

Phosphate removing by graphene oxide in aqueous solution

Tae-Sung Jun[†], No-Hyung Park^{*}, Dea-Sup So^{**}, Joon-Woo Lee^{**}, Kwang Bo Shim^{***} and Heon Ham^{***}

Korea National University of Transportation, Civil. Environmental and Transportation Engineering, Chungju 380-702, Korea

**Department of Textile Convergence of Biotechnology & Nanotechnology, Korea Institute of Industrial Technology, Ansan 426-910, Korea*

***National Nanotechnology Policy Center, Korea Institute of Science and Technology Information (KISTI), Seoul 130-741, Korea*

****Division of Materials Science and Engineering, Hanyang University, Seoul 133-791, Korea*

(Received October 15, 2013)

(Revised November 15, 2013)

(Accepted November 22, 2013)

Abstract Phosphate has been removed in waste water by chemically synthesized graphene oxide. Removing efficiency of phosphate was investigated using phosphate dispersion aqueous solution, and 70 % of phosphate was removed in phosphate dispersion solution by chemically synthesized graphene oxide solution. Removing efficiency of phosphate was increased from 70 % to 80 % with assistant of iron nano-particle in chemically synthesized graphene oxide solution. Phosphate removing capacity was up to 89.37 mg/g at initial phosphate concentration of 100 mg/l and temperature of 303 K. The Freundlich was applied to describe the equilibrium isotherms and the isotherm constants were determined.

Key words Graphene oxide, Phosphate, Adsorption, Kinetics, Isotherms, Thermodynamics

1. Introduction

With utilization of phosphate, phosphates are used for special glasses, sodium lamps, in steel production, in military applications (incendiary bombs, smoke screenings etc.), and in other applications as: pyrotechnics, pesticides, toothpaste, detergents. Among phosphate applicants, concentrated phosphoric acids, which are used in fertilizers for agriculture and farm production, make serious water pollution. When phosphate contains in drinking water, this can be a serious danger to our health because of poisonous. Hence more attention has been devoted toward the reduction of phosphate concentrations in water [1, 2].

To remove phosphate from water, the suitable removing phosphate techniques have been investigated, for instance, chemical precipitation, biological materials, membrane processes, adsorption, ion exchange and crystallization. Among many phosphate removing techniques, two methods are currently being used around the world to remove phosphorus in wastewater: biological and chemical phosphorus removal [3, 4].

Chemical phosphorus removal produces a lot more sludge than biological phosphorus removal and the dif-

ference is dependent on the type of chemical used. Biological phosphorus removal consumes more energy in terms of the aeration capacity of the process than chemical phosphorus removal. Moreover, biological phosphorus removal needs a lot more volume or space than the chemical process. Furthermore, biological phosphorus removal efficiency usually does not exceed 30 %, so that remaining phosphate should be removed by another technique [5-9].

Because membrane phosphorus removal process has low economic viability, high maintenance cost, fouling, scaling, and membrane degradation, technique of phosphorus adsorption on materials is a widely accepted for both organic and inorganic contaminants, particularly is more effective in reducing phosphate concentrations to permissible value than the other methods. Additionally, phosphorus adsorption on materials is considered a fast and inexpensive purification method. Among many adsorbents, carbon is used in the removal of various pollutants, and various carbon structures and their composites have been investigated to improve the adsorption efficacy.

Because the most important and widely used application of bulk carbon is water purification, graphene oxide (GO) was proposed phosphate adsorbent. In this study, the phosphate removal was studied by graphene oxide and polyamide. Adsorption isotherm, kinetic and thermodynamic parameters have been estimated from experimental results.

[†]Corresponding author
Tel: +82-43-841-5601
Fax: +82-43-849-1500
E-mail: tsjun@ut.ac.kr

2. Experiment

To synthesize graphene oxide, graphite powder, H_2SO_4 (98 %), H_3PO_4 (98 %), KMnO_4 (98 %) and H_2O_2 (30 wt%) were purchased and used as received.

GO was synthesized from graphite powder via a modification of Hummers and Offeman's method from graphite powders. In a typical reaction, 1 g of graphite, 12 ml of H_3PO_4 , and 36 ml of H_2SO_4 were stirred together with a Teflon-coated magnetic stirring in an ice bath. Next, 12 g of KMnO_4 was slowly added while the temperature was maintained at 0°C . Once mixed, the solution is transferred to a $35 \pm 5^\circ\text{C}$ water bath and stirred for 3 h, forming a thick paste. Next, distilled water (90 ml) was slowly dropped into the resulting paste to dilute the mixture, and then the solution was stirred for 1 h while the temperature was raised to $90 \pm 5^\circ\text{C}$. Finally, 150 ml of distilled water was added, followed by the slow addition of 10 ml H_2O_2 (30 %), turning the color of the solution from dark brown to yellow. During this final step, H_2O_2 (30 %) reduced the residual permanganate and manganese dioxide to colorless soluble manganese sulfate. The GO deposit was collected from the GO suspension by high speed centrifugation at 15000 rpm for 30 min. The obtained GO was then washed with 200 ml of HCl (5 %), and repeatedly washed with distilled water until the pH = 7. To obtain few layers GO, a low-speed centrifugation at 3,000 rpm was first used to remove thick multilayer sheets until all the visible particles were removed (3~5 min). Then the supernatant was further centrifuged at 10,000 rpm for 30 min to remove small GO pieces and water-soluble byproduct. For this experiment, at first, 25 ml of the obtained GO suspension (~6 mg GO/ml) was dispersed in 125 ml of water, followed by a sonication for 1 h (in a sonic bath) to achieve a homogeneous aqueous GO solution. Then, the final precipitates were dispersed again in 150 ml of distilled water, resulting in GO sheet suspension [10].

GO was characterized by a scanning electron microscope (SEM, JEOL, JSM 5900LV, Japan). High-resolution transmittance electron microscope (HR-TEM) was conducted on a TECNAI 20 microscope operated at 200 kV. The Ultraviolet-visible (UV-vis) transmittance and absorption spectra were performed on a Shimadzu UV-3600 Ultraviolet-visible-near infrared spectrophotometer at room temperature.

In the natural world phosphorous is never encountered in its pure form, but only as phosphates, which consists of a phosphorous atom bonded to four oxygen atoms. This can exist as the negatively charged phos-

phate ion (PO_4^{3-}), which is how it occurs in minerals, or as organophosphates in which there are organic molecules attached to one, two or three of the oxygen atoms.

For phosphate adsorption experiment, sodium phosphate (NaH_2PO_4) (Reagent) was dissolved in distilled water for the required concentration (25~125 mg/l) and used for further experiment. Batch adsorption experiments were performed using 100 ml glass bottles with addition of 0.05 g of graphene and 75 ml of phosphate solution of concentration from 25~125 mg/l. The glass bottles were sealed with Teflon and then were placed on a shaker [11].

The adsorption experiments were carried out at 100 rpm for 12 h (25°C). The temperature of the solution has been controlled to the desired value with a variation of ± 2 K by adjusting the rate of flow of thermostatically controlled water through an external glass-cooling spiral. Phosphate was measured using an UV (HUMAS HS-3300). All the experiments were repeated three times for reproducibility and the accuracy of the results are + 1 % [12-17].

3. Result and Discussion

Fig. 1(a) shows the digital image of graphene oxide dispersion (~1 mg/ml) in glass bottle. Fig. 1(b) shows the typical TEM image of graphene oxide which has a

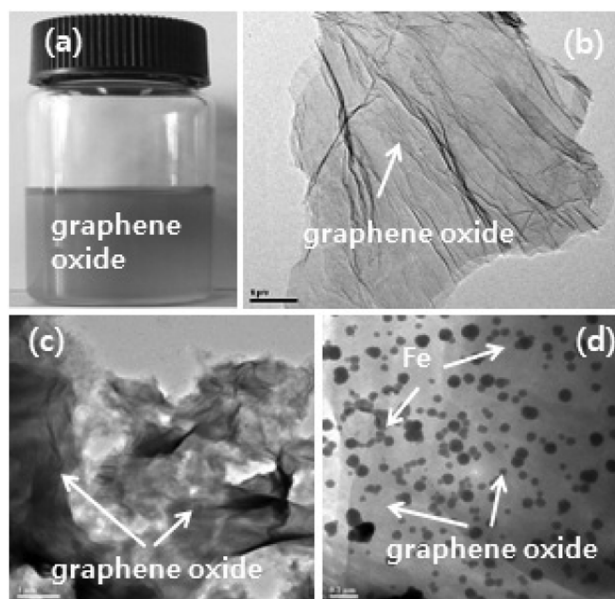


Fig. 1. (a) shows a digital image of graphene oxide solution, (b) shows a HR-TEM image of graphene oxide, (c) shows graphene oxides were aggregated with phosphate by polyamide, and (d) shows adsorption of iron nano-particles on graphene oxide.

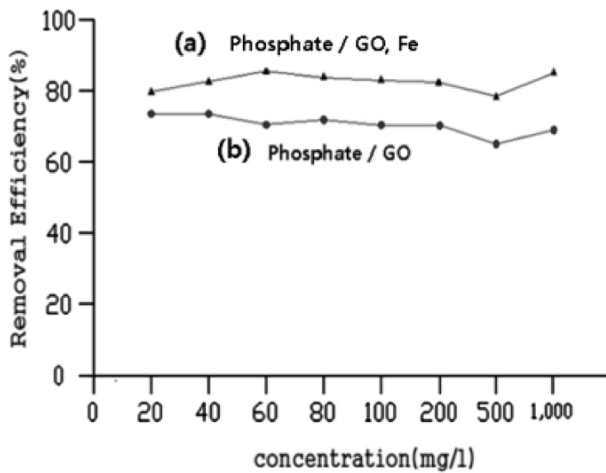


Fig. 2. (a) shows phosphate removal after aggregation with phosphate by GO and Fe. (b) shows phosphate removal after aggregation with phosphate by GO.

few tens of micro-meters. Fig. 1(c) shows TEM image of graphene oxide aggregated with polyamide. Fig. 1(d) shows adsorption of iron nano-particles on graphene oxide.

Fig. 2 shows removal efficiency of phosphate as function of polyamide concentration. To evaluate the removal efficiency of phosphate, each phosphate and polyamide concentration aqueous solution dilutes distilled water before conducting an experiment. Phosphate absorption experiments were conducted at varying initial concentration from 25–125 mg/l. Although experiments were conducted at varying experimental time from 5 minute to 24 hours, and pH from 3 to 7, removing phosphate in initial phosphate concentration has almost same and constant as shown in Fig. 2. Thus, reaction time between phosphate and graphene oxide and polyamide fixed 2 hours in this experiment, and also pH of solution fixed at 7. Because polyamide used for absorbent of phosphate and graphene oxide in aqueous solution, reaction time and pH of aqueous solution were not under the influence removing phosphate in aqueous solution.

Fig. 2(a) shows removing phosphate by graphene oxide in water as a function of polyamide concentration. Although there are some deviations of removing phosphate in each solution, most of phosphate was purified about $70 \pm 5\%$ in water. Fig. 2(b) shows the removal efficiency of phosphate by graphene oxide and iron (Fe) in water as a function of polyamide concentration. Although there are some deviations of removing phosphate in each solution, most of phosphate was purified about $80 \pm 5\%$ in water. Because iron (Fe) nano-particles in water acted with phosphate in water, phosphate removal efficiency increased in water.

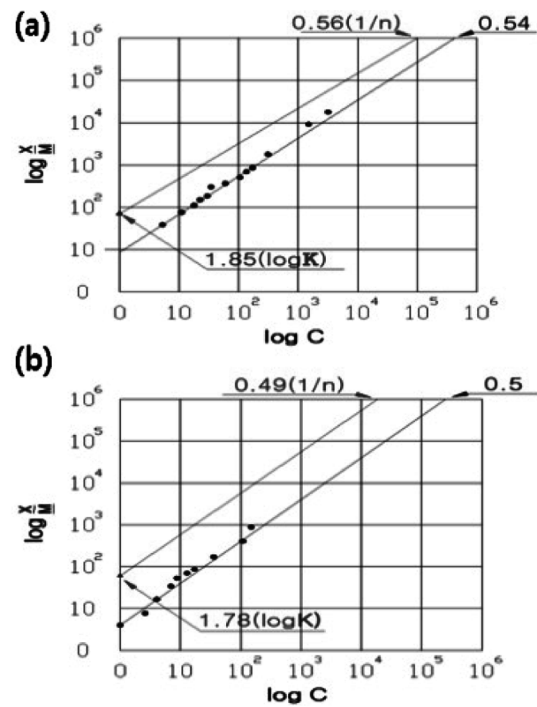


Fig. 3. (a) shows phosphate removal after aggregation with phosphate by graphene oxides. (b) shows phosphate removal after aggregation with phosphate by graphene oxides and Fe.

Fig. 3 shows Freundlich model of phosphate removal after aggregation with phosphate by graphene oxides and graphene oxides and Fe. Freundlich model is an empirical model allowing for multilayer adsorption on adsorbent. The linearized in logarithmic form and the Freundlich constants can be expressed as,

$$\log q_e = \log k_f + n \log C_e$$

where, k_f is the Freundlich constant related to adsorption capacity, n is the energy or intensity of adsorption, C_e is the equilibrium concentration of phosphate (mg/l). The values of K_f and $1/n$ obtained from the intercept and slope of the plot of $\log q_e$ versus $\log C_e$, along with the error functions at all temperatures. The values of $1/n$ were less than unity, suggesting that phosphate was adsorbed favourably by graphene at all temperatures studied. The increase in Freundlich constants with increase of temperature confirmed that adsorption was favourable at high temperatures and the process was endothermic in nature.

Fig. 3(a) and (b) show figures of the Freundlich model and correlation co-efficient calculated for adsorption isotherm model for phosphate adsorption at 100 mg/l at pH 7. Fig. 3(a) shows phosphate absorption values on surface of graphene oxide. Experimental slope value shows 0.54 and theoretical slope value shows 0.56. Fig. 3(b)

shows phosphate absorption values on surface of graphene oxide. Experimental slope value shows 0.5 and theoretical slope value shows 0.49. Because slope degree of Fig. 3(b) is lower than Fig. 3(a), phosphate can absorb on surface of graphene oxide with assistance of iron nano-particles.

4. Conclusions

Phosphate has been removed in waste water by chemically synthesized graphene oxide. Removing efficiency of phosphate was investigated using phosphate dispersion aqueous solution, and 70 % of phosphate was removed in phosphate dispersion solution by chemically synthesized graphene oxide solution. Removing efficiency of phosphate was increased from 70 % to 80 % with assistant of iron nano-particle in chemically synthesized graphene oxide solution. Phosphate removing capacity was up to 89.37 mg/g at initial phosphate concentration of 100 mg/l and temperature of 303 K. The Freundlich was applied to describe the equilibrium isotherms and the isotherm constants were determined. Freundlich model shows phosphate absorption capability of graphene oxide.

Acknowledgement

“The research was supported by a grant from the Academic Research Program of Korea National University of Transportation in 2013”.

References

- [1] X. Huang, X. Liao and B. Shi, “Adsorption removal of phosphate in industrial wastewater by using metal-loaded skin split waste”, *J. Hazard. Mater* 166 (2009) 1261.
- [2] S. Mustafa, M.I. Zamanf and S. Khan, “Temperature effect on the mechanism of phosphate anions sorption by-MnO₂”, *Chem. Eng. J.* 141 (2008) 51.
- [3] WHO (World Health Organisation), *Guidelines for Drinking Water Quality*, 4th ed., WHO, Geneva (2011).
- [4] K.A. Krishnan and A. Haridas, “Removal of phosphate from aqueous solutions and sewage using natural and surface modified coir pith”, *J Hazard. Mater* 152 (2008) 527.
- [5] S. Yeoman, T. Stephenson, J.N. Lester and R. Perry, “The removal of phosphorus during wastewater treatment: a review”, *Environ. Pollut* 49 (1998) 183.
- [6] J.P. Boisvert, T.C. To, A. Berrak and C. Jolicoeur, “Phosphate adsorption in flocculation processes of aluminium sulphate and polyaluminium-silicate-sulphate”, *Water Res.* 31 (1997) 1939.
- [7] K. Fytianos, E. Voudrias and N. Raikos, “Modelling of phosphorus removal from aqueous and wastewater samples using ferric iron”, *Environ. Pollut* 101 (1998) 123.
- [8] R.D. Neufeld and G. Thodos, “Removal of orthophosphates from aqueous solutions with activated alumina”, *Environ. Sci. Technol.* 3 (1969) 661.
- [9] H.D. Stensel, *Principles of biological phosphorus removal: Phosphorus and Nitrogen Removal from Municipal Wastewater—Principles and Practice*, H.K. Lewis: London (1991) p. 101.
- [10] A.K. Geimf and K.S. Novoselov, “The rise of graphene”, *Nat. Mater* 6 (2007) 183.
- [11] A. Demirbas, “Agricultural based activated carbons for the removal of dyes from aqueous solutions: a review”, *J. Hazard. Mater* 167 (2009) 1.
- [12] J.M. Nabais, J.A. Gomes, Suhas, P.J. Carrott, C. Laginhas and S. Roman, “Phenol removal onto novel activated carbons made from lignocellulosic precursors: influence of surface properties”, *J. Hazard. Mater* 167 (2009) 904.
- [13] S.G. Wang, W.X. Gong, X.W. Liu, Y.W. Yao, B.Y. Gao and Q.Y. Yue, “Removal of lead(II) from aqueous solution by adsorption onto manganese oxide-coated carbon nanotubes”, *Sep. Purif. Technol.* 58 (2007) 17.
- [14] A.K. Meena, G.K. Mishra, P.K. Rai, C. Rajagopal and P.N. Nagar, “Removal of heavy metal ions from aqueous solutions using carbon aerogel as an adsorbent”, *J. Hazard. Mater* 122 (2005) 161.
- [15] S.-N. Jo and S.-G. Kang, “A study on the properties of artificial aggregates containing bottom ash from the power plant and waste catalyst slag”, *J. Korean Cryst. Growth Cryst. Technol.* 22(4) (2012) 200.
- [16] G. Zhao, X. Ren, X. Gao, X. Tan, J. Li, C. Chen, Y. Huang and X. Wang, “Removal of Pb(II) ions from aqueous solutions on few-layered graphene oxide nanosheets”, *Dalton Trans* 40 (2011) 10945.
- [17] Y.-J. Choi and Y.-T. Kim, “Effect of EAF dust on the formation of ultra lightweight aggregates by using bottom ash and dredged soil from coal power plant”, *J. Korean Cryst. Growth Cryst. Technol.* 21(3) (2011) 129.