



## Adsorptive Removal of Phosphate from Aqueous Solutions using Ceria-Titania Mixed Oxide

P.K. SATAPATHY<sup>1\*</sup>, R.K. BEHERA<sup>2</sup>, A.K. NAYAK<sup>3</sup> and T. MISHRA<sup>4</sup>

<sup>1</sup>Post Graduate Department of Chemistry, North Orissa University, Baripada-757 003, India

<sup>2</sup>Department of Chemistry, BPS College, Badasahi Mayurbhanja-757 026, India

<sup>3</sup>Department of Chemistry, Government Women's College, Sundargarh-770 002, India

<sup>4</sup>ACC Division, National Metallurgical Laboratory, Jamshedpur-831 007, India

\*Corresponding author: E-mail: pramoda\_satapathy\_70@yahoo.com

(Received: 4 September 2010;

Accepted: 9 March 2011)

AJC-9727

The present study is an attempt to use ceria-titania mixed oxide as an adsorbent for removal of phosphate from aqueous solution. Physico-chemical characterization revealed that ceria-titania mixed oxide has anatase phase indicating the homogeneous distribution of cerium in the anatase crystal lattice without forming any separate cerium oxide phase. Pore size distribution study indicated the mesoporous nature of the material. The adsorption studies were carried out with respect to effect of pH, initial phosphate concentration and amount of adsorbent. Phosphate uptake was seen to increase with increasing amount of adsorbent and pH and attains maximum at pH 5.0 whereas it decreases with increasing concentration of phosphate solution. The experimental equilibrium adsorption data were fitted with Langmuir isotherm indicating monolayer adsorption.

**Key Words:** Adsorption, Phosphate, Ceria-titania mixed oxide, Adsorbent, Adsorbate.

### INTRODUCTION

Although limiting amount of phosphorous is essential for growth of organisms in most eco systems, its presence in excess may cause eutrophication and pose significant environmental problems to water resources. Generally there are three forms of phosphate namely orthophosphate, polyphosphate and organic phosphate found in aqueous solution. The municipal and industrial wastewaters mainly contain orthophosphate (up to 15 mg/L as P) together with organic phosphate. Phosphorous removal from wastewater has been widely investigated during last decade. Chemical precipitation, adsorption/ion exchange and biological removal of phosphate are common approaches that have been successfully employed. Among these methods adsorptive removal of phosphate from aqueous solution has been employed by many researchers across the globe. A wide variety of adsorbents natural and synthetic have been used so far and the search for further improvement has been continued<sup>1-7</sup>.

Cerium oxide containing materials have been the subjects of numerous investigations in recent years because of their broad range of applications in catalysis and in advanced ceramic materials<sup>8-16</sup>. The success of ceria in diverse applications is mainly due to its unique combination of an elevated oxygen transport capacity coupled with the ability to shift easily between reduced and oxidized states ( $Ce^{3+} \leftrightarrow Ce^{4+}$ )<sup>15</sup>.

Despite its widespread applications, the use of pure cerium dioxide is highly discouraged because it is poorly thermostable as it undergoes sintering at high temperatures, thereby losing its crucial oxygen storage and release characteristics<sup>15,17,18</sup>. To increase its temperature stability and ability to store and release oxygen during operations, other transition and non transition metal ions ( $Al^{3+}$ ,  $Si^{4+}$ ,  $Ti^{4+}$ ,  $Zr^{4+}$ , etc.) are normally introduced into the ceria cubic structure<sup>19-28</sup>. The redox and catalytic properties of  $CeO_2$  are strongly influenced when it is combined with other transition metals oxides like  $TiO_2$ .

The photo catalytic activity of ceria-titania mixed oxide prepared by sol gel method is well known, however its adsorption behaviour has not yet been studied. The objective of this work is to prepare the ceria-titania mixed oxide by sol-gel method and to study its feasibility as an adsorbent for phosphorous removal from wastewater.

### EXPERIMENTAL

Mesoporous  $CeO_2$ - $TiO_2$  mixed oxides with 2 and 5 wt % of  $CeO_2$  were prepared by sol-gel method using ceric ammonium nitrate and titanium(IV) isopropoxide as precursors and 1-propanol as solvent. About 400 mL of water of pH 2.5 (pH was adjusted to 2.5 by adding  $HNO_3$ ) was taken in a beaker under magnetic stirring condition at room temperature. Calculated amount of titanium isopropoxide with 20 mL of

*n*-propanol and required amount of aqueous ceric ammonium nitrate solution (about 25 mL) were taken in two separate burettes and clamped above the beaker with 400 mL water. Both the solutions were added drop by drop to the water for 20 min. Obtained white precipitate was allowed to remain under stirring condition for another 4 h. Then the solid precipitate was separated by centrifuge and dried at 100 °C in an oven. 100 °C dried samples were denoted as TiCe-2 and TiCe-5.

Stock solutions of phosphate (1000 mg/L) were prepared by dissolving  $\text{KH}_2\text{PO}_4$  in distilled water. Working solutions were prepared by suitable dilution of stock solution with distilled water as and when required for different experiment.

**Characterization of samples:** XRD patterns of all the synthesized samples calcined at different temperatures were recorded on a Siemens (model: D-500) semiautomatic diffractometer using  $\text{Cu-K}\alpha$  radiation source and Ni filter in the range of 10 to 70°. BET surface area, pore volume and pore size distribution was determined by  $\text{N}_2$  adsorption desorption method at liquid nitrogen temperature using NOVA 4000e (Quantachrome, ESA). Prior to adsorption desorption measurements, the samples were degassed at 393 K at  $10^{-4}$  torr for 5 h.

**Adsorption experiments:** The adsorption of phosphate was carried out by equilibrium experiments of batch type. In a typical experiment, 50 mL of aqueous dihydrogen phosphate solution of desired concentration was mixed with an appropriate amount of adsorbent (ceria-titania mixed oxide) in a 100 mL stoppered conical flasks. The initial phosphate concentration and amount of adsorbent were varied from 5-30 mg/L and 1.0-6.0 g/L, respectively. The solutions were adjusted to desired pH by addition of dilute NaOH or HCl: the volume of NaOH or HCl was never exceeding 0.5 mL. The flasks were shaken in a water shaker bath at room temperature with a constant stroke (100 rpm) until the solution was attained the equilibrium. A preliminary experiment revealed that about 9 h was required to attain the equilibrium. The sample was taken at regular intervals, centrifuged or filtered through Whatman 42 filter paper and the concentration of phosphate in the filtrate was determined spectrophotometrically by standard phosphovanadomolybdate method. The amount of phosphate adsorbed was determined from the ratio of phosphate in the solution and particulate phases using the following equation.

$$q_e = (C_i - C_e)V/m \quad (1)$$

where  $q_e$ ,  $C_i$ ,  $C_e$ ,  $V$  and  $m$  represent the amount of P adsorbed on the solid ( $\text{mg P g}^{-1}$ ), the initial concentration ( $\text{mg L}^{-1}$ ), the final concentration ( $\text{mg L}^{-1}$ ), volume of the solution (L) and amount of adsorbent (g) respectfully.

## RESULTS AND DISCUSSION

XRD spectra of all the synthesized materials show broad bands with standard 'd' value of anatase phase. Irrespective of cerium amount all the XRD shows the presence of only anatase phase indicating the homogeneous distribution of cerium in the anatase crystal lattice without forming any separate cerium oxide phase. BET surface area and pore size distribution was calculated from  $\text{N}_2$  adsorption desorption isotherms. All the isotherms are of type II or IV indicating the mesoporous nature of the material. In all the materials surface area is found to

increase with the increasing cerium content of the material. However average pore diameter slightly decreases with the increasing cerium content (Table-1).

TABLE-1  
TEXTURAL PARAMETERS OF THE  
SYNTHESIZED MATERIALS

Sample code	Ceria (wt %)	Titania (wt %)	Calcinations temp. (°C)	BET surface area ( $\text{m}^2/\text{g}$ )	Pore volume ( $\text{mL/g}$ )	Pore radius (Å)
Ti-Ce-2	02	98	400	122	0.324	30.61
Ti-Ce-5	05	95	400	126	0.279	30.23

## Adsorption of phosphate

**Preliminary observations:** Preliminary studies with varying initial phosphate concentration ( $5\text{-}30 \text{ mg P L}^{-1}$ ) at fixed pH 5.0 and adsorbent dose ( $2 \text{ g L}^{-1}$ ) shows the adsorption process is relatively slow and the equilibrium is attained within 9 h (Fig. 1). No further change in equilibrium concentration was observed up to 30 h. The time required to reach the equilibrium appears to be independent of initial phosphate concentration. Hence the equilibrium time is kept 9 h for all further adsorption experiments.

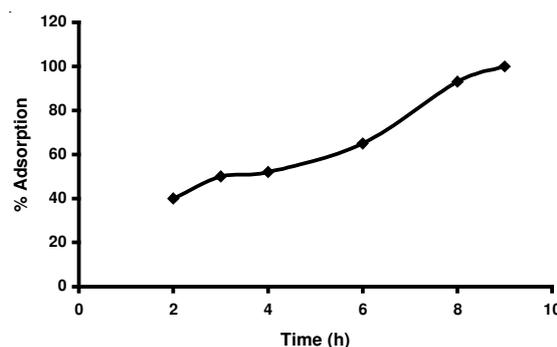
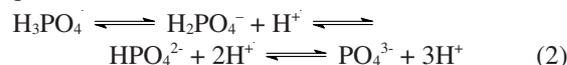


Fig. 1. Effect of contact time on phosphate adsorption over Ti-Ce-2 sample

**Effect of pH:** Phosphate exists in different ionic forms ( $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$  and  $\text{PO}_4^{3-}$ ) and the proportion of each species in an aqueous solution is a function of pH according to dissociation equilibrium of  $\text{H}_3\text{PO}_4$  as delineated below:



where  $\text{pK}_1 = 2.15$ ,  $\text{pK}_2 = 7.2$  and  $\text{pK}_3 = 12.33$ . This indicates the  $\text{H}_2\text{PO}_4^-$  is most abundant below pH 7.2, while  $\text{HPO}_4^{2-}$  is prevalent in between pH 7.2 and 12.0. Keeping these in view, the effect of varying pH on adsorption of phosphate was studied at fixed phosphate concentration ( $10 \text{ mg P L}^{-1}$ ) and adsorbent dose ( $2 \text{ g L}^{-1}$ ) and the results are presented in Fig. 2.

As evident from the Fig. 2, the phosphate adsorption increases with increase of pH, attains a maximum value at ca. 5.0 and then decreases progressively on further increase of pH up to ca. 9.0. Similar trends with adsorption maxima in between pH range 5-7 have been reported for adsorption of phosphate on several naturally occurring minerals or industrial wastes containing oxides/oxyhydroxides<sup>29,30</sup>. The present study, indicates that  $\text{H}_2\text{PO}_4^-$  is the main adsorbing species at  $\text{pH} \leq 5.0$  which gradually decreases with simultaneous increase of  $\text{HPO}_4^{2-}$  species.

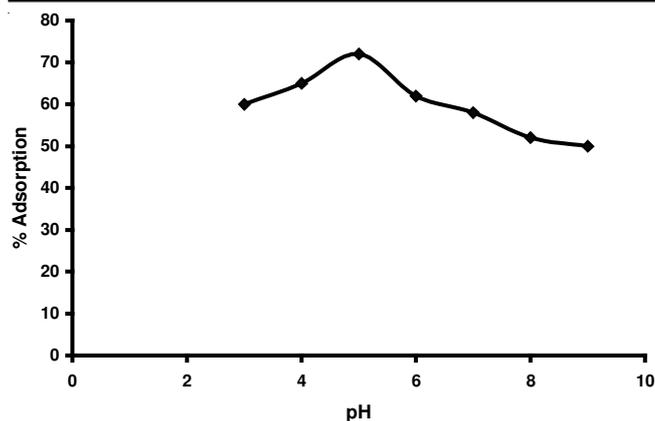


Fig. 2. Effect of pH on phosphate adsorption over Ti-Ce-2 sample

**Effect of adsorbent dose and initial adsorbate concentration:** The results of phosphate adsorption with varying amount of Ti-Ce-2 sample (1.0-6.0 g/L) and initial phosphate concentrations (5-30 mg P L<sup>-1</sup>), keeping all other parameters fixed, are illustrated in Figs. 3 and 4, respectively. The percentage adsorption of phosphate increases with increase of amount of adsorbent (Ti-Ce-2) due to increase of active sites. On the other hand the percentage of adsorption decreases with increase of initial concentration of phosphate at a constant amount of adsorbent which probable due to blockage of pores of the adsorbent.

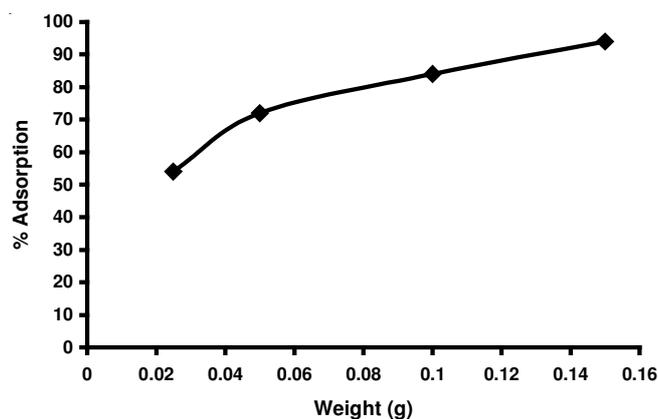


Fig. 3. Effect of Ti-Ce-2 dose on percentage of phosphate adsorbed, with initial phosphate concentration, 10 mg P L<sup>-1</sup> and pH 5.0

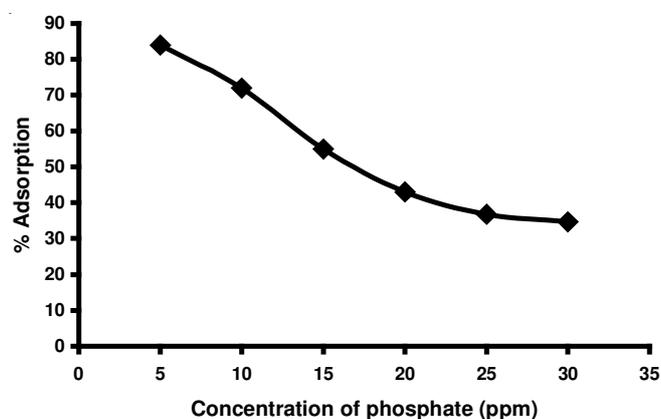


Fig. 4. Effect of initial phosphate concentration (5-30 mg P L<sup>-1</sup>) on percentage of phosphate adsorbed, with amount of adsorbent, 2 g/L and pH 5.0

**Adsorption isotherms:** Among several available models, the classical Langmuir and Freundlich models have been most extensively used to describe the equilibrium established between the adsorbate on the adsorbent and in solution. In present study, the equilibrium phosphate adsorption data were fitted to Langmuir equations (eqn. 3) (Fig. 5). The linearized form of Langmuir equation is given by:

$$C_e / q_e = 1/bQ_0 + C_e / Q_0 \quad (3)$$

where  $C_e$  is the equilibrium phosphate concentration in solution (mg P L<sup>-1</sup>),  $q_e$  is the equilibrium phosphate uptake per unit mass of adsorbent (mg P g<sup>-1</sup>),  $Q_0$  is the maximum adsorption capacity (mg P g<sup>-1</sup>) and  $b$  is Langmuir constant (energy of adsorption). The fitting of Langmuir model assumes that maximum adsorption corresponds to a saturated monolayer of adsorbate on the adsorbent surface with uniform energies of adsorption and no transmigration of adsorbate in the plane of surface.

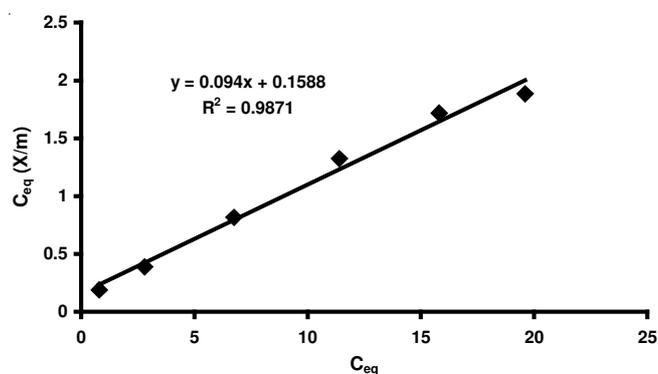


Fig. 5. Langmuir plot of adsorption of phosphate over Ti-Ce-2 sample

## Conclusion

The potential of ceria-titania mixed oxides prepared by sol-gel method, for removal of phosphate from its aqueous solution was studied. Ceria-titania mixed oxide having 2 wt % ceria was found effective an adsorbent for phosphate at pH 5.0. It was found that the percentage of phosphate adsorption increases with increasing concentration of adsorbent (Ti-Ce-2 sample) and decreases with increasing initial concentration of phosphate.

## REFERENCES

1. M. Ozacar, *Chemosphere*, **51**, 321 (2003).
2. I. Zhu and R. Zhu, *Sep. Purif. Technol.*, **54**, 71 (2007).
3. K. Karageorgiou, M. Paschalis, G.N. Anastassakis, *J. Hazard. Mater. A*, **139**, 447 (2007).
4. B. Nowack and A.T. Stone, *Water Res.*, **40**, 2201 (2006).
5. S. Mustafa, M.I. Zaman and S. Khan, *J. Colloid Interface Sci.*, **301**, 370 (2006).
6. E. Ou, J. Zhou, S. Mao, J. Wang, F. Xia and L. Min, *Colloids Surf. A*, **308**, 47 (2007).
7. K. Kuzawa, Y.-J. Jung, Y. Kiso, T. Yamada, M. Nagai and T.-W. Lee, *Chemosphere*, **62**, 45 (2006).
8. A. Trovarelli, *Catalytic Science Series 2*; World Scientific Publishing Company: London, UK (2002).
9. S. Bernal, J. Kasper and A. Trovarelli, *Catal. Today*, **50**, 173 (1999).
10. A. Trovarelli, *Catal. Rev. Sci. Eng.*, **38**, 439 (1996) and references therein.
11. T. Sato, K. Dosaka, M. Ishitsuka, E.M. Haga and A. Okuwaki, *J. Alloys Compd.*, **193**, 274 (1993).

12. M. Sahibzada, B.C.H. Steele, K. Zheng, R.A. Rudkin and I.S. Metcalfe, *Catal. Today*, **38**, 459 (1997).
13. S. Rossignol, Y. Madier and D. Duprez, *Catal. Today*, **50**, 261 (1999).
14. P. Fornasiero, G. Balducci, R. Di Monte, J. Kaspar, V. Sergo, G. Gubitosa, A. Errero and M. Graziani, *J. Catal.*, **164**, 173 (1995).
15. A. Trovarelli, C. de Leitenburg and G. Dolcetti, *Chem. Tech.*, **27**, 32 (1997).
16. K.C. Taylor, *Catalysis Science and Technology*; Springer-Verlag: Berlin, Ch. 2 (1984).
17. S.J. Schmiege and D.N. Belton, *Appl. Catal. B: Environ.*, **6**, 127 (1995).
18. R. Di Monte, P. Fornasiero, J. Kaspar, M. Graziani, J.M. Gatica, S. Bernal and A.G. Herrero, *Chem. Commun.*, **21**, 67 (2000).
19. M. Yashima, H. Arashi, M. Kakihana and M. Yoshimura, *J. Am. Ceram. Soc.*, **77**, 1067 (1994).
20. B.M. Reddy, A. Khan, Y. Yamada, T. Kobayashi, S. Loridant and J.C. Volta, *Langmuir*, **19**, 3025 (2003).
21. J. Rynkowski, J. Farbotko, R. Touroude and L. Hilaire, *Appl. Catal. A: Gen.*, **203**, 335 (2000).
22. E. Guglielminotti and F. Bocuzzi, *J. Mol. Catal. A: Chem.*, **104**, 273 (1996).
23. B.M. Reddy, A. Khan, Y. Yamada, T. Kobayashi, S. Loridant and J.C. Volta, *J. Phys. Chem. B*, **107**, 5162 (2003).
24. A. Bensalem, F. Bozon-Verduraz, M. Delamar and G. Bugli, *Appl. Catal. A: Gen.*, **121**, 81 (1995).
25. W. Liu and M. Flytzani-Stephanopoulos, *J. Catal.*, **153**, 304 (1995).
26. B.M. Reddy, A. Khan, Y. Yamada, T. Kobayashi, S. Loridant and J.C. Volta, *J. Phys. Chem.*, **106**, 10964 (2002).
27. A. Trovarelli, M. Boaro, E. Rocchini, C. de Leitenburg and G. Dolcetti, *J. Alloys Compd.*, **323**, 584 (2001).
28. B.M. Reddy, A. Khan, Y. Yamada, T. Kobayashi, S. Loridant and J.C. Volta, *J. Phys. Chem. B*, **107**, 11475 (2003).
29. S. Karaca, A. Gurses, M. Fider and Acikyildiz, *J. Hazard. Mater. B*, **128**, 273 (2006).
30. Y. Li, C. Liu, Z. Luana, X. Peng, C. Zhua, Z. Chena, Z. Zhang and J. Fan, *J. Hazard. Mater. B*, **137**, 374 (2006) and reference cited therein.