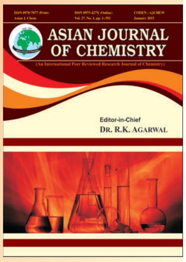
Asian Journal of Chemistry; Vol. 27, No. 7 (2015), 2477-2481

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17938



Adsorption/Desorption of Ammonium and Phosphorus on Four Substrates in Constructed Wetland

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Received: 3 May 2014; *Accepted*: 22 August 2014; *Published online*: 30 March 2015; AJC-17060

Gravel, clinoptilolite, limestone and lytag are widely used in constructed wetland in China. The results of adsorption kinetic study showed that the adsorption rate of ammonium on these four substrates was in the order: clinoptilolite > lytag > gravel > limestone, and the adsorption rate of phosphorus was: clinoptilolite > lytag > limestone > gravel. Meanwhile, pH value played an important role on removal efficiency of ammonium and phosphorus on four substrates. Clinoptilolite displayed the largest adsorption capacity of ammonium (average 0.289 mg/g) when pH was 6-8, and decreased obviously with increasing of pH until 9. When pH increased from 6 to 9, adsorption capacity of phosphorus on clinoptilolite significantly increased to 0.141 mg/g, while the value on lytag decreased from 0.138 to 0.092 mg/g. Both Freundilch and Langmuir model could well describe the adsorption behaviour of ammonium and phosphorus on the four substrates. Clinoptilolite and lytag demonstrated best removal efficiency of ammonium and phosphorus, respectively. Desorption experiments showed that gravel had the largest desorption ratio of both ammonium (27.6265 %) and phosphorus (41.7143 %). More importantly, the ammonium desorbed from lytag (35.2439 mg/L) could lead to ammonium secondary pollution, while all of the four substrates would result in phosphorus secondary pollution.

Keywords: Four substrates, Constructed wetland, Ammonium and phosphorus adsorption kinetic, pH, Desorption characteristics.

INTRODUCTION

As a novel wastewater treatment technology, constructed wetland has attracted considerable attention. Because of self-perpetuating, low-maintenance and low cost[1,2], constructed wetland is widely used to reduce biochemical oxygen demand (BOD), suspended solids (SS), ammonium (nitrogen) and phosphorus in sewage[3-5]. Although most waste water treatment plants in China have primary and secondary treatment processes, the effluent quality can't fulfill the requirement of the natural water function[6,7]. In addition, more stringent regulations will be announced in Beijing in which tertiary treatment needs to be applied to reduce effluent concentrations of ammonium (nitrogen) and phosphorus to as low as 1.0 and 0.3 mg/L, respective.

Generally substrates are used as packing skeleton as well as afford microorganism adhere in constructed wetland. More imporantly, substrates play a great role in purifying pollutants due to its great adsorption capacity and ion or ligand exchange functions[8,9]. Consequently, it is important to select those substrates with highest adsorption capacity, which is dependent upon chemical and physical properties of the material[10,11]. Apart from Fe, Al and Ca minerals, the adsorption capacity of phosphorus in constructed wetland is also controlled by both pH value and the surface area of substrate[12].

Adsorption kinetic study is widely used to explain degradation process and removal mechanism of pollutants. It is very important in designing constructed wetland and speculating removal efficiency in many countries[13,14].

Therefore, the objectives of this research were: (1) to compare the removal efficiency of pollutants on four substrates under different pH; (2) to discuss the adsorption kinetics of the four substrates to analyze ammonium (nitrogen) and phosphorus removal mechanism in constructed wetland; (3) to study the desorption characteristics on the four substrates and evaluate the ecological risk of secondary pollution.

EXPERIMENTAL

Gravel, clinoptilolite, limestone and lytag selected from a factory managing water purification filter material, were used to study adsorption characteristics of ammonium and phosphorus. The chemical components of the four substrates were shown in Table-1.

General procedure

(1) Adsorption kinetic experiment of substrates: Each of the four substrates was quantified 20 g and put into a 250 mL iodine flask respectively, then added 200 mL solution prepared with NH_4Cl (ammonia nitrogen concentration was 35 mg/L)and KH_2PO_4 (phosphorus concentration was 9.5 mg/L).

TABLE-1
CHEMICAL COMPONENT OF THE FOUR SUBSTRATES

Substrate content Content	Lytag	Clinoptilolite	Gravel	Limestone
Total Ca (mg/g)	68.5	28.3	0.0	320.6
Total Fe (mg/g)	57.1	10.1	44.4	8.6
Total Al (mg/g)	133.4	82.3	68.3	30.6
Total Mg (mg/g)	12.7	4.0	5.1	20.9
Total Mn (mg/g)	0.0	0.0	0.0	0.0
Particle size (mm)	3-5	6-10	15-25	6-10

Placed the flasks into constant temperature air oscillator and surged under the experimental conditions of 25 ± 1 °C and 125 ± 5 rpm, took samples at different time point and filtrated with 0.45 μm filtration membrane, analyzed ammonia nitrogen and phosphorus concentrations, then drew adsorption kinetic curves of the four substrates for ammonia nitrogen and phosphorus.

(2) Experiments of effect of pH on substrates adsorption: The experimental procedures were the same as the former kinetic study, but the pH was adjusted with HCl and NaOH to 6, 7, 8, 9, respectively.

(3) Sequencing batch isotherm adsorption experiments: each of the four substrates was quantified 20 g and put into a 250 mL iodine flask respectively, then added 200 mL solution prepared with NH_4Cl and KH_2PO_4 in different concentrations. Placed the flasks into constant temperature air oscillator and surged for 48 h under the experimental conditions of 25 ± 1 °C and 125 ± 5 r/min, took samples at different time point and filtrated with 0.45 μm filtration membrane, analyzed ammonia nitrogen and phosphorus concentrations, then drew isothermal adsorption curves of the four substrates for ammonia nitrogen and phosphorus.

(4) Desorption experiments of four adsorption saturation substrates: Each of the four adsorption saturation substrates was quantified 10 g and put into a 250 mL iodine flask, respectively, then added 200 mL deionized water. Placed the flasks into constant temperature air oscillator and surged for 24 h under the experimental conditions of 25 ± 1 °C and 125 ± 5 r/min, took samples and filtrated with 0.45 μm filtration membrane, analyzed ammonia nitrogen and phosphorus concentrations, then calculated the ratio and concentration of desorption.

The mineral compositions of the four substrates were determined by X-ray diffraction (XRD). The pH of the solution was determined with a pH meter (HI98128). Ammonia nitrogen was tested with Nessler's reagent spectrometry (GB7479-87). Phosphorus was determined with molybdenum-antimony anti-spectro-photometric method (GB11893-89).

RESULTS AND DISCUSSION

Adsorption kinetic of substrates: The results of kinetic study on four different substrates were shown in Fig. 1 (a) and (b).

Fig. 1(a) showed that the adsorption rates of ammonium on four substrates made a great difference. As the time prolonged, the adsorption rates of ammonium on clinoptilolite and lytag became faster, and much quicker than gravel and limestone. The adsorption rates of ammonium on the four substrates were in the order of : clinoptilolite > lytag > gravel > limestone. Fig. 1(b) revealed that the adsorption rates of phosphorus on the four substrates were also quite different, and the phosphorus adsorption rates on gravel and limestone were much lower than on clinoptilolite and lytag. The phosphorus adsorption rates were in the sequence of: clinoptilolite > lytag > limestone > gravel. Therefore, Clinoptilolite and lytag showed great adsorption performance for both ammonium and phosphorus.

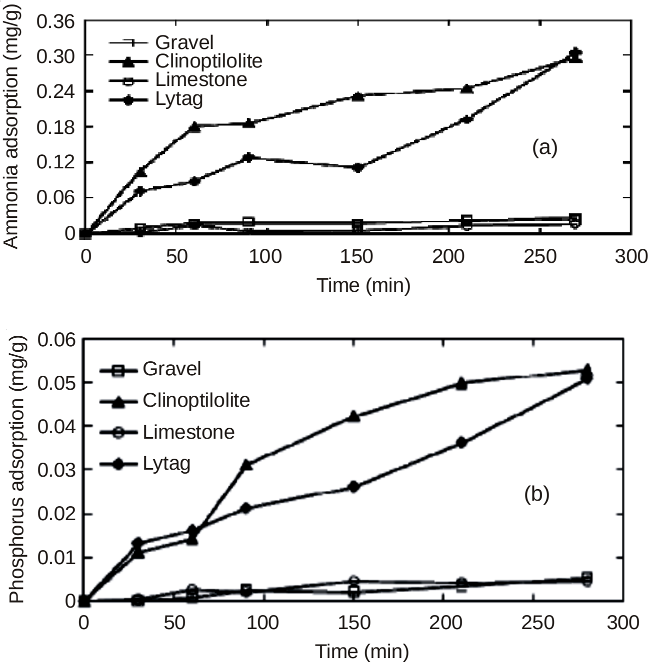

Fig. 1. Adsorption curves of ammonium and phosphorus on substrates

Different pH influence on substrates adsorption: Many researches have shown that substrate component, specific surface area, redox potential, adsorption space and pH were the main influencing factors on ammonium and phosphorus adsorption. The pH value could determine the existing forms of nitrogen and phosphorus which not only influence adsorption rate but also the removal efficiency depending on the precipitation process. The experimental results of pH influence on the four substrates adsorption were shown in Fig. 2(a) and (b).

Fig. 2(a) showed adsorption capacity of ammonium on clinoptilolite reduced significantly (from 0.285 to 0.124 mg/g) when pH increased from 8 to 9, but much higher than the other three substrates which adsorption capacities were increased slightly. Under alkali condition, NH_4^+ can change into $NH_3·H_2O$ and OH^-, and hence the adsorption competition of HPO_4^{2-} and OH^- existed. So the adsorption performance of clinoptilolite which based on ion exchange significantly decreased.

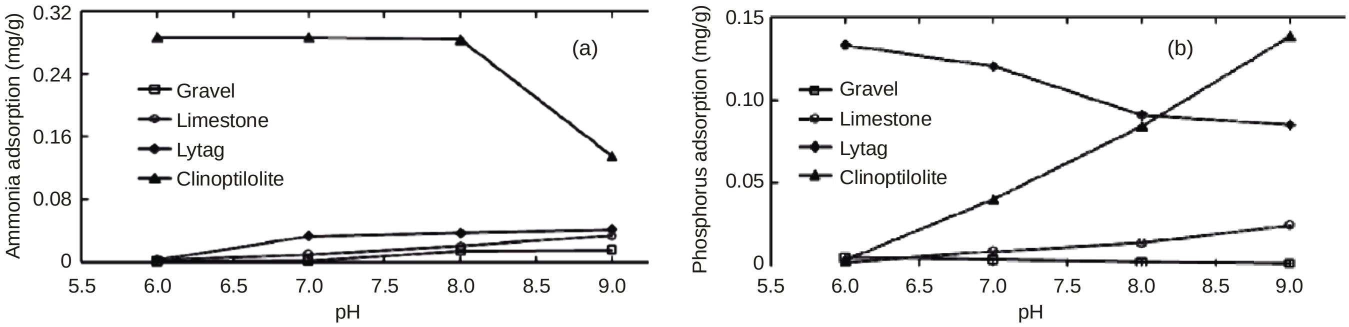

Fig. 2. pH influences on substrates adsorption of ammonium and phosphorus

Fig. 2(b) showed phosphorus adsorption capacities on clinoptilolite and lytag were much higher than on gravel and limestone. The adsorption capacities of phosphorus on clinoptilolite and limestone increased with pH increasing from 6 to 9, while the opposite was true for the gravel and lytag. When pH increased from 6 to 9, adsorption capacity of phosphorus on clinoptilolite rapidly increased to 0.141 mg/g, while lytag gradually decreased from 0.138 to 0.092 mg/g.

Many studies have mentioned that it was easy to remove phosphorus by generating precipitation with Al^{3+}, Fe^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+} and other ions or arising chemical absorption. As pH value increased, the combination between Al^{3+}, Fe^{2+} and PO_4^{3-} could be weakened, thus the colloid of containing iron or aluminum would precipitate instability or be dissolved. The decreasing of phosphorus adsorption on lytag and gravel with pH increasing can be contributed to the more amount of aluminum in them (Table-1). Meanwhile, limestone contains more calcium, $H_2PO_4^-$ can be easily transferred to HPO_4^{2-} and develop precipitation with Ca^{2+} and Mg^{2+} as pH increased. On higher pH value, NH_4^+ can be more easily changed into $NH_3{\cdot}H_2O$, therefore clinoptilolite has more adsorptive sites to significantly increase adsorption capacity of phosphorus.

Isothermal adsorption: For solid-liquid adsorption under constant temperature condition, Freundilich adsorption equation could express the correlation between adsorption quantity on solid surface and equilibrium adsorption concentration in solution. Freundilich adsorption equation is:

$$\lg G = \lg K + \frac{1}{n}\lg C$$

G was equilibrium adsorption capacity per unit mass adsorbent, C was equilibrium adsorption concentration, K reflected adsorption capacity, 1/n grossly showed ammonium and phosphorus adsorption strength of substrate, 1/n <0.5 showed adsorbate easily to be adsorbed, 1/n > 2 showed adsorbate difficult to be adsorbed. Langmuir adsorption equation could determine the theoretical maximum adsorption capacity and adsorption strength of solid medium, and could be expressed as:

$$\frac{1}{G} = \frac{1}{G_0} + \frac{A}{G_0}\frac{1}{C}$$

G_0 was equilibrium theoretical maximum adsorption capacity of adsorbent, Complex ability of substrate, maximum buffering capacity (MBC = G_0/A) could utilized to reflect ammonium and phosphorus adsorption strength and capacity on substrate. The regression parameters of ammonium and phosphorus adsorption isotherms on the four substrates were shown in Tables 2 and 3, respectively.

As can be seen in Table-2, both Freundilch and Langmuir model could describe the adsorption isotherms very well. K value was in the order: clinoptilolite > lytag > limestone > gravel. It is worth to note that the value of 1/n on clinoptilolite and limestone were less than 0.5, indicating that their great adsorption willing for ammonium. G_0 value of clinoptilolite was the biggest (2.2267), while the smallest G_0 was limestone (0.0219) which was a little lower than gravel (0.0257). MBC value was: clinoptilolite > lytag > gravel > limestone.

Clinoptilolite has the largst K value, G_0 value and MBC value than the other three substrates, representing its larger adsorption capacity and buffer capacity. According to these results, gravel or limestone is not suitable as single substrate for designing constructed wetland. More important, clinoptilolite or mixed substrates containing clinoptilolite can be selected in constructed wetland to maintain higher ammonium removal efficiency.

Table-3 displayed both Freundilch and Langmuir model could describe phosphorus adsorption on the four substrates. K value was in the order of: lytag > clinoptilolite > limestone > gravel. G_0 value was: lytag > limestone > clinoptilolite > gravel, MBC value was: lytag > clinoptilolite > limestone > gravel. Therefore, lytag possesses largest adsorption capacity of phosphorous and buffer capacity than other substrates due to larger K value, G_0 value and MBC value.

Because the phosphorus removal efficiency of constructed wetland is mainly depends on substrate adsorption, substrate with great phosphorus adsorption much be applied. But the lytag is not good enough in removing phosphorus due to no optimal G_0 value and MBC value. Therefore, all the four substrates could not be used alone in designing wetland but other substrate with ideal phosphorus adsorption capacity needed.

Desorption study: The ammonium and phosphorus desorption results on the four saturation substrates were listed in Table-4.

The desorption capacity of ammonium on lytag was 0.0289 mg/g which was much higher than the other three substrates, and limestone was the least (0.0035 mg/g). The ammonium desorption ratio of gravel was 27.6265 % which was higher than the other three substrates, and clinoptilolite was the least (0.2784 %). Therefore, clinoptilolite could be good substrate selection removing ammonium in constructed wetland due to its lower desorption capacity and desorption ratio but higher adsorption capacity. The desorption capacity

TABLE-2
AMMONIUM ISOTHERMAL ADSORPTION EQUATION AND PARAMETERS OF THE FOUR SUBSTRATES (25 °C)

Substrate	Freundlich adsorption equation			Langmuir adsorption equation			
	K	1/n	R (n = 7)	G_0 (mg/g)	A	R (n = 7)	MBC (mg/g)
Lytag	0.0344	0.5588	0.9573	0.1633	4.7133	0.9325	0.0347
Gravel	0.0051	0.5008	0.9905	0.0257	5.5952	0.9452	0.0046
Clinoptilolite	0.7818	0.4069	0.9725	2.2267	2.1320	0.9500	1.0444
Limestone	0.0089	0.2757	0.9726	0.0219	2.5699	0.9586	0.0085

TABLE-3
PHOSPHORUS ISOTHERMAL ADSORPTION EQUATION AND PARAMETERS OF THE FOUR SUBSTRATES (25 °C)

Substrate	Freundlich adsorption equation			Langmuir adsorption equation			
	K	1/n	R (n = 7)	G_0 (mg/g)	A	R (n = 7)	MBC (mg/g)
Lytag	0.0538	0.5856	0.9087	0.3725	6.7237	0.9296	0.0554
Gravel	0.0002	1.0728	0.9600	0.0175	64.8406	0.9811	0.0003
Clinoptilolite	0.0083	0.4305	0.9583	0.0473	10.2852	0.9908	0.0046
Limestone	0.0004	1.1236	0.9960	0.1305	250.4534	0.9983	0.0005

TABLE-4
AMMONIUM AND PHOSPHORUS DESORPTION RATIO OF FOUR SUBSTRATES

Parameter	Substrate			
	Lytag	Gravel	Clinoptilolite	Limestone
Ammonium theoretical adsorption capacity (mg/g)	0.1633	0.0257	2.2267	0.0219
Ammonium desorption capacity (mg/g)	0.0289	0.0071	0.0062	0.0035
Ammonium desorption ratio (%)	17.6975	27.6265	0.2784	15.9817
Ammonium desorption concentration (mg/L)	35.2439	13.8536	15.7605	9.7674
Phosphorus theoretical adsorption capacity (mg/g)	0.3725	0.0175	0.0473	0.1305
Phosphorus desorption capacity (mg/g)	0.0146	0.0073	0.0069	0.0030
Phosphorus desorption ratio (%)	3.9195	41.7143	14.5877	2.2989
Phosphorus desorption concentration (mg/L)	17.8049	14.2439	17.5399	8.3721

of phosphorus on lytag was 0.0146 mg/g which was much higher than the other three substrates, and limestone was the least (0.0030 mg/g). The phosphorus desorption ratio of gravel was 41.7143 % which was higher than the other three substrates, and limestone was the least (2.2989 %). Both desorption capacity and desorption ratio of phosphorus on limestone were less, but the adsorption capacity (0.1305 mg/g) was higher than gravel and clinoptilolite. All these characteristics showed that limestone was a good substrate to removal phosphorus in constructed wetland.

As seen in Table-4, the desorption concentration of ammonium on lytag is as high as 35.2439 mg/L, which is much as than grade II (25 mg/L) (<discharge standard of pollutants for municipal wastewater treatment plant> (GB18918-2002)). In addition, all desorption concentration of phosphorus on four substrates were much higher than grade II (3 mg/L). More importantly, it is known that the hydraulic retention time was longer than the desorption equation time of saturation substrates in practical constructed wetland,. Thus the ammonium and phosphorus concentrations would reach to the desorption concentration listed in Table-4. That could result in ecological risk of secondary pollution, which should be prudent considered when selecting the substrates for constructed wetland.

Conclusions

- The adsorption rates of ammonium on clinoptilolite and lytag were faster than gravel and limestone.
- pH plays a significant role in adsorption of ammonium and phosphorus on four substrates. Under alkali condition, both ammonium and phosphorus can be easily adsorbed onto lytag and limestone. In contrast, gravel and clinoptilolite are only good at adsorption of ammonium and phosphorus, respectively. However, ammonium can be easily adsorbed onto clinoptilolite and phosphorus can be easily adsorbed onto lytag under neutral and weak acid condition.
- In comparison of the adsorption isotherms onto four substrates, clinoptilolite had larger ammonium adsorption capacity than the other three substrates. Lytag had slightly larger phosphorus adsorption capacity than the other three substrates.
- Desorption study showed clinoptilolite had larger ammonium adsorption capacity and less saturation desorption capacity. Lytag had larger phosphorus adsorption capacity and less saturation desorption ratio. Four substrates in practical constructed wetland would lead to phosphorus desorption secondary pollution, only the concentration of ammonium treated by lytag would meet the effluent standard.

ACKNOWLEDGEMENTS

This paper was supported by Science Development Project of Beijing, D07050601490701.

REFERENCES

1. W.J. Mitsch and S.E. Jørgensen, Ecological Engineering-An Introduction to Ecotechnology, Wiley, NY, pp. 2/36-2/48 (1996).
2. R.H. Kadlec and R.L. Knight, Treatment Wetlands, Lewis Publishers, Boca Raton, FL, pp. 5/81-5/94 (1989).
3. G.A. Moshiri, Constructed Wetlands for Water Quality Improvement, Lewis Publishers, Boca Raton, FL, pp. 3/62-3/71 (1993).

4. R.H. Kadlec, P.S. Burgoon and M.E. Henderson, *Water Sci. Technol*., **35**, 263 (1997).
5. J. Vymazal, H. Brix, P.F. Cooper, M.B. Green and R. Haberl, Constructed Wetlands for Wastewater Treatment in Europe, Backhuys Publishers, Leiden, The Netherlands, pp. 3/44-3/60 (1998).
6. L.H. Cui, X.Z. Zhu and S.M. Luo, *J. China Environ. Sci*., **250**, 27 (2007).
7. X.W. He, Z. Chai, H. Wang *et al*., The 5th International Conference on Bioinformatics and Biomedical Engineering, IEEE, China, pp. 1-4 (2011).
8. M. Schreijer, R. Kampf, S. Toet and J. Verhoeven, *Water Sci. Technol*., **35**, 231 (1997).
9. Y.F. Wang, F. Lin and W.Q. Pang, *J. Hazard. Mater.*, **160**, 371 (2008).
10. T. Zhu, P. Jenssen, T. Mhlum and T. Krogstad, *Water Sci. Technol*., **35**, 103 (1997).
11. A. Drizo, C.A. Frost, J. Grace and K.A. Smith, *Water Res*., **33**, 3595 (1999).
12. W. Stumm and J. Morgan, Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters, John Wiley & Sons Inc., NY, pp. 404-408 (1981).
13. O.S. Pilipenko, L.F. Atyaksheva, E.V. Kryuchkova and E.S. Chukhrai, *Russian J. Phys. Chem. A*, **86**, 1301 (2012).
14. S. Hussain, H.A. Aziz, M.H. Isa, M.N. Adlan and F.A.H. Asaari, *Bioresour. Technol*., **98**, 874 (2006).