized bed membrane bioreactor could reduce membrane fouling rate efficiently.

To date, few studies have explained the mechanisms or given the reasons of GAC alleviating membrane fouling in membrane-coupled anaerobic reactors. Thus, it is necessary to know which kinds of organic matters are easily absorbed and removed by GAC and how GAC affect the filtration resistance distribution in membrane-coupled anaerobic reactors system. In this study, the effect of GAC addition on the performance of an expanded granular sludge bed (EGSB) was investigated. The properties of effluents were characterized. The short-term experiments on membrane fouling potentials and mechanisms were carried out in a dead-end ultrafiltration (UF) setup.

2. Materials and methods

2.1 EGSB setup

As shown in supplementary data, the performance of two lab-scale EGSBs (EGSB1 and EGSB2) fed with synthetic wastewater were examined in parallel during three months operation. GAC with the concentration of 50 g/L was added into EGSB1 at the beginning of the operation. The GAC concentration was chosen based on the study of Kim et al. (2010). EGSB2 was a control system without GAC addition. The effective working volume of each EGSB was 3 L (diameter of 50 mm and length of 1800 mm), and the effluent flow rate was set at 0.75 L/h, corresponding to a hydraulic retention time (HRT) of 4 h. Some portion of mixed

liquor on the top was recycled back to the reactor with a liquid upflow velocity of 10 m/h. Both of the reactors were inoculated with 10 g/L granular sludge (with the average particle size of 940 μm) originating from a large-scale upflow anaerobic sludge blanket of a soybean wastewater treatment plant in Harbin, China. The granular sludge was washed using deionized (DI) water for three times before inoculation.

In order to simulate the domestic sewage, the synthetic wastewater consisted of glucose (200 mg/L), sodium acetate (150 mg/L), NH_4Cl (150 mg/L), KH_2PO_4 (22 mg/L), NaHCO_3 (400 mg/L), and a mixture of trace elements. The feed solution contained 310-360 mg/L of chemical oxygen demand (COD), 35-45 mg/L of $\text{NH}_4^+\text{-N}$, 4-5 mg/L of TP, and pH value of 7.0-7.5.

2.2 Adsorbents and static adsorption tests

The GAC was made of coconut shell from Tianjin Binhai Kody Company. The particle size of GAC was between 500 and 1700 μm (screen mesh: 10 meshes to 30 meshes). It had a BET surface area of $867 \pm 10 \text{ m}^2/\text{g}$.

GAC were washed with DI water for several times until the COD of the supernatant was less than 5 mg/L (limit of detection) before used. GAC static adsorption experiment was carried out in a 1L baker with magnetic stirrer. GAC with the mass concentration of 50g/L was added in the baker. The solution stirred at 150 rpm and 25°C for 24h. The supernatant samples were taken out for COD analysis at 0, 2h, 4h, 12h and 24h, respectively.

2.3 Short-term UF tests

Bench scale short-term dead-end ultrafiltration (UF) tests were carried out to study the membrane fouling potential of the EGSB effluents during 75-80 days. The effluents samples were collected from the outlets of EGSB1 and EGSB2 (Sample 1 from EGSB1: S1; Sample 2 from EGSB2: S2) for the short-term UF tests. Each UF test was carried out in triplicates.

The filtration system consisted of a nitrogen gas cylinder, an UF cell and an electric balance and a computer (supplementary data). Flat sheet polyethersulfone (PES) UF membranes (MWCO 100 kDa, OM100076, Pall, USA) with an effective surface area of 43.01 cm² were used. The volume of the UF cell (Amicon 8400, Millipore, USA) was 350 mL without stirring. The membrane was placed at the bottom of the cell with glossy side towards the bulk solution. Nitrogen gas was used to drive the feed solution through the membrane at a constant pressure of 30 kPa . The filtrate flowed into a 500 mL beaker on the electronic balance which was connected to a computer. The weighting data were automatically logged every five seconds.

2.4 Membrane resistance model

To evaluate fouling behaviors of the membrane, Darcy's law was applied to estimate the total fouling resistances as shown in Eq. (1)

$$R_t = \frac{\Delta P}{\mu J} \quad (1)$$

Where J is the final permeate flux, ΔP is trans-membrane pressure, μ is dynamic viscosity, and R denotes the resistance.

$$R_t = R_m + R_{cp} + R_p + R_c \quad (2)$$

$$R_m = \frac{\Delta P}{\mu J_0} \quad (3)$$

$$R_{cp} = R_t - \frac{\Delta P}{\mu J_1} \quad (4)$$

$$R_c = \frac{\Delta P}{\mu J_1} - \frac{\Delta P}{\mu J_2} \quad (5)$$

As shown in equation (2), R_t , R_m , R_{cp} , R_p and R_c are total, membrane, concentration polarization layer, pore blocking and cake layer resistances, respectively (Li & Wang, 2006). R_m is determined by filtering the DI water through the clean membrane; J_0 is the permeate flux of DI water filtered through the clean membrane (from (3)); R_{cp} is calculated by filtering the DI water through the fouled membrane; and J_1 is the final permeate flux (from (4)). R_c is determined from the difference in resistance before and after gentle membrane cleaning to remove the cake layer using a sponge, and J_2 is the later flux (from (5)).

2.5 Modeling for membrane fouling process

The flux decline of UF in the dead-end cell under constant pressure could be described by different blocking mechanisms: complete blocking, standard blocking, intermediate blocking and cake filtration (Shen et al., 2010). The equations for different membrane blocking mechanisms are listed below: (1) Complete blocking: $-J+J_0=aV$; (2) Standard blocking: $1/t+b=J_0/V$; (3) Intermediate blocking: $-\ln J+\ln J_0=cV$; (4) Cake filtration: $1/J-1/J_0=dV$, where V is the volume of the feed water; a , b , c and d are all constants.

2.6 Analytical methods

COD was measured according to Standard Methods (CEPB, 2002). Turbidity was

determined by the Turbidity Meter (HI-98713-02 ISO, HANNA, US). Ultraviolet absorbance at 254 nm (UV_{254}) was determined by a spectrophotometry (SPECORD 50 PLUS, Germany). Particle size distribution was measured using MasterSizer Laser Diffraction Particle Size Analyzer (Mastersizer 2000, Malvern Instruments, England). The SMP was obtained by measuring the dissolved total organic carbon (TOC) in the effluents. The effluent sample was centrifuged at 4000 rpm for 10 min, and then filtered through a 0.45 μ m membrane. TOC concentration was evaluated using a TOC analyzer (multi N/C 2100S, Analytic Jena, Germany). The concentrations of protein in SMP (SMP_{pr}) were measured by the Lowry method (Lowry et al., 1951). The concentration of polysaccharide in SMP (SMP_{ps}) were determined by the phenol-sulfuric method (DuBois et al., 1956). The analyses were all conducted in duplicate, and their average values were reported.

The fluorescence excitation-emission (EEM) spectrometry was used for obtaining the information of the SMP, and the details could be found in Meng's paper (Meng et al., 2011). Excitation spectrum and emission spectrum was scanned from 220 to 450 nm at 5 nm increments and 250 to 550 nm at 5 nm increments, respectively.

3. Results and discussion

3.1 Effect of GAC addition on the COD removal performance of the EGSB

The results show that the COD removal by GAC static adsorption was 22% (removal of 77mg COD/L) after two hours reaction, and kept stable at around 25% (removal of 90mg COD/L) for the next 10 hours (supplementary data). This indicates that GAC could absorb part of the COD in the influent, and the adsorption

capacity of the GAC for this feed water was 6.67 mg COD /g GAC. As seen in supplementary data, the COD concentration of EGSB1 effluent (S1) dropped more sharply than that of EGSB2 effluent (S2) at the first 10 days and decreased slightly in the next 20 days. After that, S1 and S2 were stable with the concentrations of 50-60 mg/L and 90-100 mg/L, respectively. The results showed that GAC could perform well in EGSB for COD removal efficiencies with the value of 80% (higher than that of 62% in the control system). After 60 days, there were slight fluctuations in both S1 and S2 due to the temperature change (between 15 and 30 °C). The COD removal efficiency increased with increasing the temperature. The results are in line with the report of Gao et al. (2014). From the static adsorption tests, GAC adsorption saturation was reached after 4-8 hours, however, the EGSB with GAC addition still kept higher COD removal performance after 3 month operation. It is known that the COD removal depended on the GAC adsorption and anaerobic granular sludge biodegradation in EGSB1 system. The reason for this phenomenon was that GAC addition not only adsorbed partial COD, but might enhance the activity of the anaerobic granular sludge as well. Ozgun et al. (2013) review that the specific methanogenic activity of the sludge can be improved by activated carbon addition in the AnMBR because the support surface provided by activated carbon in order to protect the biomass from high shear conditions. Similarly, Johir et al. (2013) also found that GAC addition improved the COD removal from 89.2% to 95.6% in a aerobic MBR system during the synthetic wastewater treatment. The reason that the efficiencies were higher than ours might be the membrane-based treatment.

Therefore, conclusion can be drawn that EGSB with GAC addition could improve the COD removal efficiency due to the adsorption and anaerobic sludge activity improvement.

3.2 Effect of GAC addition on the characteristics of the effluents

Effluents from EGSB1 and EGSB2 were taken out for analysis during Day 75-80.

Table 1 presents the characteristics of the effluent samples (named S1 and S2) for both EGSB1 and EGSB2. GAC addition could only reduce the effluent turbidity by 6.8% compared to the control, which indicated that GAC is not able to remove the colloids and large size particles from the effluent significantly. Thus, suspended solid is still a problem to deal with in the EGSB system. Moreover, GAC addition helped to reduce the value of UV_{254} which represented the organic matters containing the functional groups such as C=C and C=O. Furthermore, in comparison with S2, the concentrations of SMP, SMP_{ps} and SMP_{pr} in S1 were 11.7 ± 0.3 , 2.6 ± 0.1 and 7.9 ± 1.2 mg/L, which reduced by 26.8 %, 27.8 % and 24.7 %, respectively. The results are in line with the review of Barker and Stuckey (1999), who stated that GAC was the most effective method for SMP removal in the aerobic activated sludge system. From the results above, it can be concluded that GAC could also help to reduce the dissolved polysaccharides and proteins in the anaerobic reactor.

Table 1

Figure 1 illustrates the particle size distribution of the effluents and Table 2 gives the detail of the data. The average particle size increased a little bit (22.6%) after adding GAC during three month operation. Normally, in aerobic system such as

submerged MBR, adding a certain amount of carriers might break up sludge flocs and cause an increase in the amount of small particles and supernatant total organic carbon, accelerating membrane fouling (Huang et al., 2008; Wei et al., 2006). However, in anaerobic system such as EGSB system, granule formation is strongly influenced by the upflow liquid velocity and HRT. Hence, a short HRT combined with high upflow liquid velocity could increase the density of the granular (Liu & Tay, 2004; Tiwari et al., 2006). Meanwhile, adding GAC could enhance the biofilm attachment. Therefore, the addition of GAC increased the average particle size in the effluent.

Figure 1

Table 2

It has been reported that SMP are complex and play an important role in membrane fouling (Meng et al., 2009). However, it is not clear that which types of proteins and polysaccharides were the main foulants and whether the GAC influences their existence in anaerobic reactors. Therefore, fluorescence excitation-emission spectrometry (EEM) was used to better understand the influence of GAC addition on the components of SMP. The fluorescence spectra data are illustrated in Figure 2 and the peak values are summarized in Table 3. There were four main peaks identified from the fluorescence spectra of SMP samples through the literatures. The first main peak was observed at excitation/emission wavelengths (Ex/Em) of 235-240/340-355 nm (Peak A), which was associated with the simple aromatic proteins such as tyrosine (Baker, 2001; Chen et al., 2003). The second main

241 peak was at the Ex/Em of 275-280/320-330 nm (Peak B), which was related to the
 242 tryptophan protein-like substances (Baker, 2001; Chen et al., 2003). The third peak
 243 at the Ex/Em of 240-260/390-445 nm (Peak C) was described as the fluorescence of
 244 fulvic-like substances (Pons et al., 2004), while the fourth peak (around the Ex/Em
 245 of 290-350/410-435 nm (Peak D)) was identified as a visible humic acid-like
 246 fluorophores (Chen et al., 2003).

247 As seen in Figure 2 (A, B and C), there were no peaks in the feed solution, which
 248 indicated that the feed solution did not contain fluorescent substances. S1 and S2
 249 contained both peaks A and C, representing the existence of aromatic protein-like
 250 substances and fulvic-like substances, respectively. There was no peak B appearing
 251 in S1 suggesting the absence of tryptophan protein-like substances. Therefore, these
 252 aromatic protein-like substances, tryptophan protein-like substances and fulvic-like
 253 substances were generated from the microbial metabolism after three months
 254 operation. Moreover, adding GAC could mainly reduce the tryptophan protein-like
 255 substances. With regard to the fluorescence peak intensity, the values of peak A and
 256 peak C of S1 were both lower than those of S2. It demonstrated that GAC addition
 257 also decreased the concentrations of aromatic protein-like substances and fulvic-like
 258 substances. Johir et al. (2011) compared the properties of SMP in a SMBR with
 259 GAC addition and a control SMBR. The effluent from both SMBRs had negligible
 260 organics, whereas SMP had organics of aminoacid type (Ex/Em: 200-250/ 330-380)
 261 and fulvic acid type substances (Ex/Em: 200-250/ 380-500). However, the peak
 262 intensities of the GAC addition sample were lower than the control one. As such, no

263 matter in aerobic or anaerobic processes, GAC addition could help to reduce the
 264 aminoacid-like substances and fulvic-like substances by adsorption. Overall, adding
 265 GAC in EGSB mainly reduced tryptophan protein-like substances, and following by
 266 aromatic protein-like substances and fulvic-like substances.

267 Figure 2

268 Table 3

269 ***3.3 Effect of GAC addition on the UF membrane fouling potential***

270 ***3.3.1 Flux decline***

271 A short-term dead-end UF system was applied to investigate the membrane
 272 fouling potential of membrane-coupled EGSB process. The feed solutions were
 273 collected from the effluents of two EGSBs during Day 75-80. Figure 3(A) shows the
 274 flux decline tendencies of the effluent samples. The fluxes of both curves dropped
 275 rapidly in the first 60 ml, and after this decreased slowly. The flux decline of S2 was
 276 more severe than S1. Similarly, Kim et al. (2010) also found that GAC addition
 277 reduced the TMP growth rate under a constant flux in an anaerobic fluidized bed
 278 membrane bioreactor. The results of flux decline are quite in line with the reduced
 279 concentrations of SMP in the effluents. Nevertheless, the GAC addition had less
 280 improvement on the turbidity (or suspended solid) of the effluent. Therefore, it can
 281 be concluded that the main reason for GAC mitigating membrane fouling was that it
 282 could improve COD removal and help to reduce SMP in the effluent, but not the
 283 suspended solid. Especially, GAC addition effectively reduced the tryptophan
 284 protein-like substances, and aromatic protein-like and fulvic-like substances came

285 second.

286 **3.2.2 Fouling model and filtration resistance analyses**

287 Classic filtration models were applied to evaluate the fouling potential of EGSB
 288 effluents. The simple regression results of the four models are given in Figure 4. The
 289 R^2 values of S1 and S2 were around 0.65 under complete blocking model (Figure 4
 290 a1 and b1). The values were between 0.92 and 0.98 under standard blocking and
 291 intermediate blocking models (Figure 4 a2, b2, a3 and b3). However, they were both
 292 greater than 0.99 under the cake filtration model (Figure 4 a4 and b4), which
 293 elucidated that the primary fouling model of EGSB effluents was the cake filtration.
 294 The results above also indicated that the average particle size of the effluents was
 295 200-300 μm , which was much larger than the pore size of the membrane (0.01 μm).
 296 Hence, the SMP of the both effluents mainly contributed to the gel cake layer on the
 297 membrane surface. Some previous research also revealed that the cake layer
 298 formation were the main fouling mechanism in membrane-coupled anaerobic
 299 reactors or AnMBRs (Choo & Lee, 1996; Robles et al., 2013).

300 In addition, filtration resistances were analyzed to better understand the alleviation
 301 of membrane fouling by GAC addition. Figure 3 (B) shows the total resistance (R_t)
 302 variation of S1 and S2 with the specific volume. The R_t values of S2 were larger than
 303 S1 from the beginning to the end which coincide with the results of flux decline.
 304 Figure 3 (C) presents the resistance distribution of the two effluents at the end of the
 305 filtration. The R_t of S1 and S2 were $26.2 \times 10^{11} \text{ m}^{-1}$ and $38.5 \times 10^{11} \text{ m}^{-1}$, respectively,
 306 indicating that GAC addition into EGSB reduced the R_t by 32.0 %, compared to the

control one (S2). The membrane resistance (R_m) and pore blocking resistance (R_p) for both effluent were almost the same, with the values of around $3.0 \times 10^{11} \text{ m}^{-1}$ and $0.1 \times 10^{11} \text{ m}^{-1}$, respectively. However, GAC addition into EGSB significantly decreased the cake layer resistance (R_c) proportion by 53.5 % and the values of R_c of S1 and S2 were $7.7 \times 10^{11} \text{ m}^{-1}$ and $16.6 \times 10^{11} \text{ m}^{-1}$, respectively. Overall, adding GAC into EGSB could alleviate cake layer fouling, whereas the main fouling mode of membrane-coupled EGSB process was cake layer filtration regardless of GAC addition.

Figure 3

Figure 4

Based on our experimental results, schematic illustration of membrane fouling mechanism of EGSB effluents for both EGSBs are proposed in supplementary data. And this work may be useful to better understand the membrane fouling potential and develop fouling control strategy during the membrane-coupled anaerobic process. Although the GAC addition has the potential of mitigating membrane fouling of membrane-coupled EGSB process, the studies on the long-term UF process will be conducted in our further study with the real domestic wastewater.

4. Conclusion

GAC addition improved the COD removal efficiency. It alleviated effluent membrane fouling during short-term UF tests. The reason was that GAC addition reduced the SMP, SMP_{ps} and SMP_{pr} by 26.8%, 27.8% and 24.7%, respectively, but not suspended solids. EEM analyses revealed GAC primarily help to reduce the

tryptophan protein-like substances, and aromatic protein-like and fulvic-like substances came second. Furthermore, resistance analysis demonstrated that GAC mainly decreased the R_c with the reduction of 53.5%. This work provided a useful fouling control strategy that a certain concentration GAC could be considered to add into anaerobic reactors during the membrane-coupled anaerobic process.

Acknowledgement

This work was support by the National Natural Science Foundation of China (51038003), the Funds for Creative Research Groups of China (51121062), Industry-University-Research Collaboration Project of Guangdong Province & Chinese Ministry of Education (2012B091000029), Key Breakthrough Project of Guangdong & Hong Kong (2012BZ100021) and Industry-University-Research Collaboration Project of Chancheng District (2012107101169).

References:

- [1] Baker, A. 2001. Fluorescence Excitation–Emission Matrix Characterization of Some Sewage-Impacted Rivers. *Environmental Science & Technology*, **35**(5), 948-953.
- [2] Barker, D.J., Stuckey, D.C. 1999. A review of soluble microbial products (SMP) in wastewater treatment systems. *Water Research*, **33**(14), 3063-3082.
- [3] Chen, W., Westerhoff, P., Leenheer, J.A., Booksh, K. 2003. Fluorescence Excitation–Emission Matrix Regional Integration to Quantify Spectra for Dissolved Organic Matter. *Environmental Science & Technology*, **37**(24), 5701-5710.
- [4] Choo, K.H., Lee, C.H. 1996. Membrane fouling mechanisms in the membrane-coupled anaerobic bioreactor. *Water Research*, **30**(8), 1771-1780.
- [5] DuBois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F. 1956. Colorimetric Method for Determination of Sugars and Related Substances. *Analytical Chemistry*, **28**(3), 350-356.
- [6] Gao, D.-W., Hu, Q., Yao, C., Ren, N.-Q. 2014. Treatment of domestic wastewater by an integrated anaerobic fluidized-bed membrane bioreactor under moderate to low temperature conditions. *Bioresource Technology*, **159**(0), 193-198.
- [7] Guo, W., Ngo, H.H., Li, J. 2012. A mini-review on membrane fouling. *Bioresour Technol*, **122**, 27-34.
- [8] Huang, X., Wei, C.-H., Yu, K.-C. 2008. Mechanism of membrane fouling control by suspended carriers in a submerged membrane bioreactor. *Journal of Membrane Science*, **309**(1-2), 7-16.
- [9] Johir, M.A., Shanmuganathan, S., Vigneswaran, S., Kandasamy, J. 2013. Performance of submerged membrane bioreactor (SMBR) with and without the addition of the different particle sizes of GAC as suspended medium. *Bioresour Technol*, **141**, 13-8.
- [10] Johir, M.A.H., Aryal, R., Vigneswaran, S., Kandasamy, J., Grasmick, A. 2011. Influence of supporting media in suspension on membrane fouling reduction in submerged membrane bioreactor (SMBR). *Journal of Membrane Science*, **374**(1-2), 121-128.
- [11] Kim, J., Kim, K., Ye, H., Lee, E., Shin, C., McCarty, P.L., Bae, J. 2010. Anaerobic Fluidized Bed Membrane Bioreactor for Wastewater Treatment. *Environmental Science & Technology*, **45**(2), 576-581.
- [12] Li, X.-y., Wang, X.-m. 2006. Modelling of membrane fouling in a submerged membrane bioreactor. *Journal of Membrane Science*, **278**(1-2), 151-161.
- [13] Lin, H.J., Xie, K., Mahendran, B., Bagley, D.M., Leung, K.T., Liss, S.N., Liao, B.Q. 2009. Sludge properties and their effects on membrane fouling in submerged anaerobic membrane bioreactors (SAnMBRs). *Water Res*, **43**(15), 3827-37.
- [14] Liu, Y., Tay, J.H. 2004. State of the art of biogranulation technology for wastewater treatment. *Biotechnol Adv*, **22**(7), 533-63.
- [15] Lowry, O.H., Rosebrough, N.J., Farr, A.L., Randall, R.J. 1951. PROTEIN MEASUREMENT WITH THE FOLIN PHENOL REAGENT. *Journal of Biological Chemistry*, **193**(1), 265-275.
- [16] Meng, F., Chae, S.R., Drews, A., Kraume, M., Shin, H.S., Yang, F. 2009. Recent advances in membrane bioreactors (MBRs): membrane fouling and membrane material. *Water Res*, **43**(6), 1489-512.
- [17] Meng, F., Zhou, Z., Ni, B.J., Zheng, X., Huang, G., Jia, X., Li, S., Xiong, Y., Kraume, M. 2011. Characterization of the size-fractionated biomacromolecules: tracking their role and fate in a

- 384 membrane bioreactor. *Water Res*, **45**(15), 4661-71.
- 385 [18] Ozgun, H., Dereli, R.K., Ersahin, M.E., Kinaci, C., Spanjers, H., van Lier, J.B. 2013. A review of
- 386 anaerobic membrane bioreactors for municipal wastewater treatment: Integration options,
- 387 limitations and expectations. *Separation and Purification Technology*, **118**, 89-104.
- 388 [19] Pons, M.N., Le Bonte, S., Potier, O. 2004. Spectral analysis and fingerprinting for biomedica
- 389 characterisation. *J Biotechnol*, **113**(1-3), 211-30.
- 390 [20] Robles, A., Ruano, M.V., Ribes, J., Seco, A., Ferrer, J. 2013. A filtration model applied to
- 391 submerged anaerobic MBRs (SAnMBRs). *Journal of Membrane Science*, **444**(0), 139-147.
- 392 [21] Shen, Y., Zhao, W., Xiao, K., Huang, X. 2010. A systematic insight into fouling propensity of
- 393 soluble microbial products in membrane bioreactors based on hydrophobic interaction and
- 394 size exclusion. *Journal of Membrane Science*, **346**(1), 187-193.
- 395 [22] Stuckey, D.C. 2012. Recent developments in anaerobic membrane reactors. *Bioresour Technol*,
- 396 **122**, 137-48.
- 397 [23] Tiwari, M., Guha, S., Harendranath, C.S., Tripathi, S. 2006. Influence of extrinsic factors on
- 398 granulation in UASB reactor. *Applied Microbiology and Biotechnology*, **71**(2), 145-154.
- 399 [24] Wang, Y., Leslie, G.L., Waite, T.D. 2014. Impact of iron dosing of membrane bioreactors on
- 400 membrane fouling. *Chemical Engineering Journal*, **252**(0), 239-248.
- 401 [25] Wei, C.-H., Huang, X., Wang, C.-W., Wen, X.-H. 2006. Effect of a suspended carrier on
- 402 membrane fouling in a submerged membrane bioreactor. *Water Science & Technology*, **53**(6),
- 403 211.
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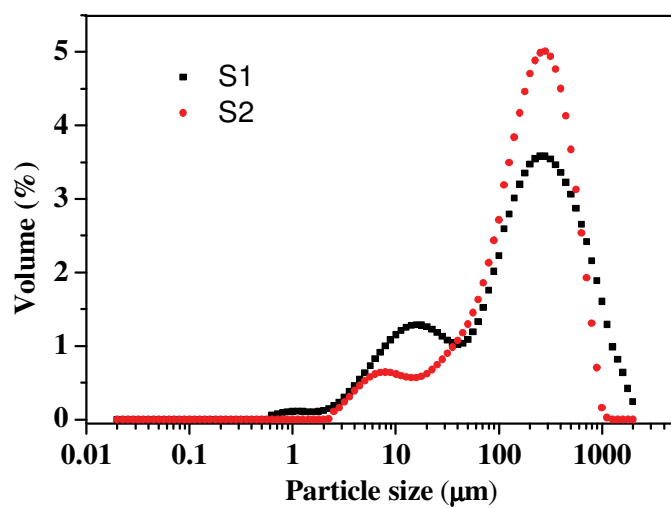
Figure captions

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408 **Figure 1 Particle size distributions of EGSB effluents**409 **Figure 2 Effect of GAC addition on the EEM fluorescence spectra of EGSB**410 **effluents: (A) EGSB1 effluent: S1; (B) EGSB2 effluent: S2**411 **Figure 3 Effect of GAC addition on the membrane fouling potential of EGSB**412 **effluents: (A) Normalized flux declines; (B) The total filtration resistance**413 **variation of the effluents with the specific volumes; (C) Total filtration**414 **resistance distributions**415 **Figure 4 Fitting the flux decline to the four fouling models (a: S1; b: S2): (1)**416 **complete blockage; (2) intermediate blocking; (3) standard blocking; and (4)**417 **cake filtration**

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421 **Figure 1 Particle size distributions of EGSB effluents**

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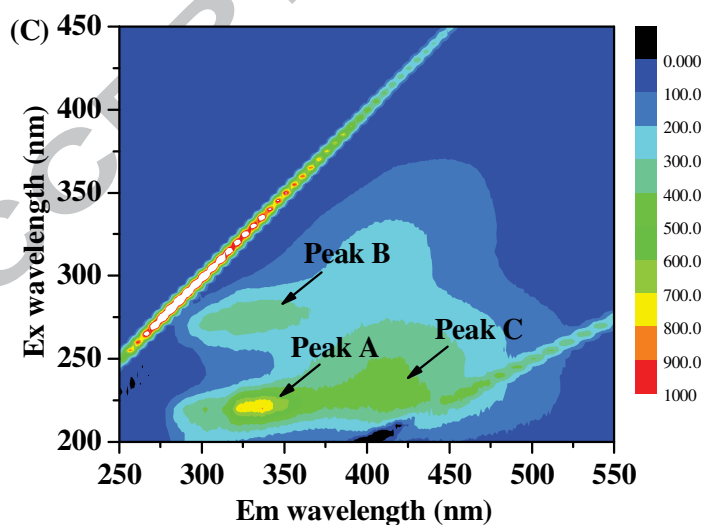
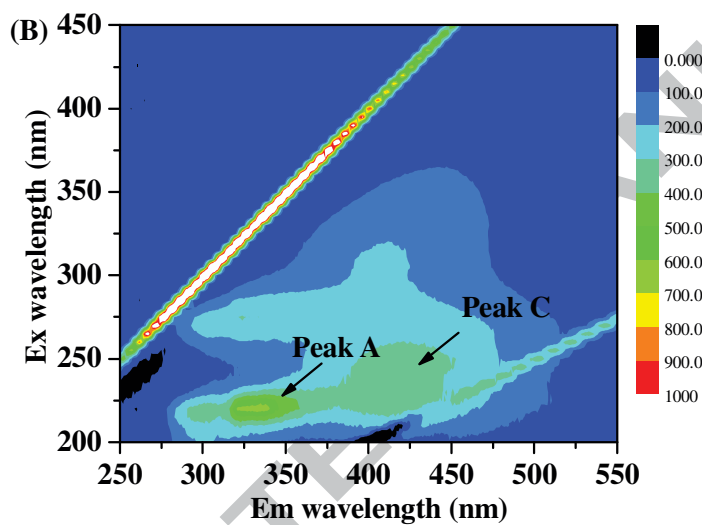
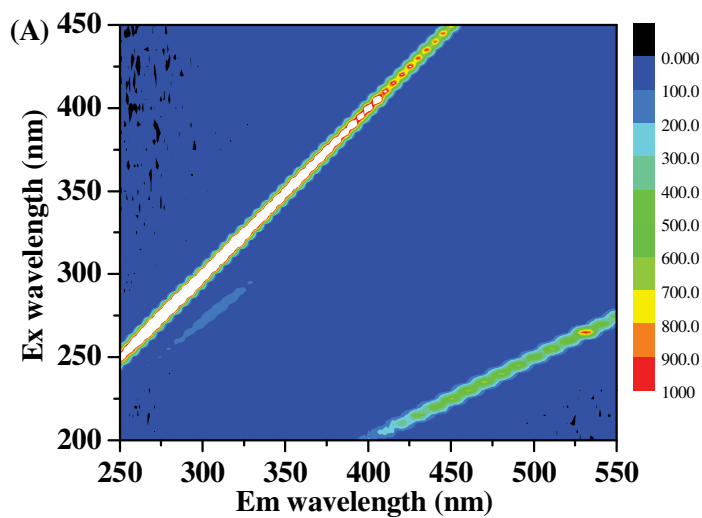


Figure 2 Effect of GAC addition on the EEM fluorescence spectra of EGSB

431 **effluents: (A) Feed water; (B) EGSB1 effluent: S1; (C) EGSB2 effluent: S2**

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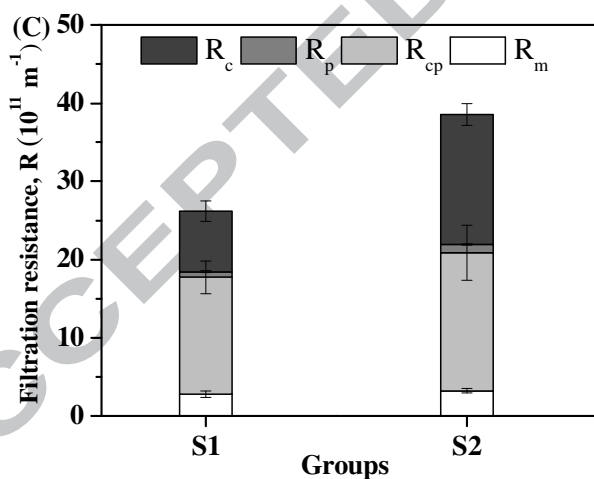
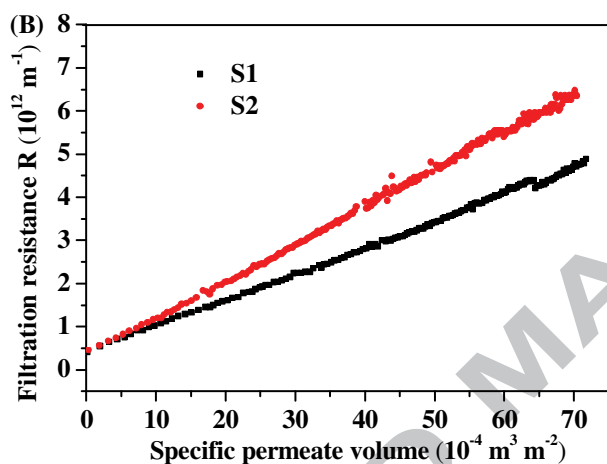
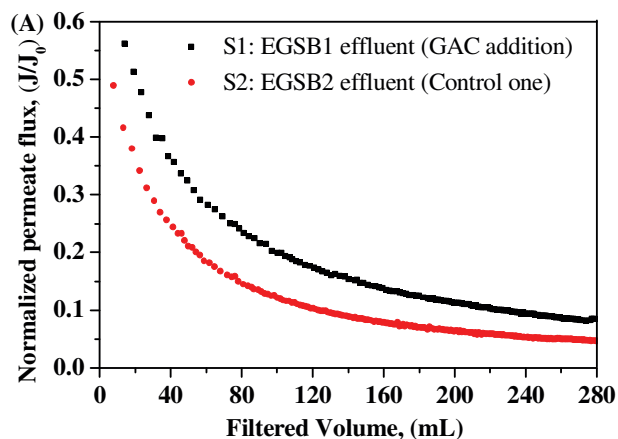
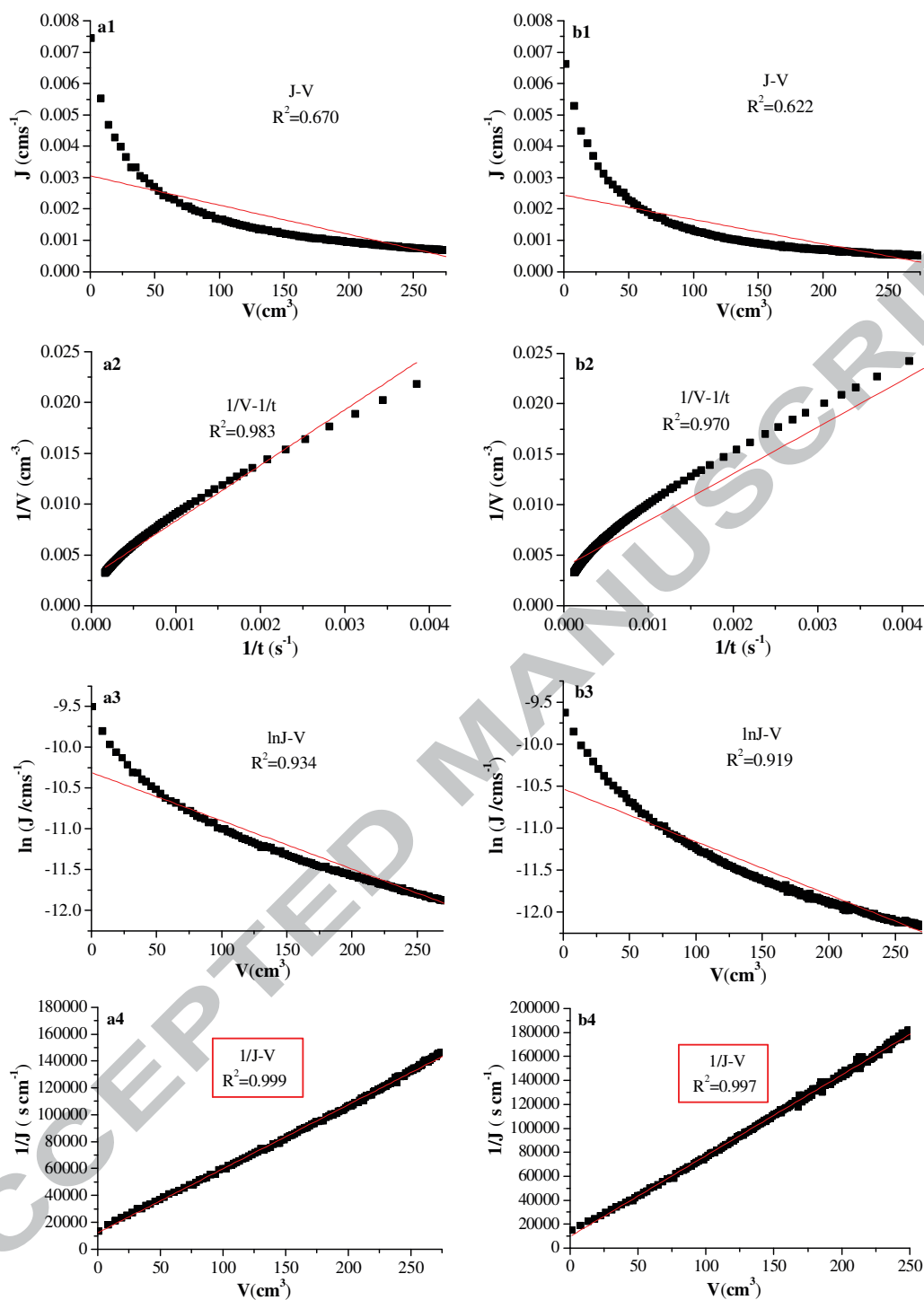


Figure 3 Effect of GAC addition on the membrane fouling potential of EGSB effluents: (A) Normalized flux declines; (B) The total filtration resistance variation of the effluents with the specific volumes; (C) Total filtration resistance distributions



439 **Figure 4 Fitting the flux decline to the four fouling models (a: S1; b: S2): (1)**
 440 **complete blockage; (2) intermediate blocking; (3) standard blocking; and (4)**
 441 **cake filtration**

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Table captions

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444 **Table 1** The characteristics of the effluent samples445 **Table 2** Particle size of the EGSB effluent samples (μm)446 **Table 3** Fluorescence spectral parameters of effluent samples

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448 **Table 1 The characteristics of the effluent samples**

Effluent samples	Turbidity (NTU)	UV ₂₅₄	SMP (mg/L)	SMP _{ps} (mg/L)	SMP _{pr} (mg/L)
S1	37.2±2.3	0.048±0.001	11.7±0.3	2.6±0.1	7.9±1.2
S2	39.7±1.1	0.067±0.000	16.0±0.2	3.6±0.3	10.5±1.6

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456 **Table 2 Particle size of the EGSB effluent samples (μm)**

	Average particle size	d (0.1)	d (0.5)	d (0.9)
S1	280.5	10.3	171.5	711.8
S2	228.8	21.8	184.7	499.1

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463 **Table 3 Fluorescence spectral parameters of effluent samples**

Sample	Peak A		Peak B		PeakC	
	Ex/Em	Intensity	Ex/Em	Intensity	Ex/Em	Intensity
S1	220/333	617.2	--	--	230/416	385.0
S2	220/334	737.4	275/305	425.6	230/404	539.0

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Highlights

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- Adding GAC alleviated membrane fouling of a membrane-coupled EGSB process
- It reduced the concentrations of SMP, SMP_{ps} and SMP_{pr} by 26.8%, 27.8% and 24.7%
- It primarily reduced tryptophan proteins, aromatic proteins and fulvic substances
- GAC addition mainly decreased the cake layer resistance proportion by 53.5%