Journal of Ceramic Processing Research. Vol. 17, No. 10, pp. 1095~1099 (2016)

J O U R N A L O F
Ceramic Processing Research

Investigation on the Preparation and properties of reticulate porous ceramic for organism carrier in sewage disposal

Shulin Wang[a], Mei Zhou[b], Lingke Zeng[b] and Wubin Dai[a,*]
[a]*School of Materials Science and Engineering, Wuhan Institute of Technology, Wuhan, 430205, P. R. China.*
[b]*School of Materials Science and Engineering, South China University of Technology, Guangzhou, 510640, P. R. China*

The purpose of this study is to prepare cheaper and higher performance reticulate porous ceramic (RPC) which is quite suitable for using in organic carrier. The RPC was made by clay through the polymeric foam replication process. The X-ray powder diffraction (XRD) phase analysis indicated that the RPC was mainly comprised mullite when sintered at 1350 °C. The surface status of different component RPCs were also observed under scanning electron microscopy (SEM). The bio-film properties of RPC with different component and pore size were evaluated by the removal rates of COD_{Cr} and NH_3-N. The results illustrated that the RPC had high effectiveness on the adsorption of micro-organism, the removal rates of COD_{Cr} and NH_3-N were all reached to ~90%. The bio-film effect was associated to porosity, pore size and surface status of the RPC. Moreover, the porosity and pore size played more importantly role than the surface status in the process of bio-film for the RPC carriers. In fact, the RPC carriers with more porosity and suitable pore size achieve better sewage treatment effect.

Key words: Reticulate porous ceramic, Polymeric foam replication process, Organism carrier, Sewage disposal, Materials characterization.

Introduction

From the perspective of environmental protection, it is widely believed that industrial waste water should be treated before exhausting outside. Based on this consideration, it is a feasible way to use bio-film to treat the wastewater, such as the method sewage disposal [1]. Biological immobilization is considered as a kind of new and rising technology in the field of modern biological engineering, which can produce bio-film efficiency and make the efficient bacterium fully deal with the noxious organic compound. The preparation process (i.e., chosen of bio-carriers) is the key point of the new bio-immobilized technology [2]. Till up now, on the one hand, many of materials are used as bio-carriers, such as PVC, PE, PS, PP, rubber, polyurethane, and so on [3]. Although those organic carrier materials have advantages of designable and processable, they also have disadvantages of poor biocompatibility, difficult biofilm fixation and low space utilization. On the other hand, inorganic materials such as sand, glass, zeolite, ceramic, activated carbon, slag, sponge iron, etc. are also frequently used as biological carrier and normally, they are more cheaper, high mechanical strength, chemical stability and similarly, there are also some disadvantages such as poor permeability, flow resistance, easy blockage and so on [4, 5].

Among all the experimental methods, the most popular one (invented by Schwartzwalder and Somers [6]) of preparing RPC is the so-called 'replication' process or more specifically, the 'polymeric sponge' process [7]. RPC prepared in this method are normally cellular structures composed of a three-dimensional interconnected pores network of struts and well-known for high porosity, high strength, acid and alkali resistant [8-11]. These highly porous materials have many applications not only such as filters for molten metal, hot gas and diesel engine exhausts filters, catalyst carriers, biomaterials, thermal insulators for furnaces and aerospace applications, gas combustion burners and lightweight building materials [12-19] but also were selected to immobilizing microalgae for sewage disposal [20]. Recently, Florina Corina Patcas research group had compared the CO oxidation over three kinds of structured carriers, namely ceramic foams, honeycombs and beads, their results indicated that ceramic foam and honeycomb ceramic have a better quality and energy transfer characteristics, and foams were superior over particle beds from the perspective that foams combined high mass transfer and low-pressure drop [21]. Meanwhile, by using RPC, honeycomb ceramic, beads and pall rings as carriers in the aerated biological ceramicite filters, Dr. Jiang Fan research group came to a conclusion that the sequence is RPC > honeycomb ceramic > beads > pall rings when comparing the removal rates of COD_{Cr} and NH_3-N, respectively [22]. The main work studied in this work was conducted to prepare cheaper and high

*Corresponding author:
Tel : +86-131-2507-0238
Fax: +86-(0)27-87-19-56-61
E-mail: wubin.dai@foxmail.com

performance RPC for organic carrier and discuss their basic properties, such as pore size and component influence over the treated result of waste water.

Materials and Methods

Preparation for the RPC

Commercial poly-urethane foams (PU) in the form of 5, 9, 13 and 23 ppi pore size (50mm × 50mm × 25 mm, Luoyang JINLING Mesh foam Factory, PRC) were adopted in this study. The industrial clay powder (median diameter 11.46 μm, Foshan Oceano Ceramic Co., Ltd., PRC) was used as the raw material. A commercial silica sol (SiO_2: 21 wt. %, Na_2O: 0.3 wt. %, PH = 8.5-10, Shanghai Changquan Silica Gel desiccant Co., Ltd., PRC) was employed as a binder. The slurries of the mixtures were prepared in distilled water and the components of the slurry were exhibited in Table 1.

In this study, the RPC was prepared by polymeric foam replication process. This method involved coating a reticulated polymeric sponge by immersed it into thixotropic ceramic slurry. The sponge was compressed to ensure filling of the void space with slurry, and then usually passed through a set of squeezing device (such as rollers) to remove the excess slurry. After removal of the excess slurry and drying, the sponge was burned out and at the same time ceramic material was sintered, resulted in a replica of the original sponge. After, the effective specific surface area of the sintered bodies was determined by PoreMaster 60 (Quantachrome Corporation, USA). The phase composition of the sintered bodies was determined by standard powder XRD. The cell geometry and structure of the RPCs were characterized by optical camera and its surface morphology was observed by SEM.

Sewage treatment

The bio-film forming experiment was processed by using of BASS bio-film reactor. Its useful volume was 1.8L, and the filling ratio of bio-carriers was fixed at 50%. The chemical oxygen demand (COD_{cr}) of water sample was obtained by rapid digestion determination on type XJ-1COD digestion instrument. Ammonia nitrogen (NH_3-N) was analyzed by use of Nessler's reagents dec'trophotometry on type UV9100 UV-VIS spectro-scope. The sewage samples were collected from the sewage of South Lake and the mixed wastewater from lab and office of SCUT.

The process of micro-organism adhesions was tested under condition of air/water ration which was set at 5: 1 and hydraulic retention time lasted 2 hrs. The influent and effluent of the COD_{Cr} and NH_3-N were measured at about 9:30a.m. per day, respectively. The bio-film of carriers were described by biodegradation effect on sewage substrate, the removal rate was calculated by using the Eq. (1) as shown below:

$$R\% = \frac{V(I) - V(E)}{V(I)} \tag{1}$$

where $R\%$ is the removal rate and $V(I)$ and $V(E)$ are the value of influent and effluent, respectively. It can be considered as a signal of the development of bio-film when the removal rate of the COD_{Cr} and NH_3-N reached to 70%.

Table 1. Components of the slurry.

Components	Clay powder	Distilled water	Silica sol
Mass percent (%)	45-70	30-55	0-3.5

Results and Discussion

Phases analysis and surface description of the RPC

XRD results indicated that the phase compositions of the RPC were related to the sintering temperature. As can be seen from the Fig. 1, the phase compositions changed from quartz (Fig. 1(a)) to mainly mullite (Fig. 1(e), still mixed with a little amount of quartz) following the temperature increasing from 1200 to 1500 ºC. The sample almost formed mullite when sintered temperature higher than 1350 ºC and accompanied by the non-crystallization (glass) phase increasing which means that the RPC was over burned.

The surface micrographs of the samples mullite, carbofrax and alumina RPCs are shown in Fig. 2. Obviously, there are irregular scaly on the surface for the sample mullite RPC as can be seen from Fig. 2(a). Fig. 2(b) indicates that the surface of alumina RPC was smooth and had some micron pores, the grain size of alumina was about 2-10 μm. Fig. 2(c) exhibited that numerous of pores and aperture (in micrometers) on the surface for the sample carbofrax RPC. Typically, the carbofrax and mullite RPCs have rough surface and

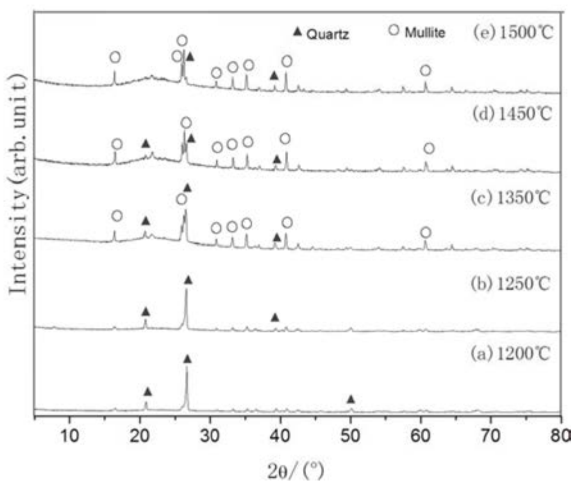

Fig. 1. XRD pattern for the sample sintered at different temperature: (▲) quartz and (○) mullite.

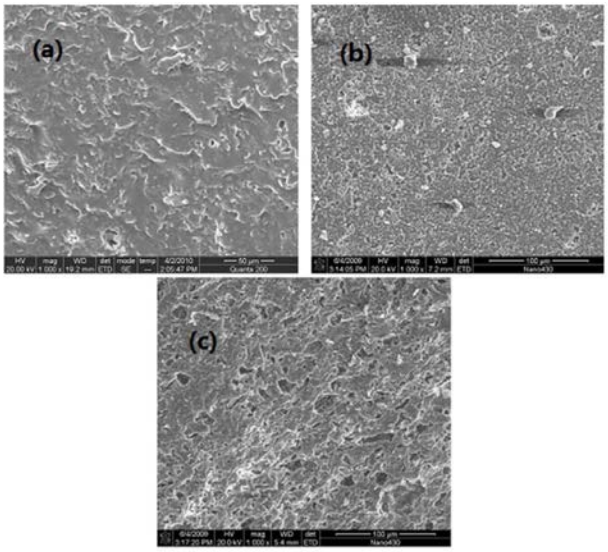

Fig. 2. SEM of the RPC surface: (a) mullite RPC, (b) alumina RPC and (c) carbofrax RPC.

Table 2. The RPC used as bio-carriers in sewage treatment experiment.

RPC	Main component	Pore size (ppi)	Porosity (%)	Effective specific surface area (m^2/g)
A-1	$3Al_2O_3.2SiO_2$	5	82	0.0041
A-2	$3Al_2O_3.2SiO_2$	9	83	0.0041
A-3	$3Al_2O_3.2SiO_2$	13	84	0.0041
A-4	$3Al_2O_3.2SiO_2$	23	81	0.0041
B -1	Al_2O_3	13	84	0.0036
C -1	SiC	13	84	0.0054

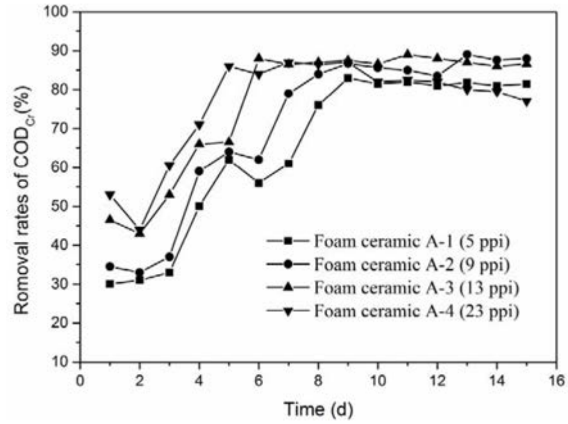

Fig. 3. COD_{Cr} removal rates of different pore size mullite RPC carriers.

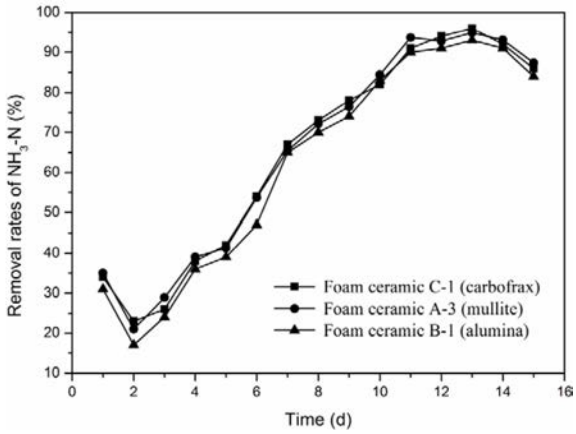

Fig. 4. NH_3-N removal rates of different pore size mullite RPC carriers.

irregular porous. Consequently, the different surface characters would lead to the different effective specific surface area. As listed in the Table 2, the effective specific surface area for the sample mullite RPC was 0.0041 m^2/g and the carbofrax RPC was 0.0054 m^2/g, while the alumina RPC was 0.0036 m^2/g, respectively (the effective surface area in this work refers to the surface area ignoring the pores size below 10 microns when calculated by the intrusive mercury curve).

COD_{Cr} removal rates of the RPC carriers

Separately, at this step, the different carriers are put into the bio-film reactor. The different pore size mullite RPC samples (named A-1, A-2, A-3 and A-4, respectively) degradation rate curves of COD_{Cr} are shown in Fig. 3. Meanwhile, the degradation rate curves for the same samples under NH_3-N are shown in Fig. 4. As shown in the Fig. 3, the A-3 and A-4 carriers absorbed the organic pollutants caused much higher substrate degradation rate (first abscissa data). However, the degradation rate dropped for the saturation adsorption (second abscissa data) when the RPC saturated with pollutants. Then, due to the increase of bio-film, substrate degradation rate increased gradually following the time. From a global perspective, the A-4, A-3, A-2 and A-1 substrate degradation rate of COD_{Cr} successively reached their peaks at the value about 85% (sixth abscissa data). Similarly phenomena are also observed as can be seen in the Fig. 4, substrate degradation rate of NH_3-N reached their maximum values at about 90% (eleventh coordinate). After, the values for the samples A-3, A-2 and A-1 keep in stability, but the values of A-4 dropped gradually in the rest of the stage (Fig. 3). The reason associated to these phenomena is because the pore size of the A-4 RPC was so small that the inner pores could be blocked by the abscission of the bio-film, which decreased the velocity of flow. Thus, it leads to lower substrate degradation rate for the bio-film insufficient supplemental oxygen and nutrients. Although these RPC carriers are in the same components, have identical surface morphology (Fig. 2(a)) and similar specific surface area, they are different in pore size and porosity. The pore size sequence is A-1 > A-2 > A-3 > A-4 while the porosity sequence is A-3 > A-2 > A-1 > A-4. In general, the A-3 RPC had more effective bio-film colonization for sewage disposal, so

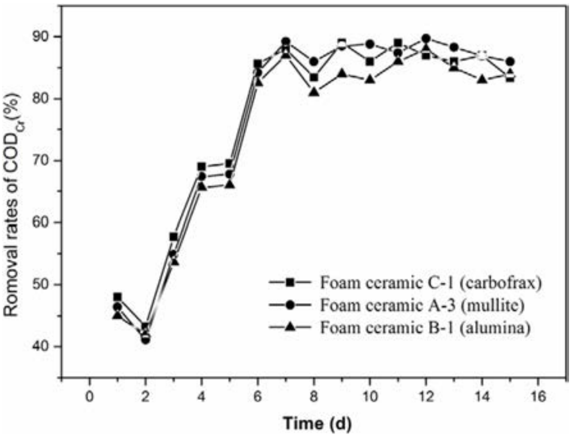

Fig. 5. COD_{Cr} removal rates of different component RPC carriers.

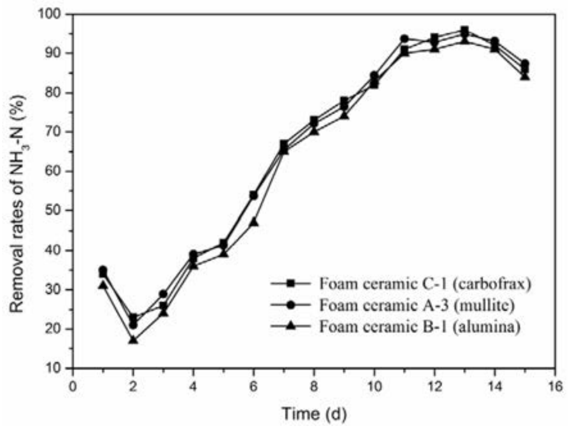

Fig. 6. NH_3-N removal rates of different component RPC carriers.

the substrate degradation rate of RPC carriers is related to their porosity and pore size. The RPC carriers with more porosity and suitable pore size achieve better sewage treatment effect.

In the same way, the RPC samples C-1, B-1 and A-3 degradation rate curves of COD_{Cr} and NH_3-N are shown in Fig. 5 and Fig. 6, respectively. As shown in the Fig. 5 and Fig. 6, the COD_{Cr} and NH_3-N removal rate for the samples C-1, B-1 and A-3 successively reached to the value at about 70% while their effects on development of bio-film were approximate. The reason for these phenomena is because these RPC carriers were in the same porosity and pore size, but different in surface characters and specific surface area which causes carbofrax and mullite RPCs have rougher surface. Therefore, carbofrax and mullite RPCs can decrease the flow velocity on the surface and providing a safe habitat to accrete for microorganism growth and regeneration. Because their specific surface area was not obviously different for carbofrax and mullite RPCs, it is safe to say that the factors of porosity and pore size would play main role in bio-film process instead of surface status for these carries.

Conclusions

By using the raw material clays and through the process of polymeric foam replication, the RPC was mainly composed by mullites when sintered at 1350°C. When used as the sewage biological treatment carriers, the RPC has a good biocompatibility which induces easily to hang film and backwashing. The removal rates of COD_{Cr} and NH_3-N are all reach to the value at about 90% in the bio-film forming study. Although the effects of the bio-film are related to porosity, pore size and surface status of the RPC, the porosity and pore size play more important role than the surface status of these carriers in bio-film process. The RPC carriers with more porosity and suitable pore size achieve better sewage treatment effect. The 13 ppi carbofrax RPC with highest porosity, effective specific surface area and suitable pore size had better sewage biological treatment performances than other samples while the 13 ppi mullite RPC had no difference.

Acknowledgements

This work has been supported by the Fundamental Research Funds for the Central Universities (Grant No. 2015ZM035), Hubei Province Science and Technology Support Project (Grant No. 2014BAA102) and Project of Technology Innovation in Hubei Province (Grant No. 2016ACA160).

References

1. S. Zhang, C. Li, S.F. Li, Q. Sun, Z.X. Guo and Y. Jia, Appl. Phys. Lett. 104 (2014) 172111.
2. P. Miranzo, E. Garcia, C. Ramirez, J. Gonzalez-Julian, M. Belmonte and M. I. Osendi, J. Eur. Ceram. Soc. 32 (2012) 1847-1854.
3. Y.C. Fan, W. Jiang and A. Kawasaki, Adv. Funct. Mater. 22 (2012) 3882-3889.
4. F. Inam, T. Peijs and M.J. Reece, J. Eur. Ceram. Soc. 31 (2011) 2853-2859.
5. L. Kvetkova, A. Duszova, P. Hvizdos, J. Dusza, P. Kun and C. Balazsi, Scr. Mater. 66 (2012) 793-796.
6. C. Balazsi, Z. Shen, Z. Konya, Z. Kasztovszky, F. Weber, Z. Vertesy, L.P. Biro, I. Kiricsi and P. Arato, Compos. Sci. Technol. 65 (2005) 727-733.
7. K. Schwartzalder and A.V. Somers, Method of Making Porous Ceramic Articles, U.S. Pat. 3090094, 1963.
8. S.B. Bhaduri, Adv. Perform. Mater. 1 (1994) 205-209.
9. E.J. Williams and J.R. Evans, J. Mater. Sci. 31 (1996) 559-563.
10. V. Singh, D. Joung, L. Zhai, S. Das, S.I. Khondaker and S. Seal, Prog. Mater. Sci. 56 (2011) 1178-1271.
11. P. Kun, O. Tapaszto, F. Weber and C. Balazsi, Ceram. Int. 38 (2012) 211-216.
12. S. Zuercher, K. Pabst and G. Schaub, Appl. Catal. A-Gen, 357 (2009) 85-92.
13. Z. Taslicukur, C. Balaban and N. Kuskonmaz, J. Eur. Ceram. Soc, 27 (2007) 637-640.
14. J. Lévêque, D. Rouzineau and M. Prévost, Chem. Eng. Sci. 64 (2009) 2607-2616.

15. E.C. Bucharsky, G. Schell, R. Oberacker and M.J. Hoffmann, J. Eur. Ceram. Soc. 29 (2009) 1955-1961.
16. L. Frank, G.C. Williams, Appl. Surf. Sci. 3 (1979) 409-415.
17. A.H. Cheryl, B.W. William, Mater. Lett. 4 (2004) 397-402.
18. Y. Yang, Y. Wang, W. Tian, Z. Q. Wang, Y. Zhao, L. Wang, and H.M. Bian, Mat. Sci. Eng. A: Struct. 508 (2009) 161-166.
19. P. Colombo, Key Eng. Mater. 206-213 (2002) 1913-1918.
20. I. Moreno-Garrido, Bioresource Technol. 99 (2008) 3949-3955.
21. F.C. Patcas, G.I. Garrido and B. Kraushaar-Czarnetzki, Chem. Eng. Sci. 62 (2007) 3984-3990.
22. F. Inam, H. Yan, M.J. Reece and T. Peijs, Adv. Appl. Ceram. 109 (2013) 240-247.