

Phosphorus Removal in Wastewater Using Activated Ca-Loess Complex

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Abstract

In many instances phosphorus is a limiting factor for eutrophication in streams, and lakes. Because wastewater treatment plant itself may be the main phosphorus source in a natural water body, removal of phosphorus in final effluent of wastewater treatment processes is required.

Amongst various technologies for phosphorus removal in wastewater, adsorption technology was investigated using activated Ca-loess complex. Ca was added in loess to enhance adsorption capacity and intensity of phosphorus. Ca added loess was activated at a high temperature of 400 °C which turned out to be the optimum temperature. Activated Ca-loess complex below 400 °C had not enough strength to be applied as an activated Ca-loess pallet column in wastewater treatment process. Ca-loess complex which activated above 400 °C lost its adsorption capacity as the loess surface was glassified when the activation temperature reached above 400 °C. Even if adsorption capacity of activated Ca-loess was not very high due to the lack of abundant pores on its surface, adsorption intensity was still high because it was activated with added Ca in loess.

Activated loess was made by pallets. The activated loess pallets were filled in a column, and were applied in wastewater treatment process. Using an activated Ca-loess pallet column, total phosphorus (T-P) was reduced from about 0.5 mg/l to lower than 0.1 mg/l in wastewater treatment, and ionic phosphorus (phosphate) was completely removed for the four months of pilot plant operation.

Key words : phosphorus, loess, activation, Ca, phosphate

요약문

강이나 호수로 유입되는 인(P)이 종종 부영양화의 가장 큰 제한요소로 작용한다. 그런데 하수처리장의 방류수가 자연수계에 인의 중요한 공급처로 작용하는 경우가 많기 때문에 하수처리장의 최종 처리수에서 인의 제거가 요구된다.

하수에서 인을 제거할 수 있는 많은 기술 중에서, 활성 칼슘-황토의 복합체를 이용한 흡착기술을 연구하였다. 칼슘을 황토에 첨가하여 인의 흡착 용량과 흡착강도를 증가시켰다. 칼슘을 첨가한 황토를 최적 온도로 밝혀진 400 °C의 고온에서 활성화시켰다. 400 °C 미만에서 활성화시킨 칼슘-황토는 하수처리 공정의 활성칼슘-황토 복합체를 이용한 처리조에 적용하기엔 강도가 부족하였다. 반면 400 °C 초과 온도에서 활성화시킨 칼슘-황토 복합체는 복합체 표면이 유리화되어 흡착용량이 감소하였다. 활성칼슘-황토 복합체는 표면에 충분한 기공이 발달하지 못하여 인의 흡착용량에 한계는 있으나 칼슘을 첨가하였기 때문에 흡착강도는 높았다.

활성칼슘-황토는 입자형 복합체로 만들어졌다. 제조된 복합체를 흡착칼럼에 채워 하수처리공정에 적용하였다. 활성칼슘-황토의 복합체를 충전한 칼럼을 파일럿 플랜트에 적용한 결과 0.5 mg/l의 인의 농도를 0.1 mg/l로 낮출 수 있었고, 이온성 인을 4개월의 운전기간 동안 완전하게 흡착시켜 제거할 수 있었다.

주제어 : 인, 활성, 황토, 칼슘, 이온성 인

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1. Introduction

Importance of removing phosphorus in wastewater treatment is being acknowledged significantly because in many cases phosphorus may be the control factor in eutrophication of natural water body such as streams, and lakes. Phosphorus can be removed by a biological process such as A2O (Anaerobic-Anoxic-Oxic Process), and many other particular processes. To raise phosphorus removal in wastewater treatment, advanced technologies have been investigated (Hu et al., 2003; Wu et al., 2010). Wu et al. tried to find higher phosphorus removal technology using granular sludge (Wu et al., 2010), while Hu et al. found that enriched nitrifying bacteria could remove phosphorus effectively (Hu et al., 2003). On the other hand wetland was suggested for removing phosphorus from agricultural run-off which is a non-point source (Lu et al., 2009).

However, Chemical precipitation is usually used to remove phosphorus in wastewater treatment. Recently various technologies were suggested for removing phosphorus in wastewater treatment (Guan et al., 2009; Xiong et al., 2010; Yin et al., 2011). Guan et al. assessed phosphorus removal abilities for loess, cin-der, and limestone (Guan et al., 2009). It was reported that calcium plays an im-portant role in adsorption of phosphorus in wastewater (Xiong et al., 2010; Yin et al., 2011). It seems that ionic reaction be-tween calcium and phosphorus may be an important mechanism in removing phos-

phorus in wastewater for those materials containing calcium such as sepiolite, peat, and limestone (Guan et al., 2009; Xiong et al., 2010; Yin et al., 2011). Iron (Fe) is also known to be effective in remov-ing phosphorus in wastewater (Fu et al., 2009; Gutierrez et al., 2010; Moelants et al., 2011). Gutierrez et al. found that iron salts can remove phosphorus and sulfide at the same time if they were applied at influent step of wastewater (Gutierrez et al., 2010; Moelants et al., 2011). Govern-ing mechanisms of phosphorus removal by iron salts were complexation between iron and phosphorus, and then the adsorption of phosphorus on their complex (Fu et al., 2009; Gutierrez et al., 2010; Moelants et al., 2011). Other technologies such as ionic exchange, electrochemical coagulation, crystallization, and adsorption by a com-posite metal oxide have been investigated for removing phosphorus in wastewater as well (Awual et al., 2011; Bian et al., 2011; Tran et al., 2012; Liu et al., 2012).

Adsorption technology using adsorbent has also been reported (Khadhraoui et al., 2002; Xiong et al., 2010). Khadhraoui et al. found that Ca-based sorbent was ef-fective in removing phosphorus, and the adsorption capacity could be enhanced by the generated pores on its surface (Khadhraoui et al., 2002). Peat was also used as an adsorbent for removing phos-phorus in wastewater by using its porous characteristics (Xiong et al., 2010). It was known that adsorbed phosphorus on ad-sorbent is hardly desorbed for regenera-tion (Yin et al., 2011).

In this investigation, activated loess adsorbent was developed to remove phosphorus in wastewater. Loess was mixed with Ca to enhance adsorption capacity and its intensity. Loess mixed with Ca was activated at an optimum temperature of 400 °C. Activated Ca-loess complex was made as pallets to be applied in adsorption column of a wastewater treatment process. Activated loess pallet column was applied in the pilot plant of domestic wastewater for about four months.

2. Material and Methods

2.1 Materials

For phosphate adsorbing metals (adsorbents), activated calcium and loess complex was used as a supporting media. CaCl_2 (Yakuri Pure Chemicals, Japan) was used in preparing activated calcium and loess complex. Loess was grinded and sieved with STANDARD TESTING SIEVE 75 μm (No. 200). Sieved loess was mixed with 1M of CaCl_2 200 ml and 0.5 M of HCl 40 ml. KH_2PO_4 (Shinyo pure chemicals, Japan) was used for phosphate sample solution.

2.2 Adsorbent Preparation

Loess 1 kg was mixed with 1M CaCl_2 200 ml and 0.5 M HCl 40 ml (5 : 1). Calcium-loess complex (Loess mixed with calcium) was made in a form of stick with about 20 ~ 40 cm length and 5 mm of diameter (a in Fig.1). The stick type loess was dried for 2 hours in electric oven at 105 °C, and cut to around 4 ~ 5 mm as pallets (b in Fig. 1). Pallets of calcium-loess complex about

5mm in diameter (loess pallet hereafter) were made by being heated at various temperatures for 2 hours. Ca-loess pallets were activated by heating for 2 hours and cooling in desiccator for 24hours. Sticks of Ca-loess complex and its pallets were shown in Fig. 1.



Fig. 1. Sticks of Ca-loess complex (a), and their pallets (b)

2.3 Experimental Methods

Pallets (Fig. 1 (b)) were heated in various temperatures from 300 °C to 800 °C for 2 hours. Heated pallets were cooled in desiccator for 24 hours. As such the pallets were activated for adsorbing phosphate in water. In order to estimate adsorption capacities, activated Ca-loess pallets by various temperatures were introduced in different 300 ml of bottles filled with 1 mg/l of phosphate as T-P (Total Phosphorus). The bottles which contains loess pallets activated in different temperatures, and which were filled with 1 mg/l of phosphate solution were shaken by shaking incubator (Daeil Engineering DSK 522S, Korea) in 20 °C with 180rpm for 1 hour. Removal rates of phosphate by loess pallets, which were activated differently, were calculated to estimate the optimum activation temperature.

2.3.1 Isotherm Test

Isotherm test has been performed to understand the characteristics of activated loess pallets in adsorbing phosphorus in water. Pallet 5 gs were put in 300 ml of bottles filled with 0.1, 0.5, 1.0, 5.0, and 10 mg/l of phosphate solutions each. Phosphate solution has been prepared using KH_2PO_4 (Shinyo pure chemicals, Japan). Bottles were shaken by shaking incubator (Daeil Engineering DSK 522S, Korea) at 20 °C with 200 rpm for 2 hours. Water used in synthesizing samples of phosphorus solution for isotherm tests was prepared by that tap water was distilled, and followed by passing through activated carbon column and ion exchange resin. pH of the prepared water was 5.15. Freundlich isotherm model was applied in the experiment.

2.3.2 Field Application

Activated loess pallets were applied in domestic wastewater treatment using a pilot plant. A schematic pilot plant diagram is presented in Fig. 2. Raw water was treated by DAF (Dissolved Air Flotation) without coagulant, and the effluent was introduced into MBR (Membrane Bioreactor) system. Effluent of MBR system was again treated by DAF with coagulant to remove phosphorus. To remove phosphorus in very low level, activated loess pallets adsorption was employed. Phosphate was mainly removed by adsorption in loess column. Size of the column was D 15 cm × H 200 cm with flow rate of 100 ml/min. Ca-loess pallet (12 kg) was filled

in the column which having a volume of about 7,000 cm³ with D 15 cm × H 125 cm. Contact time (adsorption period) of the phosphorus with Ca-loess pallet was about 70 min. Phosphorus contained in floc was finally removed by microfiltration. Even though various processes have been used in the pilot plant for domestic wastewater treatment, phosphorus removal by Ca-loess pallet column was the main focus in this investigation. The pilot plant was set up in nearby domestic wastewater treatment plant.

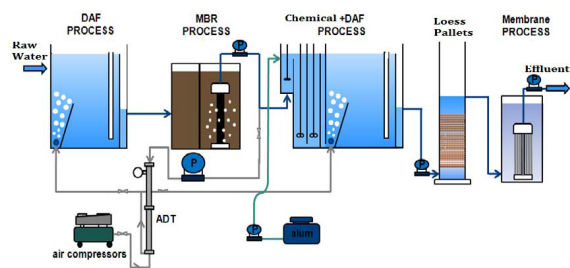


Fig. 2. Schematic diagram of the experimental process

3. Results and Discussion

3.1 Activation Temperature

Ca-loess complex were activated in various temperatures from 300 °C ~ 800 °C to find the optimum activation temperature. Results of the activations are shown in Fig. 3. The highest removal rate of T-P (phosphate) occurred at 350 °C as shown in Fig. 3. However, loess pallets activated below 350 °C were crushed down or disorganized during operation in the pilot plant. Even if phosphorus removal rate by loess pallets activated in 350 °C was highest with 67 %, it was determined that the optimum activation temperature was 400

℃ with removal rate of 51 % due to be lack of strength of loess pallets activated below 400 ℃. Loess pallets activated at 400 ℃ had enough strength to last the whole application process in the pilot plant. Loess pallets not only should have large surface area for phosphorus to be adsorbed, but they should also have enough strength to avoid being worn down by handling impact during application.

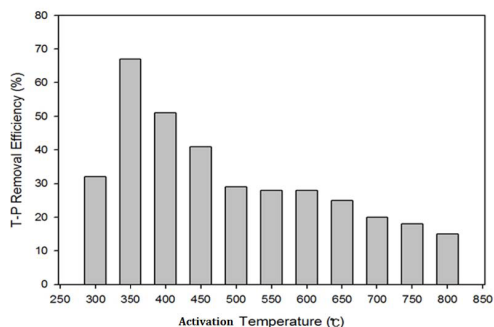


Fig. 3. Removal rates of T-P (Phosphate) by loess pallets activated in various temperatures

Reason for the decrease in phosphorus removal rate by the Ca-loess seems to be because pallets activated in high temperature seems to loose soil characteristics, and gain glass characteristics with activation temperature. SEM (Scanning Electron Microscope JSM-820 Jeol, Japan) images of loess pallets activated in different temperatures (a, c, e), and those (b, d, f) after phosphate adsorption are presented in Fig. 4. Pallet activated at low temperature (350 ℃) like (a) in Fig.4 has more rough surface, and looks more porous than the others such as (c) and (e) in Fig. 4. Surface of activated pallets was getting smoother with the increase in activating temperature as it may be observed in Fig. 4. It seems that loess is changing to glass matter at

higher temperature, and it loses surface area and active adsorption sites on surface of pallets. Phosphorus adsorbed surface of the used loess pallets are shown in b, d, f in Fig. 4. Adsorbed amount of phosphorus should depend on the surface area under the same condition. It was proved that removal rate of loess pallets activated at 350 ℃ was higher than those activated at higher temperature such as 400 and 800 ℃. Surface of the activated Ca-loess pallets after phosphorus adsorption became smoother than the original ones before phosphorus adsorption as it may be observed in Fig. 4. Due to the loss of soil characteristics of Ca-loess pallet by activation at high temperature, active functional groups such as -OH may be covered by glassified material on the surface of Ca-loess pallet as it can be interpreted

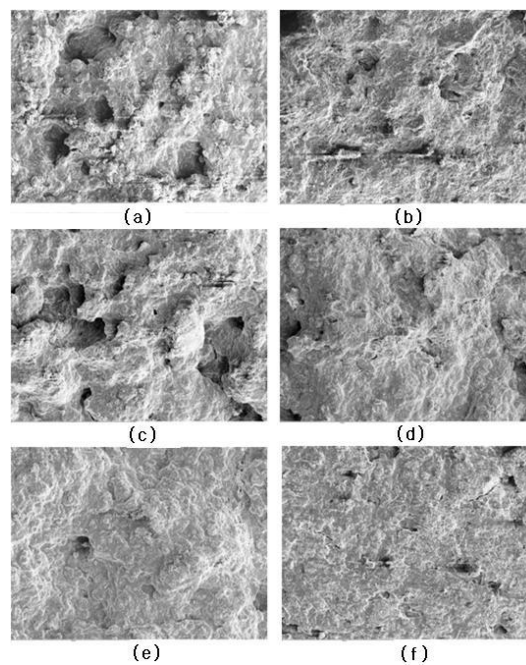


Fig. 4. SEM images (magnification: x 200) before and after phosphate adsorption of loess pallets activated in different temperatures (a),(b) 350 ℃; (c),(d) 400 ℃; (e),(f) 800 ℃

in Fig. 4. Loosing functional group may be another reason why removal rate of phosphorus by Ca-loess pallets is decreasing with active temperature.

3.2 Isotherm Test

Isotherm test has been performed for the Ca-loess pallets activated at 400 °C which is believed to be the optimum activation temperature. Result of the isotherm test is presented in Fig. 5. The result shows very good co-relations between adsorption and equilibrium concentrations. Freundlich Model, $x/m = K_f C_e^{1/n}$ was applied in the experiment. x is an amount of phosphate adsorbed in mg on the surface of loess pallets, m is weight of loess pallets in grams, K_f and $1/n$ are experimental constants, and their values were obtained with 0.03, and 0.41 in the isotherm test. C_e is equilibrium concentration. K_f value represents adsorption capacity of the loess pallets. However, the value 0.03 of K_f obtained was not so high due to the lack of number of pores on the surface of loess pallets. $1/n$ represents adsorption intensity. $1/n$ of 0.41 obtained was relatively high because loess pallets were activated with Ca and other minerals such as Al, and Fe which are contained in loess itself. Activated loess pallets have low adsorption capacity, and high adsorption intensity. Because phosphorus concentration is low in tertiary effluent, and loess is abundant and cheap, activated loess pallets may be used in removing phosphorus at very low level of concentration in final effluent of wastewater treatment.

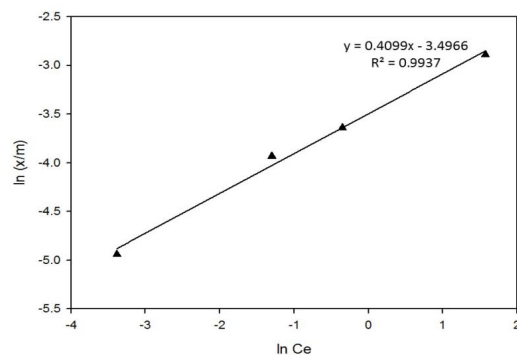


Fig. 5. Applied Freundlich model in the isotherm test for activated loess pallets

3.3 Pilot Test

Pilot plant was set up in nearby domestic wastewater treatment plant. Raw water from influent of the wastewater treatment plant was pumped into a storage tank of the pilot plant. After about two months of adjustment period from Dec. 1, 2010 to Feb. 15, 2011, pilot plant has been operated for four months until June 21, 2011. During the operation T-P (Total Phosphorus) and phosphate concentrations were monitored along with other water quality parameters. T-P and phosphate were the main focus in the investigation. Loess pallet column was set up on the wastewater treatment process as shown in Fig. 2. Domestic wastewater was treated by DAF (without chemical) - MBR - DAF (with coagulant) process. Effluent of DAF was introduced into activated loess pallet column. To remove phosphorus in extremely low level, micro-membrane has been used to remove particulate phosphorus even if activated loess column was the main focus in the investigation. Raw water quality is shown in Table 1.

Table 1. Raw Water Quality Parameters of the Pilot Plant

Parameters	Concentrations (mg/l)
Alkalinity (as CaCO ₃)	147
SS	56
BOD ₅	132.39
COD _{Mn}	135.87
COD _{cr}	164.18
T-N	26.87
T-P	3.84
PO ₄ -P	0.71

Average T-P concentration in raw water was 3.84 mg/l, which was then removed down to about 0.5 mg/l by series of processes until DAF process. The experiment attempted to lower the T-P concentration further using activated loess pallet column. Loess pallet was made through a series of processes. It was first mixed with MgCl₂, and then it was reformed as pallets, which were followed by activation at 400 °C. Loess pallet has pores and functional groups on its surface, which were generated by activation. Surface of loess pallets are charged by Ca²⁺ and Al³⁺, and more of mineral cations. Phosphorus ion (phosphate) can be combined with these positively charged cations, and particulate phosphorus may also be transported into pores on the surface. Removal mechanisms of phosphorus in water by loess pallet may be these three principles which are ionic reaction between phosphate and functional groups on surface, transport of ionic and particulate phosphorus from bulk solution into pores of pallets, and adsorption of particulate phosphorus on surface

of pallets. Fig. 6 shows T-P concentrations at effluent of each unit operation in the series of processes. T-P concentrations in raw water fluctuated all the way during the operation. T-P was removed up to about 0.5 mg/l until DAF with chemical (coagulant). It is being required to lower this T-P concentration down to lower than 0.1 mg/l to prevent receiving waters such as streams and lakes from eutrophication. Activated loess pallet column could remove T-P from about 0.5 mg/l in effluent of DAF with coagulant down to 0.1 mg/l. Ionic and particulate T-P were removed together as it can be seen in Fig. 6. T-P in effluent of loess column has been treated very stably. Even though T-P could be further removed by microfiltration, it was not feasible in the economic point of view.

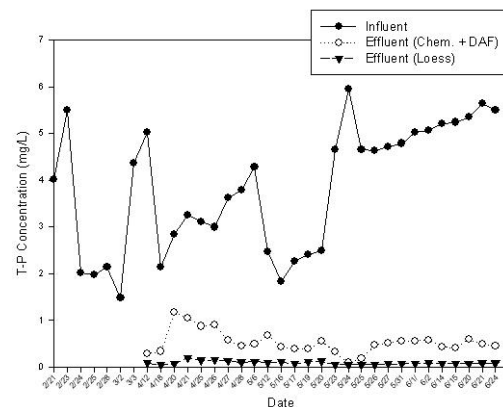


Fig. 6. T-P concentrations at each process of the pilot plant

Phosphate concentrations were also monitored along with T-P concentrations at each unit operation of the processes. Ionic phosphorus (phosphate) could be virtually removed completely by activated loess pallet column. Phosphate can

be removed by ionic combination between phosphate and functional groups on surface of loess pallets. Because loess pallet was activated with Ca^{2+} , and other cationic metal ions like Al^{3+} and Fe^{3+} contained in loess itself, ionic phosphorus (phosphate) may be adsorbed first, and then particulate phosphorus can be adsorbed by mass transport on surface and into pores of loess pallets. Results of the pilot plant operation are shown in Fig. 7. Ionic phosphorus was virtually removed completely by loess pallet column as it can be observed in Fig. 7.

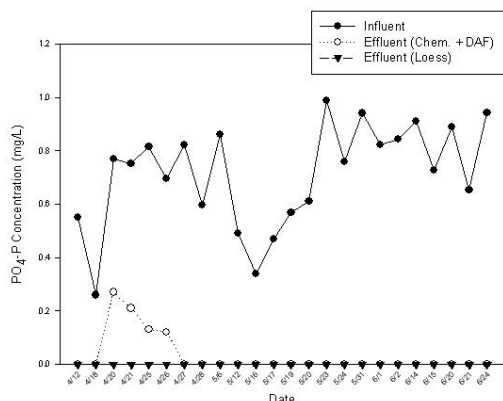


Fig. 7. PO₄-P concentrations at each process of the pilot plant

Total phosphorus can be removed up to about 0.5 mg/l by DAF with coagulant, which is traditional technology. DAF with other technologies has been devised in wastewater treatment plants to remove T-P. If T-P is to be removed fur-

ther, new technology should be employed like adsorption by activated loess pallet developed in the investigation. T-P was removed down to lower than 0.1 mg/l, and ionic phosphorus was removed completely by the developed loess pallet column in the pilot plant of domestic wastewater treatment as it can be seen in Table 2. Results of the pilot plant operation are shown in Table 2.

4. Conclusion

By traditional wastewater treatment technologies such as MBR (Membrane Bioreactor) - DAF with chemical process, total phosphorus (T-P) was removed down to about 0.5 mg/l in domestic wastewater treatment. If T-P is required to be removed further, new technology needs to be employed.

Loess mixed with Ca was activated at various temperatures. Even though the highest adsorption capacity of activated Ca-loess complex was obtained at 350 °C, hardness of the loess pallets was not strong enough, so that optimum activation temperature was determined at about 400 °C.

Activated Ca-loess pallets were developed as a new technology to adsorb phosphorus in tertiary effluent of wastewater

Table 2. Concentrations and Removal Rates of T-P and PO₄-P Treated by the Pilot Plant Operation

Unit	DAF		MBR		Coagulation+DAF		Ca+Loess		Membrane	
	mg/l	Removal rate(%)	mg/l	Removal rate(%)	mg/l	Removal rate(%)	mg/l	Removal rate(%)	mg/l	Removal rate(%)
T-P	1,866	48 %	1,407	61 %	0,542	85 %	0,099	97 %	0,026	99%
PO ₄ -P	0,526	72 %	0,753	60 %	0,08	96 %	0,001	100 %	N.D.	100%

treatment plant in the investigation. Using activated loess pallet column total phosphorus could be lowered below 0.1mg/l in final effluent of the pilot plant of domestic wastewater treatment. Ionic phosphorus (phosphate) could also be removed completely within 4months of operation in the pilot plant.

References

- J. Y. Hu, S.L. Ong, W.J. Ng, F. Lu, and X.J. Fan, (2003). A new method for characterizing denitrifying phosphorus removal bacteria by using three different types of electron acceptors. *Water Research* 37, 3463-3471.
- Chang-Yong Wu, Yong-Zhen Peng, Shu-Ying Wang, and Yong Ma. (2010). Enhanced biological phosphorus removal by granular sludge: From macro- to micro-scale. *Water Research* 44, 807-814.
- S.Y. Lu, F.C. Wu, Y.F. Lu, C.S. Xiang, P.Y. Zhang, and C.X. Jin. (2009). Phosphorus removal from agricultural runoff by constructed wetland. *Ecological Engineering* 35, 402-409.
- Baohua Guan, Xin Yao, Jinhui Jiang, Ziqiang Tian, and Shuqing An. (2009). Phosphorus removal ability of three inexpensive substrates: Physicochemical properties and application. *Ecological Engineering* 35, 567-581.
- J.B. Xiong, and Q. Mahmood. (2010). Adsorptive removal of phosphate from aqueous media by peat. *Desalination* 259, 59-64.
- Hongbin Yin, Ye Yun, Yinlong Zhang, and Chengxin Fan. (2011). Phosphate removal from wastewaters by a naturally occurring calcium-rich sepiolite. *Jour. of Hazardous Materials* 198, 362-369.
- Fu Ying, and Yu Shui-li. (2009). Characterization and phosphorus removal of polysilicic-ferric coagulant. *Desalination* 247, 442-455.
- Oriol Gutierrez, Donglee Park, Keshab R. Sharma, and Zhiguo Yuan. (2010). Iron salts dosage for sulfide control in sewers induces chemical phosphorus removal during wastewater treatment. *Water Research* 44, 3467-3475.
- N. Moelants, I.Y. Smets, and J.F. Van Impe. (2011). The potential of an iron rich substrate for phosphorus removal in decentralized wastewater treatment systems. *Separation and Purification Technology* 77, 40-45.
- Md. Rabiul Awwal, and Akinori Jyo. (2011). Assessing of phosphorus removal by polymeric anion exchangers. *Desalination* 281, 111-117.
- Dejun Bian, Shengshu Ai, Jing Liu, Yan Zuo, and Xi Tian. (2011). Treatment of phosphorus wastewater using crystallization method. *Jour. of Environmental Sciences* 23, s106-s109.
- Nam Tran, Patrick Drogui, Jean-Francois Blais, and Guy Mercier. (2012). Phosphorus removal from spiked municipal wastewater using either electrochemical coagulation or chemical coagulation as tertiary treatment. *Separation and Purification Technology* 95, 16-25.
- Ting Liu, Kun Wu, and Lihua Zeng. (2012). Removal of phosphorus by a composite metal oxide adsorbent derived from manganese ore tailings. *Jour. of Hazardous Materials* 217-218, 29-35.
- M. Khadhraoui, T. Watanabe, and M. Kuroda. (2002). The effect of the physical structure of a porous Ca-based sorbent on its phosphorus removal capacity. *Water research* 36, 3711-3718.
- J.B. Xiong, and Q. Mahmood. (2010). Adsorptive removal of phosphate from aqueous media by peat. *Desalination* 259, 59-64.
- Hongbin Yin, Ye Yun, Yinlong Zhang, and Chengxin Fan. (2011). Phosphate removal from wastewaters by a naturally occurring, calcium-rich sepiolite. *Jour. of Hazardous Materials* 198, 362-369.