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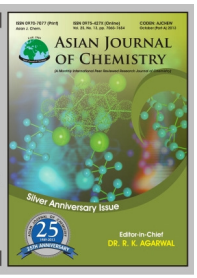

Study on Novel Materials for Nitrogen and Phosphorus Removal from Aqueous Phase

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The study on novel adsorption materials has significant practical value for the removal of nitrogen and phosphorus from eutrophicated natural water bodies. In this research, a novel material was developed by using cement, zeolite, sludge and peat, which showed high mechanical strength and excellent adsorption capacity under optimum conditions. Batch experiments and biological aerated filter were employed to evaluate the efficiency of removal of nitrogen and phosphorus. The batch experimental results showed that the adsorption capacity of this novel material was affected by temperature and reaction time. Long term run of biological aerated filter showed that when stable biological film was formed, 30 % of ammonia (NH_4^+), 28 % of total nitrogen (TN), 55 % of total phosphorus (TP) and 60 % of chemical oxygen demand (COD) in the feed water were removed and the effluent met the requirement of water quality standard for landscape water from recycling of city effluent in China (GB18921-2002).

Key Words: Novel materials, Adsorption, Nitrogen and phosphorus removal, Biological aerated filter.

INTRODUCTION

Nitrogen and phosphorus are two major nutrients leading to continual eutrophication in lakes, rivers, coastal regions and other enclosed water bodies in China. Recently, the concentration of 0.03 mg/L was found to be critical phosphorus concentration that trigged eutrophication in enclosed water bodies[1]. Excess nitrogen is responsible for increasingly serious environmental problems such as eutrophication, toxicity to aquatic life which include convulsion, coma and death[2]. With economy development and living standard improvement, many enclosed scenic water bodies are built in new residential areas for the purpose of recreation and beautifing environment. However, due to low mobility, low self purification capacity, exogenous pollution with high concentrations of nitrogen and phosphorus, the dissolved oxygen decreases sharply which further leads to massive death of aquatic life, fragile ecosystem and eutrophication. In warmer seasons, the bad smell greatly weakens various water bodies functions.

Physico-chemical and biological processes are traditional treatment methods for removal of nitrogen and phosphorus from wastewater. Although physico-chemical methods are of high efficiency in removal of nitrogen and phosphorus, their high operational cost and secondary pollution limit their applications. Biological processes are often very effective, but require large construction areas, high investment and strict operational conditions, thus leading to high total cost[2,3].

The method of adsorption has attracted much attention due to its low cost, high efficiency, relatively simple operation and wide application. Different kinds of adsorption materials have been widely investigated such as activated carbon, zeolite *etc*. Zeolites including mordenite, clinoptilolite, synthesized zeolites and modified zeolites, have been reported as significant adsorbents for removal of NH_4^+ due to their unique properties such as rich porous structure, large specific surface area, selectivity as well as high ion-exchange and adsorption capacity[4-14]. In China, there are abundant resources of peat deposit with complex composition mainly containing lignin, cellulose and humic acid, the peats carrying different types of functional groups involved in chemical binding of pollutants and resulted in effective phosphorus removal[15-18]. Some other materials such as cement[19,20], sludge-based adsorbents[21-23] have also been discussed as potential adsorbent for pollutants removing, such as phosphate, metals and organics. However, there are still some problems that need to be solved for removal of nitrogen and phosphorus from enclosed scenic water bodies using adsorption materials. Developing novel materials with the characteristics of low cost, low energy cost, unmodified, less secondary pollutant, recycling and high mechanical strength is a promising research area.

The purpose of this research is to develop novel adsorption materials by using zeolites, cement, peat and sludge as raw materials and find optimized ratio of raw materials for high mechanical strength and high adsorption capacity.

Determine the adsorption properties of the developed adsorption materials for N and P removal, the work include exploring adsorption kinetics, adsorption isotherm and effect of temperature on adsorption. Evaluate the removal efficiency of N, P and COD by biological aerated filter constructed with the developed materials.

EXPERIMENTAL

Zeolite used in this research was bought from Zhejiang province, China, with a grain size of 1-3 mm. Cement was obtained from Shanghai Hailuo Cement Co, China. Peat was obtained from Shengyuan Peat Development Co, in Jilin Province of China with a particle size range of 0.20-0.45 mm. Sewage sludge was from Quyang sewage treatment plant in Shanghai, which was pretreated by microwave under a certain condition, later smashed and sieved (US mesh 200). Foaming agent was obtained from Shandong Shiyong Architecture Co, China. The total elemental analysis was performed by a Spectro X-Lab 2000 X-Ray fluorescence spectrometer (Germany, Spectro). The zeolite had the following chemical composition (w %): SiO_2 = 65.40, Al_2O_3 = 10.90, CaO = 3.7, Na_2O = 2.00, K_2O = 1.40, Fe_2O_3 = 0.95, SrO = 0.09, TiO_2 = 0.09, P_2O_5 = 0.01, MgO = 0.05, H_2O = 11.33 and SiO_2/Al_2O_3 = 6.00. The cement had the following chemical composition (w %): $3CaO{\cdot}SiO_2$ = 55.2, $3CaO{\cdot}Al_2O_3$ = 9.8, $2CaO{\cdot}SiO_2$ = 20.3, $4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ = 6.7. The peat had a chemical composition (w %) of Na_2O = 2.10, Al_2O_3 = 6.20, SiO_2 = 73.5, SO_3 = 0.14, K_2O = 2.20, CaO = 2.89, TiO_2 = 0.88, Fe_2O_3 = 6.55. All chemicals were analytical reagent grade (NH_4Cl, KH_2PO_4 and $C_6H_{12}O_6$). The newly prepared materials were characterized by XL-30 ESEM scanning electron microscope (USA, EDAX). The biological film formed on surface of the developed material in BAF reactor was observed by Leica DVM2500 Optical Microscope (Germany, Leica).

Preparation: The preparation procedure of new type materials consisted of two steps: Microwave-treated sludge (or peat), zeolite and cement were fully mixed in different proportions, then a certain amount of water and foaming agent were added and finally the mixture was extruded and molded. The molded materials were immersed in water for 7 days with a constant temperature of 293 ± 1 K. The material made of microwave-treated sludge, zeolite and cement was defined as SZC while the other material with peat, zeolite and cement was defined as PZC.

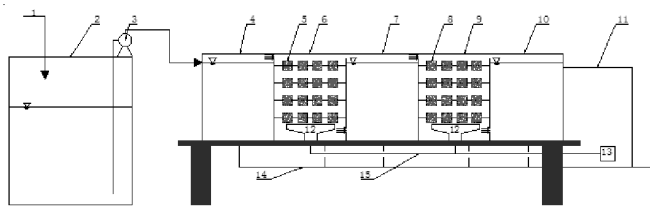
Adsorption experiments

Effect of temperature: The effect of temperature (278, 298 and 318 K) on N, P adsorption by adsorbent (SZC and PZC) were investigated with fixed amount of adsorbent under same initial N, P concentrations in flasks. The flasks were capped and agitated in a temperature controllable shaker with a shaking speed of 150 rpm. At the end of 72 h treatment period, the suspension was filtered with 0.45 μm membranes and the amount of adsorbed N, P from the solution were measured and calculated.

Adsorption kinetics: The adsorption kinetics of nitrogen and phosphorus were carried out at room temperature (298 K). 6 g adsorbent (SZC and PZC) were added into 100 mL varying initial concentrations of N and P in 200 mL Erlenmeyer flasks and agitated on a shaker with a shaking speed of 150 rpm at 298 K. Samples were taken in triplicate at the intervals of 0, 1, 2, 4, 6, 8, 10, 12, 24, 36 and 72 h after adsorption started, then filtered with 0.45 μm membranes and analyzed for residual N and P. Blank samples without adsorbent but containing all other reagents were carried out simultaneously to evaluate N and P losses caused by other factors.

Adsorption isotherms: 6 g adsorbents (SZC and PZC) were added into 200 mL Erlenmeyer flasks containing 100 mL solution with various concentrations of N and P. The flasks were capped and agitated on a thermostated shaker with a shaking speed of 150 rpm at 298 K. After a equilibration period of 24 h, the suspensions were filtered with 0.45 μm membranes, the amount of adsorbed N and P were measured and calculated. Blank samples without adsorbent but containing all other reagents were also analyzed.

Removal of N, P, COD by biological aerated filter constructed with the novel materials: Biological aerated filter reactor packed with the developed novel material was run with synthetic wastewater at room temperature (298-303 K) to examine the efficiency of N, P and COD removal, the formation of biofilm and biological regeneration capacity of the novel material. The schematic diagram of process configuration was shown in Fig. 1. The synthetic wastewater contained 8-12 mg/L of NH_4^+, 8-12 mg/L of TN, 1.2-2.0 mg/L of TP and 160-200 mg/L of COD. The pH and dissolved oxygen were adjusted to 6.9-7.2 and 4.5-5.5 mg/L, respectively. During the experiment period, the synthetic wastewater was continuously pumped from a water tank by metering pump at a flow rate of 12 L/h. The hydraulic retention time (HRT) was 1 h. The operation mode was lateral water inlet and outlet, which could keep dynamic flow. Synthetic wastewater was pumped into equalization basin 1 by metering pump, which later flow into the SZC packed pool through overflow, after that the water flow into equalization basin 2 through the bottom of a baffle, then flow into PZC packed pool through overflow. The treated water was discharged into basin 3 through bottom of the baffle. The experiment was operated to cultivate biofilm without adding activated sludge. Synthetic wastewater was fully contacted with the novel materials for biofilm attaching. Oxygen was provided for a total of 6 h per day at the time of 9:00-11:00 am, 1:00-3:00 pm and 5:00-7:00 pm, respectively, with aeration plate by an aerator. With the formation of biofilm, facultative anaerobic environment was formed in SZC-packed pool and PZC-packed pool with a constant DO concentration of 1.2 mg/L.



1. Stimulated water, 2. Tank, 3. Metering pump, 4. Equalization basin 1, 5. SZC, 6. SZC packed pool, 7. Equalization basin 2, 8. PZC, 9. PZC packed pool, 10. Basin 3, 11. Discharging pipe, 12. Aeration plate, 13. Aerator, 14. Blow-down, 15. Aeration pipe.

Fig. 1. Schematic diagram of BAF packed with new type of materials

Detection method: NH_4^+, total nitrogen, PO_4^{3+} and COD were determined using HACH standard reagents. HACH DRB

200 digester and HACH DR2700 Spectrophotometer were from HACH company (USA, HACH). pH was measured by pH meter (METTLER TOLEDO FE20, USA). Dissolved oxygen (DO) and temperature were measured by HACH oxygen meter. Compressive Strength was tested by universal testing machine (China, SHT4106).

RESULTS AND DISCUSSION

Optimization: Composition of the novel material was investigated and optimized from the aspects of N and P removal, mechanical strength, energy and material consumption, which was shown in Figs. 2-4. The results indicated that: With the increasing of cement content, the mechanical strength and adsorption capacity for P increased, but adsorption capacity for N decreased. With the increasing of zeolite content, adsorption capacity for N increased, adsorption capacity for P kept unchanged and compressive strength first increased and then decreased. With the increasing of sludge (peat) content, the mechanical strength decreased, the adsorption capacity for N and P first increased and then kept unchanged. With economic consideration of materials consumption, the optimum mass ratio of cement, zeolite and sludge (peat) was 1:2:0.05 for SZC and PZC to effectively remove N and P and to keep high mechanical strength, which was employed in the following experiments.

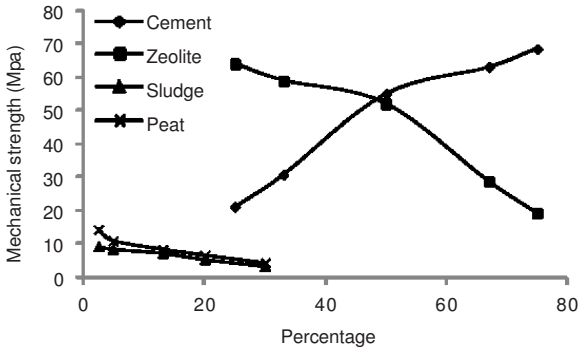


Fig. 2. Values of mechanical strength with different percentage for all kinds of raw materials

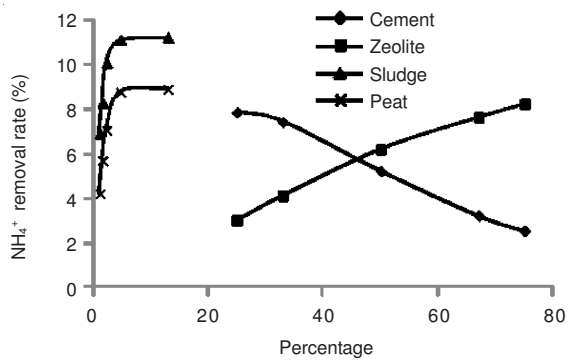


Fig. 3. Values of NH_4^+ removal rate with different percentages for all kinds of raw materials

Effect of temperature: The adsorption capacity of N and P by SZC and PZC were investigated under different temperatures. As shown in Table-1, the adsorption capacity of N and P decreased for 11.6-16.9 % when the temperature i ncreased from 278-318 K, which indicated that the adsorption

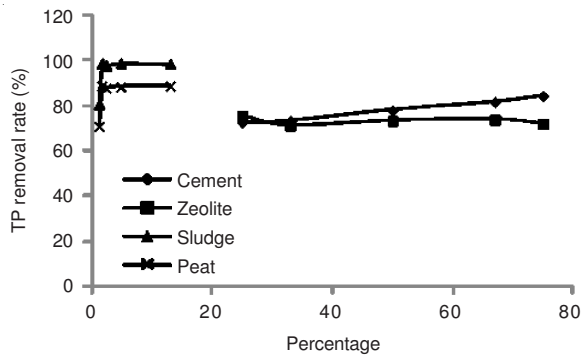


Fig. 4. Values of total phosphorus removal rate with different percentages for all kinds of raw materials

TABLE-1
EFFECT OF TEMPERATURE ON N AND P ADSORPTION BY SZC AND PZC[a]

Temp. (K)	Adsorbed N By SZC (mg/g)	Adsorbed N by PZC (mg/g)	Adsorbed P by SZC (mg/g)	Adsorbed P by PZC (mg/g)
278	0.406	0.214	0.351	0.331
298	0.377	0.192	0.324	0.305
318	0.359	0.178	0.296	0.288

[a]6.0 g adsorbents were placed in 200 mL solution containing 50 mg/L concentration at 150 rpm for 72 h under different temperatures.

of N and P by SZC and PZC were spontaneously exothermic process of free energy decrement. Compared with PZC, SZC had a higher adsorption capacity for both N and P under all test temperatures. The adsorption capacity of SZC for nitrogen was 87.9-101.7 % higher than PZC, however the difference was not so significant for P adsorption.

Adsorption kinetics: Adsorption kinetics experiments were done and several models were used to simulate the process. Possible mechanisms of adsorption such as mass transfer, diffusion, physical and chemical reaction were promoted. The analysis of adsorption rates was proved to be effective for practical operation. The adsorption processes of N and P on novel materials SZC and PZC were shown in Figs. 5 and 6.

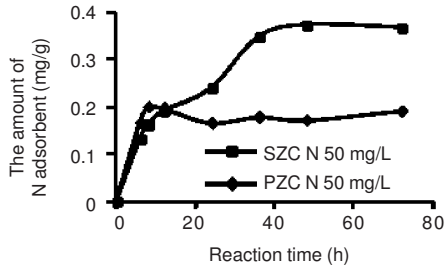


Fig. 5. Kinetics of NH_4^+ adsorption on SZC and PZC. The adsorption was investigated at initial NH_4^+ concentration of 50 mg/L and shaking speed of 150 rpm at 278 K

The adsorption of N on SZC could be divided into two stages. In the first stage, N adsorption increased quickly with the reaction time until 12 h and finally reached 60 % of the saturated adsorption capacity. In the second stage, the adsorption increased slowly with time until 72 h, when SZC reached its maximum adsorption capacity. The phenomenon that most of the N adsorption occurred in 12 h was due to the specific surface characteristics of SZC. The slow adsorption process

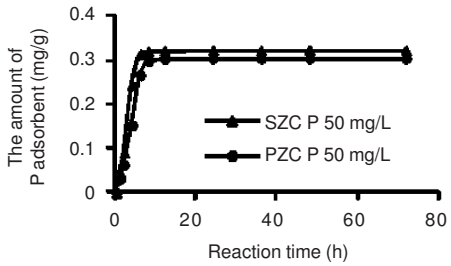


Fig. 6. Kinetics of PO_4^{3+} adsorption on SZC and PZC. The adsorption was investigated at initial PO_4^{3+} concentration of 12 mg/L and shaking speed of 150 rpm at 278 K

in the second stage was possibly related with slow diffusion rate of adsorbed N into inner surface and some surface chemical reactions. The P adsorption on SZC could also be divided into two stages of fast adsorption and slow equilibrium. During the first stage of fast adsorption, the P adsorption increased fast with time and the adsorption achieved 90 % of the saturated capacity in 4 h. The second stage of slow equilibrium process lasted to 72 h, during this time the SZC reached its maximum adsorption capacity slowly. Most P adsorption (> 90 %) occurred in 4 h and might be related to specific surface characteristics. The possibility of surface precipitation to form Ca, Fe and Al phosphates was the reason that cause slow adsorption process.

For novel material PZC, similarly a fast adsorption of 12 h and a slow equilibrium process of 72 h were observed. During the fast adsorption period, the adsorption capacity increased quickly with time until 90 % of the saturated capacity. The slow equilibrium stage lasted for 60 h and a certain degree of desorption was observed. Specific characteristics might be the reason for fast adsorption at the beginning while the slow equilibrium process might be related to N diffusion and surface chemical reactions. The desorption of N could be attributed to the specific characteristics of raw materials. P adsorption process on SZC was similar to PZC and possible mechanism might be the same.

Adsorption experiments for different initial N and P concentrations (N: 10, 20, 30, 40, 50 mg/L and P: 3, 5, 7, 9, 12 mg/L) with same dosage of adsorbent (SZC and PZC) was conducted, the typical adsorption curves were shown in Figs. 5 and 6, respectively. The matching of different kinetics models showed that N and P adsorption fitted well with pseudo-second kinetics model and the correlation coefficients (R^2) was ranging from 0.991 to 0.998.

Isotherm kinetics: The study of adsorption isotherm were essential to determine how N, P was contacted with SZC or PZC, which was very useful to optimize the utilization of SZC or PZC. Langmuir and Freundlich models are frequently used to describe adsorption equilibrium of many contaminants in aqueous solution and were applied in this research as well. The Langmuir equation reflected the adsorption of molecules on solid surface at a certain temperature.

The linear equation of Langmuir models is as following:

$$\frac{C_e}{q_e} = \frac{1}{bq_{max}} + \frac{C_e}{q_{max}} \quad (1)$$

where q_e (mg/g) is the amount of N or P absorbed on adsorbents (SZC or PZC) at equilibrium, C_e (mg/L) is N or P concentration in the solution after equilibrium, q_{max} (mg/g) and b are the maximum adsorption capacity and the Langmuir constant related enthalpy of the process, respectively.

The essential feature of Langmuir isotherm can be expressed by separation factor (R_L), a dimensionless constant, which is defined as following:

$$R_L = \frac{1}{1 + bC_0} \quad (2)$$

where b denotes the Langmuir constants and C_0 is the initial concentration of N or P. The parameter R_L is considered to be more reliable indicator for the adsorption process. There are four probable R_L values: (i) for irreversible adsorption, R_L = 0; (ii) for favorable adsorption, $0 < R_L < 1$; (iii) for linear adsorption, $R_L = 1$ (iv) for unfavorable adsorption, $R_L > 1$[6,7].

The linear equation of Freundlich model was given as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \quad (3)$$

where q_e (mg/g) is the amount of N or P absorbed on adsorbents (SZC or PZC) at equilibrium, C_e (mg/L) is N or P concentration in the solution after equilibrium, K_f is Freundlich constant related to the adsorption capacity and n is an empirical parameter involving the intensity of adsorption. 1/n ranges from 0 to and indicates favorable adsorption[24].

For N adsorption, the experimental data of SZC and PZC fitted both the Langmuir and Freundlich models well. But the correlation coefficients of Langmuir was 0.9893 and 0.9895 for SZC and PZC, respectively, which were higher than the correlation coefficients of Freundlich, which were 0.9585 and 0.9782. The results indicated that the adsorption of N on SZC and PZC might be mono layer adsorption. The value of R_L were calculated, which was ranging from 0.445 to 0.800 for SZC and 0.860 to 0.969 for PZC, indicating that the adsorption process was favorable. For P adsorption, the experiment data of SZC and PZC fitted both Langmuir and Freundlich model well. Yet the correlation coefficients of Langmuir was 0.9654 and 0.9950 for SZC and PZC, which were higher than the correlation coefficients of Freundlich of 0.9346 and 0.9575. Similar to N adsorption, the P adsorption on both SZC and PZC might be monolayer adsorption. The value of RL were calculated to be ranging from 0.006-0.025 for SZC and 0.015-0.056 for PZC, indicating that the process was favorable adsorption.

Removal of N, P, COD by biological aerated filter constructed with the novel materials: The removal efficiency of NH_4^+, total nitrogen, total phosphorus and COD by biological aerated filter based on new materials were shown in Figs. 7-10. Through observation and analysis, the whole experiment process was divided into three stages: The adsorption of both nitrogen and phosphorus by the novel materials reached equilibrium. Stable biofilm was formed on surface of the novel material without adding activated sludge. After stable biofilm was formed, removal of N, P and COD occured through the mechanisms of biodegradation by bacteria and adsorption on bio-regenerated materials.

During the first stage, maximum removal rate of NH_4^+, total nitrogen, total phosphorus and COD by SZC and PZC materials were achieved in day 5, which were 40, 30, 48 and

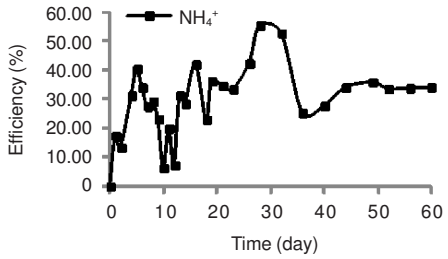


Fig. 7. Removal of NH_4^+ by BAF based on SZC and PZC

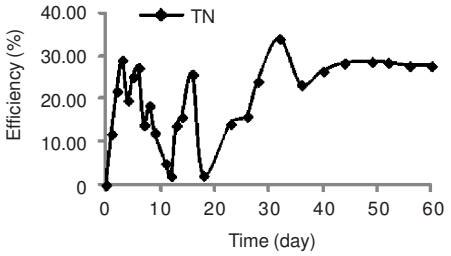


Fig. 8. Removal of TN by BAF based on SZC and PZC

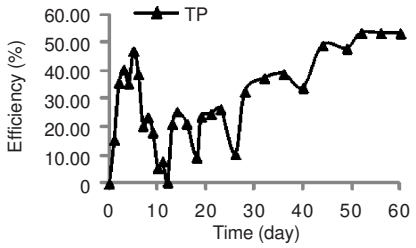


Fig. 9. Removal of TP by BAF based on SZC and PZC

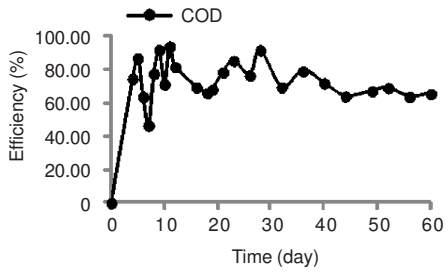


Fig. 10. Removal of COD by BAF based on SZC and PZC

90 %, respectively. During the period of day 6-12, the novel materials were saturated with N and P, leading to the minimum removal rate at day 12. The mechanism for N, P and COD removal might include adsorption, filtering and chemical precipitation by SZC and PZC at this stage.

During the second stage of day 13-40, a large amount of microorganisms grew rapidly on surface of novel materials without adding activated sludge, forming tawny floccules gradually. Because of the continuous biofilm growth, removal efficiency increase with time, which resulted in a stable effluent quality. Removal efficiency of N, P and COD began to reach a steady state. Through observation by optical microscope, a large amount of protozoa appeared at the surface of SZC and PZC, including *Rotifera, Epistylis plicatilis* and *Suctoria* that indicated the good condition of biofilm.

During the third stage of day 40-60, biofilm was fully grown, the adsorption material of SZC and PZC were regenerated. Pollutants in simulated wastewater was removed by both biologically- regenerated materials and biofilm. Removal rates of NH_4^+, total nitrogen, total phosphorus and COD by BAF were kept at 30, 28 55 and 60 %, respectively. Concentrations of NH_4^+, total nitrogen, total phosphorus and COD in effluent were below 5, 5, 0.4 and 30 mg/L, which met the discharge requirement of Water Quality Standard for Landscape Water from Recycling of City Effluent in China (GB18921-2002).

Mechanism: After the BAF reactor reached its steady state in day 40, biofilm was sampled from surface of the novel materials SZC and PZC, respectively and observed by optical microscope to further analyze the mechanism of pollutants removal. A control sample of SZC or PZC without biofilm was also investigated by optical microscope. Microbiological analysis of biofilm with optical microscope was conducted to detemine the condition of formed biofilm. As shown in Fig. 11, all kinds of typical *Protist* and *Metazoans* were found on surface of SZC and PZC, this provided evidence for the formation of stable biofilm on surface of SZC and PZC and it was the biofilm that resulted in high effluent quality.

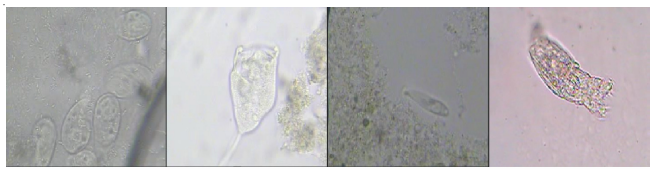


Fig. 11. Microscope pictures of typical protist and metazoan, showed from left to right: *Groveling ciliate, Vorticella, Litonotus* and *Rotifera*

Furthermore, SZC and PZC were characterized by SEM. Figs. 12 and 13 showed that tiny channels existed on surface of SZC, resulting in high optical transparency and large specific surface area, which made microorganism easier to attach on the surface of SZC. For PZC, a certain amount of fractures, porosities and large specific surface area were observed by SEM, which made it easy for microorganism to grow on the surface. Considering the observation of typical *Protist* and *Metazoans* in Fig. 11, both SZC and PZC were excellent carrier for biofilm forming as well as good materials for N and P removing.

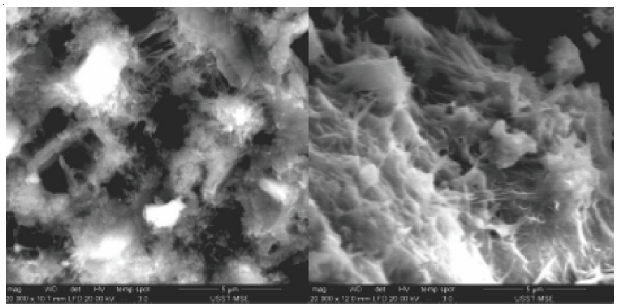


Fig. 12. SEM photographs of raw SZC (left) and SZC covered by biofilm (right)

The mechanism of NH_4^+ adsorption by SZC and PZC included physical adsorption, ion exchange and biodegradation. Physical adsorption was caused by surface structure, molecular forces and static electricity. Novel materials contained positive ions such as Ca^{2+}, Na^+ and Mg^{2+}. Ion exchange was a process of internal cations replaced by NH_4^+ in wastewater, which could be expressed as:

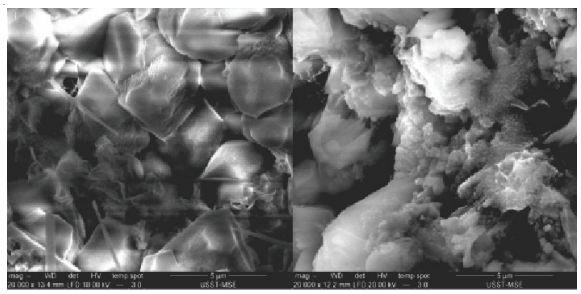


Fig. 13. SEM photographs of raw PZC (left) and SZC covered by biofilm (right)

$$R - M^{n+} + nNH_4^+ \rightleftharpoons R - nNH_4^+ + M^{n+} \quad (4)$$

where R represented anions in novel materials, M represented cations in novel materials, such as Ca^{2+}, Na^+ and Mg^{2+}, n represented charge number.

During the period of day 40-60, the removal and concentration of NH_4^+ and total nitrogen in effluent kept the same with a biofilm in good condition (Figs. 7 and 8), which indicated that simultaneous nitrification and denitrification (SND) occured on surface of the biofilm[25]. All of NH_4^+ adsorbed and decomposed by biofilm were transformed into N_2, without generation of any other nitric oxides. In addition, the novel materials could be automatically regenerated biologically, which prolonged its life.

Mechanism of removal of total phosphorus by SZC and PZC included physical adsorption, chemical precipitation and biodegradation. Physical adsorption was achieved by abundant pores and molecule forces. Rich chemical groups and many elements were present in sludge, peat and cement, which could induce phosphate precipitation. In this experiment, anaerobic-aerobic environment was created through alternating aeration, P in wastewater was removed by P accumulating bacteria through adsorption and metabolism, resulting in qualified effluent. However in this process, P was transfered into micro-organisms and thus extra sludge should be discharged from the reactor in order to remove P from the system.

Conclusion

The optimum mass ratio of cement, zeolite and sludge (peat) was 1:2:0.05 for both SZC and PZC, which exhibited significant N, P adsorption capacities and high mechanical strength. Temperature and reaction time were two main factors affecting N and P removal. The N, P adsorption from aqueous by SZC and PZC decreased with increasing temperature due to spontaneously exothermic process of free energy decrement. N, P adsorption consisted of two stages of fast adsorption and slow equilibrium, which could be attributed to specific surface characteristics, diffusion and surface chemical reaction. The N, P adsorption by SZC and PZC fitted Langmuir equation well, which were favorable adsorption with R_L values between 0 and 1. BAF tests confirmed that SZC and PZC were effective in removing NH_4^+, total nitrogen, total phosphorus and COD from synthetic wastewater. The mechanism for N removal included physical adsorption, ion exchange and biodegradation, while the P removal could be attributed to physical adsorption, chemical precipitation and biodegradation. After stable biofilm was formed, the water quality could meet GB18921-2002: Water Quality Standard for Landscape Water from Recycling of City Effluent in China. It was proved that SZC and PZC were excellent N, P adsorption materials, which was easy to form biofilm and could be considered as potential materials for N and P removal in enclosed scenic water bodies.

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