Phosphate removing by graphene oxide in aqueous solution

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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 difference 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.
2. Experiment

To synthesize graphene oxide, graphite powder, H$_2$SO$_4$ (98%), H$_3$PO$_4$ (98%), KMnO$_4$ (98%) and H$_2$O$_2$ (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$_3$PO$_4$, and 36 ml of H$_2$SO$_4$ 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 ± 5°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 ± 5°C. Finally, 150 ml of distilled water was added, followed by the slow addition of 10 ml of H$_2$O$_2$ (30%), turning the color of the solution from dark brown to yellow. During this final step, H$_2$O$_2$ (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 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 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.

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
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 ± 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 ± 5 % in water. Because iron (Fe) nanoparticles in water acted with phosphate in water, phosphate removal efficiency increased in water.

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

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.

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References


