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PHOSPHATE REMOVAL FROM AQUEOUS SOLUTIONS BY ADSORPTION ONTO AMMONIUM-FUNCTIONALIZED MESOPOROUS SILICA

Mémoire présenté
à la Faculté des études supérieures de l'Université Laval
dans le cadre du programme de maîtrise en génie agroalimentaire
pour l'obtention du grade de maître es sciences (M.Sc.)

Département des sols et de génie agroalimentaire
FACULTÉ DES SCIENCES DE L'AGRICULTURE ET DE L'ALIMENTATION
UNIVERSITÉ LAVAL
QUÉBEC

2009

Résumé long

Les activités agricoles génèrent des effluents riches entre autres en composés phosphorés dont le contrôle constitue un enjeu important du fait de leur implication directe dans le phénomène d'eutrophisation des milieux aquatiques. L'élimination des composés phosphorés se trouvant dans les effluents d'origine agricole et agroalimentaire est conventionnellement effectuée au moyen de traitements biologiques ou de traitements physicochimiques. Les premiers sont souvent complexes, longs à opérer et délicats car ils dépendent de plusieurs facteurs tels que la température, le pH, la concentration en oxygène dissous et la balance des nutriments dans l'eau en plus de générer des boues volumineuses dont il faut disposer. Les traitements physicochimiques les plus employés impliquent la précipitation des espèces phosphorés qui nécessite un contrôle rigoureux du pH et l'ajout de réactifs chimiques souvent coûteux. De plus, ces traitements produisent un précipité insoluble de phosphore métallique qui est non recyclable. Le procédé d'adsorption peut constituer une alternative intéressante et prometteuse du fait qu'il ne produit pratiquement pas de boues en plus de permettre la récupération et la réutilisation des phosphates. Divers adsorbants ont été développés et utilisés pour l'enlèvement des ions phosphate mais leur capacité d'adsorption reste toujours faible et le temps pour atteindre l'équilibre est élevé ce qui nécessite impérativement le développement de nouveaux matériaux adsorbants.

Dans cette étude, la silice mésoporeuse SBA-15 possédant une grande surface spécifique, une structure bien définie et une porosité élevée a été utilisée comme adsorbant pour les ions phosphate dissous. En effet, une fois synthétisée, cette silice a été fonctionnalisée en surface avec des groupements amines via la technique de greffage post-synthétique. L'acidification du matériau obtenu a permis de transformer les groupements amines en ammonium responsables du processus d'adsorption par attraction électrostatique. Les tests d'adsorption ont été effectués en batch et les solutions filtrées ont été analysées par HPLC ionique équipé d'une colonne Ionpac AS18 et d'un détecteur de conductivité. L'effet des paramètres opératoires tels que la température, le pH, le temps, la charge en adsorbant, la concentration initiale en ions phosphate, la charge en groupements amine ainsi que le type d'amine de la SBA-15 fonctionnalisée, la présence d'autre anions et cations ainsi que la régénération de l'adsorbent ont été investigués. Les résultats montrent qu'une capacité maximale de 27 mg P/g a été obtenue à 5°C. L'adsorption atteint un maximum à pH 4 avec

une capacité d'adsorption de 31.5 P mg/g. L'équilibre d'adsorption a été atteint au bout de 10 min. L'augmentation de la charge en adsorbant avait un effet positif sur les pourcentages d'adsorption. La quantité adsorbée de P augmente avec l'augmentation de la concentration de mono- di- et tri-ammonium jusqu à 40% avec un maximum de ~70 mg P/g d'adsorbant. La capacité d'adsorption n'a pas changé après cinq cycles d'adsorption-désorption.

Extended abstract

The agricultural activities generating effluents rich in phosphate compounds which control constitutes a major concern due to their direct involvement in the eutrophication of the aquatic environments. The elimination of phosphate compounds from agricultural and agri-food effluents are conventionally carried out by biological or physicochemical treatments. The former are long and complex to be operated. In addition their efficiency in removing phosphate could be influenced by several factors such as temperature, pH, concentration of dissolved oxygen, and the balance of the nutrients in water. As for physicochemical treatments, they often involve precipitation which requires a rigorous control of pH and the addition of expensive chemical reagents, and at the end they give a complex of insoluble phosphorus precipitate which can not be recycled. Adsorption process can be a promising alternative for phosphate removal especially in producing little sludge volumes as well as the ability to reuse recovered phosphates. Various adsorbents were developed and tested for phosphate removal but their adsorption capacity is still weak, the time to attain the equilibrium is relatively high which necessitates the development of new adsorbents.

In this study, SBA-15 mesoporous silica having a large specific surface area, a well defined structure and a high porosity was used as adsorbent for dissolved phosphates removal. Indeed, once the bare silica was synthesized, it was functionalized with amine groups *via* the grafting technique. The acidification of grafted SBA-15 transforms the amine groups into ammonium equivalents responsible for the adsorption by electrostatic attraction. The adsorption tests were carried out in batch and the filtered solutions were analyzed by ionic HPLC equipped with Ionpac AS18 column and conductivity detector. The effect of the operating parameters including temperature, pH, time, adsorbent loading, the initial phosphate concentration, amine type and loading on the SBA-15, the presence of other anions and cations as well as the regeneration of the adsorbent were investigated. The results showed that a maximum capacity of 27mg P/g was obtained at 5°C. At ambient temperature, maximum adsorption was reached at pH 4 with a capacity of adsorption of 31.5 mg P/g. Adsorption equilibrium was reached within 10 min. The increase in adsorbent loading had a positive effect on adsorption percentage. The adsorbed P increased with increasing the concentration of mono-, di-and tri-ammonium until 40% leading to a maximum adsorption capacity of ~ 70

mg P/g adsorbent. The adsorption capacity did not change after five cycles of adsorption-desorption.

Résumé court

Le développement de nouveaux adsorbants pour l'adsorption des ions phosphate présents dans les effluents agricoles et agroalimentaires pourrait représenter une alternative intéressante pour réduire l'eutrophisation des eaux de surface. Dans ce travail, la SBA-15 est synthétisée *via* greffage post-synthétique pour l'adsorption des ions phosphate monovalents ($H_2PO_4^-$) présents dans des solutions aqueuses synthétiques. L'effet des conditions opératoires telles que la température, la charge en adsorbant, la concentration initiale en ions phosphate, le pH, la présence d'autres anions et cations ainsi que la régénération de l'adsorbant ont été investigués. Les résultats montrent qu'une capacité maximale de 27mg P/g a été obtenue à 5°C avec la SBA-15 fonctionnalisée avec des groupements mono-ammonium. L'augmentation de la charge en adsorbant avait un effet positif sur les pourcentages d'adsorption. L'adsorption atteint un maximum à pH 4. La présence d'autres anions et cations n'avait pas un effet significatif sur l'adsorption. La capacité d'adsorption n'a pas changé après cinq cycles d'adsorption-désorption.

Short Abstract

The development of an efficient adsorbent for phosphate removal from wastewater to prevent the eutrophication in surface waters is very important. In this study, ammonium-functionalized SBA-15 silica was synthesized via post-synthesis grafting. This material was used as an adsorbent for monovalent phosphate ion ($H_2PO_4^-$) removal from synthetic aqueous solutions. The effects of operating conditions such as temperature, adsorbent loading, initial anion concentration, pH, the presence of competitive ions on the adsorption performances and the regeneration of the adsorbent were investigated. Results showed that adsorption capacity decreased with increasing temperature. A maximum capacity of 27mg P/g was obtained at 5°C. At ambient temperature, the maximum removal of phosphate was reached at pH 4. The adsorption was almost unaffected by the presence of competitive ions. Regeneration tests showed that the adsorbent retained its capacity after 5 adsorption–desorption cycles.

Dédicace

A celui qui m'indiqué la bonne voie….

À mon père

A celle qui a attendu avec patience les fruits de son amour…

À ma mère

A celui qui m'a soutenue avec confiance…

À MOUSTAFA

Aux rayons de soleil…..

À mes enfants AHMED et RYM

Avec beaucoup d'amour, de tendresse et en douceur, je dédie ce travail à vous tous.

Abir Elnemr, 2008

Remerciements

Je tiens à remercier sincèrement ma directrice, la *Dre. Safia Hamoudi* pour m'avoir donné l'opportunité de travailler avec elle, pour ses conseils, pour son amitié à mon égard ainsi que pour son côté humain et professionnel. Sa présence était pour moi indispensable.

J'adresse également mes remerciements à mon co-directeur, le *Dr. Khaled Belkcemi* de m'avoir accueillie dans son laboratoire. L'intérêt qu'il a porté à mon travail et la confiance qu'il m'a constamment témoignée a été pour moi très motivants.

Je remercie également la petite famille du laboratoire qui m'a accueillie et intégrée pendant toute la durée de ma maîtrise. En l'occurrence, je remercie *Rabih Saad, Zahir Dehouche, Nassima Kemache, Nasima Chorfa et Hassen Bouasker* pour la bonne humeur que vous avez assurée tout au long de cette année.

Finalement, je remercie toute ma famille et mes amis.

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CHAPTER 1: INTRODUCTION

Ecosystems that were severely disrupted by invasion of human activity attract a lot of attention among environmentalists. Eutrophication of aqueous systems by phosphate ions is one of the major environmental problems. The presence of phosphorous species in surface waters can lead to abundant development of aquatic plants, growth of algae, with some kinds of them being toxigenic, thus causing eutrophication. Excessive increase in algae and a decrease in water quality are the main results of eutrophication, which can lead to health problems and loss of property value (Seviour et al., 2003; Zeng et al., 2004; Karageorgiou et al., 2006).

Phosphates are very important basic materials in agricultural and other industrial applications. They are often present in low concentrations in water, almost solely as organic phosphate, inorganic phosphate (orthophosphates) and polyphosphates (Zeng et al., 2004; Karageorgiou et al., 2006). Their release to surface water is of environmental concern; this essential nutrient is usually considered as the growth limiting factor of aquatic vegetation in surface waters with a critical level of 0.01 mg L^{-1} for dissolved P and 0.02 mg L^{-1} for total P (Moon et al., 2007).

In order to meet effluent quality standards, it is desirable that water treatment facilities remove phosphorus from wastewaters, before they are returned to the environment. Total removal or at least a significant reduction of phosphorus is obligatory, if not fulfilled, in most countries (de-Bashan and Bashan, 2004). Wastes containing phosphorus most meet the maximum discharge limits. In the province of Québec (Canada), these limits are determined on a plant-by-plant basis, but a typical effluent total unfiltered phosphorus target is between 0.8 and 1.0 mg P L (Galarneau and Gehr, 1997). Various techniques have been used for phosphate removal. The broad categories of phosphate effluent treatment include physical, chemical and biological methods (Ozacar, 2003; de-Bashan and Bashan, 2004; Karageorgiou et al, 2006; Kuzawa et al., 2006).

Chemical removal techniques are the most effective and well-established methods up to date, including phosphate precipitation with calcium, aluminum, and iron salts. Chemical precipitation gets the operations difficult, if not impossible, to recycle in an economical industrial level. Besides, the cost associated with the use of metal salts and pH-controlling additives may hinder the widespread application (de-Bashan and Bashan, 2004; Karageorgiou et al., 2006). Because of chemical phosphate removal problems, biological removal with denitrifying phosphate accumulating organisms open opportunities for recovering most of the phosphorus and beneficial applications of the product. However to operate a successful biological phosphate removal process, it is imperative that the incoming wastewater contains the correct balance of nutrient carbon sources and pH. Moreover temperature and dissolved oxygen concentration to ensure the healthy sludge population prevailing in the reactors should be adjusted (Mulkerrins et al., 2004). Various physicochemical methods have been suggested including reverse osmosis, electro-dialysis, contact filtration and adsorption (Ozacar, 2003). Adsorption is one of the techniques, which is comparatively more useful and economical for phosphate removal especially with the application of low cost and easily available adsorbent materials (Hano et al., 1997; Ozacar, 2003; Karageorgiou et al., 2006; Kuzawa et al., 2006; Karaca et al., 2004).

Considerable research is being conducted to optimise these processes, as well as to explore innovative treatments for the removal of phosphate from the aqueous environment. Adsorption has been used as an alternative method for phosphate removal in wastewater treatment since the 1960s. For several reasons, the use of inorganic adsorbents seems to be a promising alternative (Ozacar, 2003). Although, adsorption process has some advantages, such as less production of sludge and easy operation, the process has not been applied widely because the suspended solids contained in the feed water accumulate in and clog the adsorbent bed and most adsorbents cannot be reused (Kuzawa et al., 2006). Various adsorbents have been developed for phosphate removal such as aluminum oxide (Hano et al., 1997), calcite (Karageorgiou et al., 2006), hydrotalcite (Kuzawa et al., 2006), alunite (Ozacar, 2003), layered double hydroxides (Das et al., 2006), dolomite (Karaca et al., 2004), and metal-loaded orange waste (Biswas et al., 2007).

Periodic mesoporous silica characterized by large specific surface area, high pore volume, uniform pore size distribution and controlled pore structure, which could be obtained through the coupling of inorganic and organic components can be used for the purpose of several pollutants removal from wastewaters (Sayari and Hamoudi, 2001; Hoffmann et al., 2006). The aim of this study is to investigate periodic mesoporous silica especially SBA-15 functionalized with ammonium groups for the adsorptive removal of phosphate from aqueous solutions in a laboratory scale.

CHAPTER 2: LITERATURE REVIEW

2. 1. Eutrophication

Eutrophication is a major international environmental problem caused by the enrichment of an aquatic ecosystem with chemical nutrients such as nitrogen and phosphorous compounds. It is considered one of the important forms of pollution because it promotes excessive plant growth and decay. Blooms of cyanobacteria and eukaryotic algae occur as a consequence of the presence of nutrients. Decay of resulting algal blooms consumes oxygen and prevents light infiltration, as the algae begin to die and decompose the biological oxygen demand spikes, resulting in anoxia and causing severe water quality problems including increased purification costs, loss of livestock and the possible lethal effect of algal toxins on drinking water (Bartram et al., 1999; Wang et al., 2007). All respiring plants and animals require oxygen and it is replenished in daylight by photosynthesizing plant and algae. Under eutrophic condition, dissolved oxygen greatly increases during the day, but is greatly reduced after dark by the respiring algae. When dissolved oxygen levels decline to hypoxic levels, fish and other marine animals suffocate. As a result, creatures such as fish and shrimp die off. In extreme cases, anaerobic conditions ensue, promoting growth of bacteria such as *Clostridium botulinum*, which produce toxins deadly to birds and mammals (Horrigan et al., 2002). It is now clear that the consumption of eutrophied water poses a serious medical threat since some of the cyanobacteria are toxigenic, and the symptoms caused by exposure to these toxins while often trivial, may be very serious, leading to death in some cases (Seviour et al., 2003). Eutrophication can occur in any aquatic system including rivers, lakes and marine environments (Ou et al., 2007).

The term 'nutrients' refers to those elements that are essential for primary production by plants or other photosynthetic organisms typically compounds containing nitrogen, phosphorus, or both. Phosphorus input is considered more critical since many of the cynobacteria are diazotrophic, capable of satisfying their N requirements from fixation of atmospheric N_2 (Seviour et al., 2003), also phosphorus in the form of phosphates is the easiest to be removed or controlled than nitrogen and is present in water in smaller quantities than nitrogen. In general, phosphorus concentrations above 1 mgP/l are sufficient to stimulate eutrophication in lakes (Deliyanni et al., 2007). According to environment Canada, lakes with total phosphorus concentrations above 0.03 mg/L are subject to rapid eutrophication.

Phosphates occur in the natural environment and are essential nutrient for all living organisms: plants, animals and human beings. The types of phosphates found in waters include organic phosphates, inorganic phosphate (soluble orthophosphates), and polyphosphates (Kioussis et al., 1999; Ayoub et al., 2001; Zeng et al., 2004; Karageorgiou et al., 2006). The mains sources of phosphates in agriculture runoff include (Figure 2.1):

- natural run-off from the soil and the weathering of rocks
- run-off of inorganic fertilizer
- run-off of manure from farms
- run-off from erosion

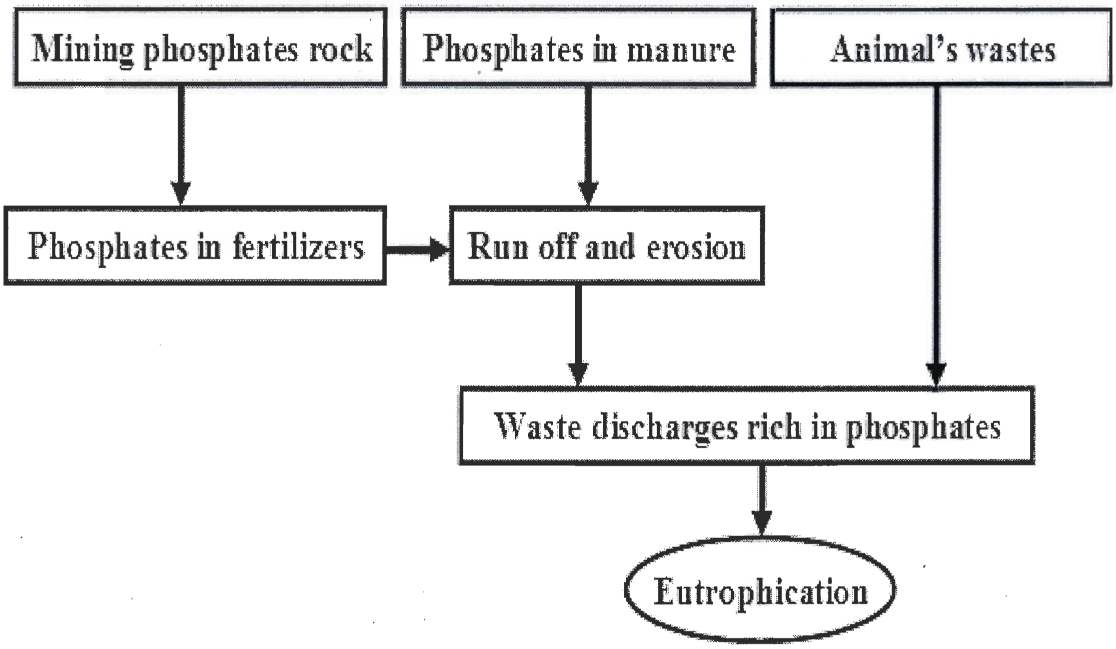

Figure 2.1. Eutrophication of water with agriculture wastes rich in phosphate.

Phosphate input into water may be classified into two categories; the point sources and non- point sources, wastewater treatment plants and permitted industrial discharges are called point sources that are regulated by monitoring loads at the ends of their discharge pipes and setting strict limits. Whereas, non point sources include: natural decomposition of rocks and minerals, storm water runoff, agricultural runoff, erosion and sedimentation, atmospheric deposition, and direct input by animals/wildlife (Carpenter et al., 1998; Krishnan and Haridas, 2007). In general, the non-point source pollution typically is significantly higher than the point sources of pollution. Phosphorus is most commonly found in rock formations as phosphate salts. Phosphate salts that are released from rocks through weathering usually dissolve in soil water and will be absorbed by plants. It was found that phosphorus lost to surface waters increases linearly with the amount of phosphorus in the soil. Thus, much of the nutrient loading in soil eventually makes its way to water. In addition, nutrients from human activities (phosphate fertilizers or manure) tend to migrate from land either to surface or negligibly to ground water. Today, many commercial processes for phosphate removal are being used; others are under investigation and development (Raike et al., 2003).

2. 2. Methods for phosphate removal from aqueous solutions

Large quantities of phosphate present in wastewaters are one of the main causes of eutrophication that negatively affects many natural water bodies, both fresh and marine. Two main methods are currently being used around the world for phosphate removal. These encompass physicochemical and biological methods.

2. 2. 1. Biological methods

Biological phosphate removal has become an established process in modern wastewater treatment. The basic conditions required for the Bio-P process as shown in Figure 2.2 are alternating anaerobic and aerobic conditions together with a supply of easily degradable organic matter during the anaerobic phase (Henze et al, 1995; Gillberg et al, 2003). In this process, the wastewater containing phosphates is introduced to specific bacteria, called polyphosphate accumulating organisms (PAO), in an anaerobic tank (nitrate and oxygen are absent) prior to the aeration tank. Under these conditions, the PAO are encouraged to grow and consume large quantities of polyphosphate within their cells (up to 20% of their mass). The phosphate is removed from this process as a result of sludge wasting.The biomass enriched in these bacteria is separated from the treated water at the end of the process and the phosphorus is thus removed, this biomass has a high fertilizer value.

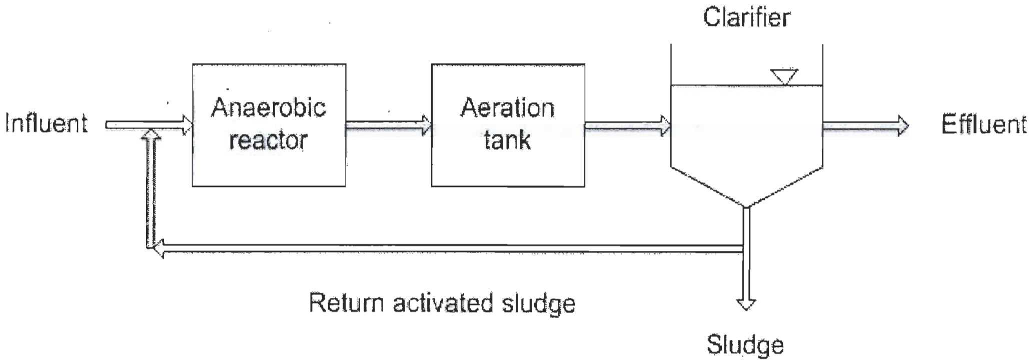

Figure 2.2. The principal steps of biological phosphate removal.

Several attempts to intentionally use specific microorganisms to remove phosphate ions were reported (Meijer et al., 2002; de-Bashan and Bashan 2004; Srivastava and Srivastava, 2006). Several advantages of this process are: reduced chemical costs, less sludge production as compared to chemical precipitation, and the absence of coagulant metal ions in the resulting sludges. However, the removal efficiency of phosphates in biological treatment usually does not exceed 30%, which means that remaining phosphate should be removed by another technique (Sommariva et al., 1996). Also, this method recognizes that the incoming wastewater presents correct balance of nutrient, carbon sources and optimal pH. Additionally, careful consideration must be given to the system temperature and dissolved oxygen concentration to ensure the healthy sludge population prevailing in the bioreactors (Mulkerrins et al., 2004).

2. 2. 2. Physicochemical methods

Apart from phosphorus removal by biological methods, the other main methods applied are physicochemical treatments. Various physical and chemical methods have been used including cross-flow filtration (Akay et al., 1998), crystallization (Momberg and Oellermann., 1992), coagulation (Zhou et al., 2008), electrodialysis, reverse osmosis, ion exchange, adsorption (Yeoman et al., 1988) and chemical precipitation. Phosphate removal is currently achieved largely by chemical precipitation usually with salts of iron, alum, or lime (Penetra et al., 1999).

2. 2. 2. 1. Chemical precipitation

Removal of phosphates by the use of chemical precipitation is based on the fact that certain metal salts have the ability to aggregate particles into such sizes that they can be removed. This is facilitated by the fact that phosphate ions in wastewater are negatively charged while aluminum and iron salts are generally positively charged. In this process, the effluents containing phosphate ions react with salts of ferric ions, aluminum ions, or lime to have metal-phosphate precipitates or precipitates together with numerous other waste materials as sludge in the end of reaction. The precipitation process depends largely on numerous factors like; initial aluminum or organics concentration, pH, temperature, ionic strength and presence of other ionic species (Georgantas et al., 2006). The following equations represent the reactions of precipitation (Arvin, 1983):

Aluminum ions combine with phosphate ions as shown by the following reaction:

$$\mathbf{Al^{3+} + PO_4^{3-} \rightarrow AlPO_4 \downarrow}$$

The reaction of ferric ions can be illustrated by the following reaction:

$$\mathbf{Fe^{3+} + PO_4^{3-} \rightarrow FePO_4 \downarrow}$$

The reactions involved in the use of lime to precipitate phosphorus are as follows:

$$\mathbf{10Ca^{2+} + 6PO_4^{3-} + 2OH^{-} \rightarrow Ca_{10}(PO_4)_6(OH)_2}$$

Baker et al. (1998) reported that iron /calcium oxides could remove 99% of phosphates from effluent within one hour. While Yi and Lo (2003) mentioned that calcium-phosphorus precipitation for phosphate removal is low cost and easy to handle. There are several important disadvantages to chemical phosphorus removal:

- The high costs of the consumed chemicals.
- A significant increase of the excess sludge production (metal-hydroxides and metal phosphates) which is difficult to handle.
- The accumulation of ions (increased salt content) may seriously restrict the reuse of the effluent.

- Chemical precipitation renders the operation difficult, if not impossible; to recycle phosphate in an economical industrial level.
- During the process, if aluminum and iron are used, neutral to acidic environments are required. On the other hand, an alkaline condition is important in the case of precipitation by calcium. This means an increasing in chemicals use (Deliyanni et al., 2007).

Therefore, it is important to search for a process of phosphate removal that separates it from other waste components, so that it can be recycled as a fertilizer or an ingredient in other valuable phosphorus products (de-Bashan and Bashan, 2004). Alternative phosphorus removal technology may be useful in phosphorus removal as a recyclable product especially with the exhausted resources of phosphorus. One of the most interesting alternatives belongs to physicochemical approaches is the adsorption technology. Adsorption has been used as an alternative method for phosphate removal since long time ago (Ozacar, 2003).

2.3. Adsorption method

2.3.1. Adsorption: a general overview

Adsorption could be simply defined as the preferential concentration of one component of a system at an interface, where the local concentration of one or more components or both phases is different from those in the bulk phases (Myers, 1999). Or with another term, it is the accumulation of gases and liquids on the surface of a solid. Adsorption is classified into two main categories: physical and chemical, the main differences between of them are:

- Physical adsorption is the result of relatively weak Van der Waal's interaction forces between the solid surface and the adsorbate, so physical adsorption is easily reversed. Unlike physisorption, chemisorption is difficult to reverse (a significant quantity of energy usually is required to remove chemically adsorbed molecules) because its result of chemical bond formed between the adsorbate molecule and the adsorbent.
- Physical adsorption requires very low activation energy so that the rate of adsorption is very high, even at low temperatures. Chemical adsorption however requires high activation energy: the rate of adsorption is low and depends upon the temperature of adsorption.

- Physical adsorption is characterized as a non specific and occurs between any adsorbate-adsorbent systems, while chemisorptions are specific.

The type of adsorption that takes place in an adsorbate-adsorbent system depends upon the reactivity of the surface, the nature of the adsorbate, the nature of the adsorbent and the temperature of adsorption.

2.3.2. Adsorption equilibrium

Adsorption equilibrium is a dynamic concept achieved when the rate at which molecules adsorb onto a surface is equal to the rate at which they desorb. When a solid surface is in contact to a liquid, the liquid molecule in contact with the surface of the solid is adsorbed with a high rate of adsorption since the whole surface is bare. But, as more and more of the system is covered, the available bare surface decreases and so does the rate of adsorption. With time, the rate of adsorption continues to decrease while the rate of desorption increases until equilibrium is reached between the rate of adsorption and the rate of desorption (Myers, 1999).

Until now the statistical theories developed to represent adsorption equilibrium for gas – solid systems were applied for liquid solid systems, the most commonly used equilibrium models beins Langmuir, Freundlich and Temkin isotherm equations.

2.3.3. Adsorption of phosphate ions

Adsorption process is an easy operation producing less sludge than other processes. Recently, different adsorbents were used for phosphate removal such as; activated alumina, aluminum hydroxide (Tanada et al., 2003), flay ash (Agyei et al., 2002), blast furnace slag (Agyei et al., 2002; Johansson and Gustafsson 2000), alunite (Ozacar, 2003), aluminum hydroxide and iron oxide tailings (Zeng et al., 2004), metal-loaded orange waste (Biswas et al., 2007) etc….

On the other hand, these adsorbents showed insufficient adsorption capacities, long time to attain the equilibrium (Table 2.1) and most adsorbent can not be reused (regenerated) as well as poor selectivity and limited surface area. Therefore it is imperative to search for new materials to adsorb phosphates. Mesoporous silica's are attractive materials to researchers seeking for adsorbents of low concentration ions in the environment. Because of the low efficiency of silica surface itself in adsorption as well as the poor characteristics in catalytic activity, it should be functionalized before using for that purpose (Yoshitake et al., 2002). SBA-15 mesoporous silica has received considerable attention because of its unique large surface area, well-defined pore size and shape (Sayari et al., 2004; Guli et al., 2007).

Table 2.1. Adsorbents used for phosphate removal.

Adsorbent	Equilibrium Time (min)	Adsorption capacity (mg P/g)	pH	Temperature (°C)	References
Zr(IV)- loaded SOW gel	1440	57	7	ND	Biswas et al., 2008.
Zirconium ferrite	1440	13	7	ND	Biswas et al., 2008.
Zr(IV)-loaded MUROMAC	1440	43	7	ND	Biswas et al., 2008.
Red mud	≈200	0.58	5.5	40	Huang et al., 2008.
Steel slag	300	≈8.67	6.7-6.9	20	Liu et al., 2008.
Metal-loaded orange waste	120	5.3	5.2	25	Xiong et al., 2008.
Fe-coated natural & engineered sorbents	600	14.13	3	30	Biswas et al., 2007.
Nanocrystalline akagenite	60	0.5	5	20	Boujelben et al., 2007.
Mesoporous ZrO_2	240	19.86	7	25	Deliyanni et al., 2007.
Zeolite	240	50			Onyango et al., 2007.
Calcined LDHS	240	14	6	30	Das et al., 2006.
Dolomite	15	≈15.67	≈3.54	20	Karaca et al., 2006.
Modified palygorskites	120	9	7.2	25	Ye et al., 2006.
Activated carbon	180	2.2	4	35	Namasivayam et al., 2004.
Calcined alunite	120	0.22	5	25	Özacar 2003.
Aluminum oxide hydroxide	50	≈11.6	2	ND	Tanada et al., 2003.
Polymer hydrogels	120	15	7.6	ND	Kioussis et al., 2000.

2.4. Mesoporous silica materials

The ordered mesoporous materials (OMM) with pore size between 2 to 50 nm were discovered in 1992 by researchers working for the Mobil Corporation. Among them, materials having purely siliceous framework are known as ordered mesoporous silicas of the M41 family materials (Beck et al., 1992). The OMS family has grown significantly, which is reflected by the development of materials with various porous structures (Figure 2. 3) and chemical composition formed by coupling organic templates and inorganic and/or hybrid organic-inorganic precursors, e.g., tetraethlorthosilicate (TEOS) and organosilanes (Hoffmann et al., 2006).

In 1998, researchers at the University of California in Santa Barbara announced that they had produced silica with much larger 46-300 angstrom pores (Zhao, et al., 1998). The material was named Santa Barbara Amorphous type material, or SBA-15. These materials also have a hexagonal array of pores. The researchers who invented these materials planned to use them as molecular sieves. Today, mesoporous silica has many applications in medicine, catalysis (Corma, 1997), drug delivery, separation (Grun et al., 1996), biomolecular immobilization (Diaz and Balkus, 1996) and adsorption of gas and liquid (Schmidt et al., 1995; Mercier and Pinnavaia, 1997, 1998; Ho et al., 2003). These applications demand precise control of the pore size, accessibility, stability, morphologies and surface functionalization of the mesoporous silicas. SBA-15 is stable in acidic, basic or hydrothermal conditions. Control over the morphology of SBA materials can be obtained by variations in the synthesis parameters or through the use of co-solvents, co-surfactants, or various salts.

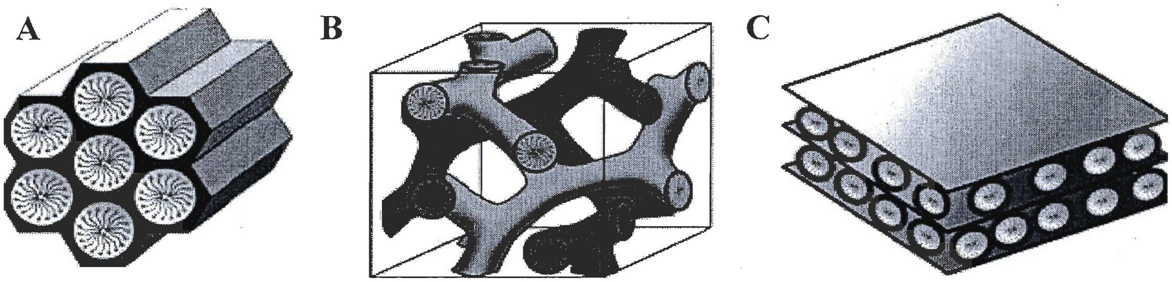

Figure 2.3. Structures of mesoporous M41s materials: A) MCM41 B) MCM-48 and C) MCM-50 (Hoffman et al., 2006).

2.4.1. Synthesis of mesoporous silica materials

The Mobil researchers suggested the liquid crystal templating mechanism (LCT) for the M41s family (e.g. Mobil composite material, or MCM-41) with a uniform hexagonal array of pores which had sizes between 15 and 100 Å with a large internal surface area up to 1000 m^2/g (Beack et al., 1992; Kersge et al., 1992; Chen et al., 1993; Trewyn, et al., 2007). The liquid crystal structure formed by the surfactant molecules serves as organic templates for assembly of the mesostructured silica. In general, according to Beck et al., (1992) and Kersge et al., (1992), the M41s family of mesoporous molecular sieves has been synthesized by combining appropriate amounts of:

- A silica source (e.g. tetraethyl orthosilicate (TEOS), fumed silica, or sodium silicate),
- A cationic surfactant (e.g. cetyltrimethyl ammonium bromide (CTAB)),
- A basic catalyst (e.g. trimethyl ammonium hydroxide (TMAOH), and
- Solvent (water, ethanol…).

This mixture, aged at temperature usually over 100°C for 24 to 144 hours, results in an organic-inorganic mesostructured solid precipitate that can be separated from the synthesis liquor by filtration. The occluded surfactant can be removed by calcination conducted generally at about 500°C under a flowing gas.

According to LCT mechanism, the Mobil researchers proposed the mechanistic pathway for the 2D hexagonal structured MCM-41 (Figure 2. 4). The hexagonal lyotropic liquid crystalline (LC) phase is formed first and then the inorganic precursor species deposit on the micellar rods of the LC phase.

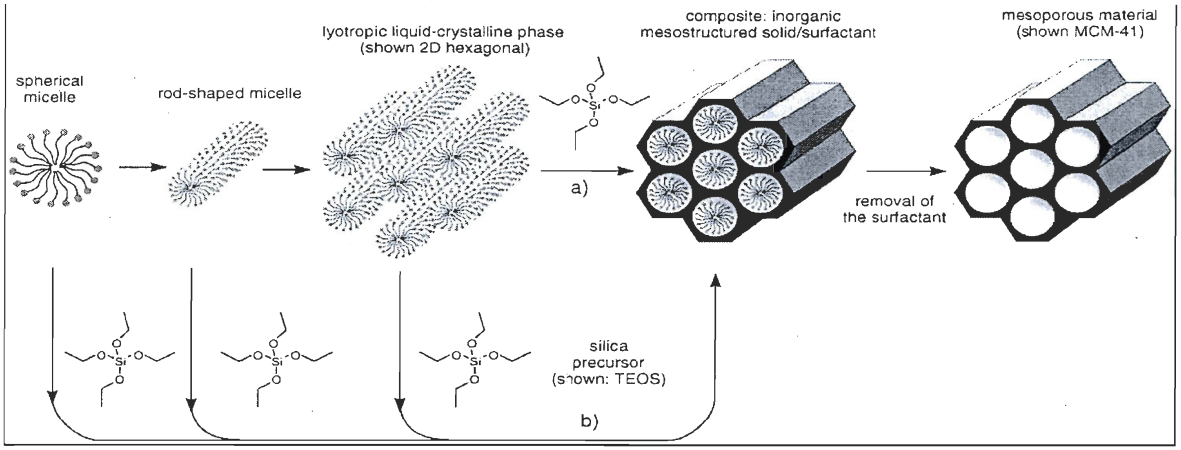

Figure 2.4. Synthesis of mesoporous materials by structure-directing agents: a) true liquid crystal template mechanism, b) cooperative liquid-crystal template mechanism (Hoffman et al., 2006).

2.4.2. Functionalization of mesoporous silicas

An attractive approach to obtain high capacity adsorbents on the basis of OMS materials include their functionalization with organic groups of specific properties for desired environmental applications. The resulting materials should possess functional groups over the entire surface capable to interact selectively with target pollutants. The selectivity could be achieved by suitable choice of functional groups. The combination of the properties of organic and inorganic building blocks within a single material is particularly attractive from the viewpoint of materials scientists because of the possibility to combine the enormous functional variation of organic chemistry with the advantages of a thermally stable and robust inorganic substrate (Hoffmann et al., 2006). By functionalization process, the polarity of the pore surfaces of an organic matrix could be adjusted by the addition of organic building blocks, which extends considerably the diversity of materials that can be used. A lot of organic functionalities such as alcohols, thiols, sulfonic, carboxylic and amines can be added which allow chemical and biochemical reactions to be carried out on a stable, solid inorganic matrix (Hoffmann et al., 2006).

Chemical functionalization of OMS via covalent bonding of organic molecules can be achieved in three general ways: (1) post synthesis modification of the pore surface called also «grafting», (2) simultaneous condensation of silica recognized as «co-condensation», and (3) the use of bissilylated organic precursors that lead to periodic mesoporous organasilicas (PMOs) (Sayari and Hamoudi, 2001; Hoffmann et al., 2006).

2.4.2.1. Post synthetic functionalization of silicas «grafting»

Grafting refers to the modification of the inner surfaces of OMS (order mesoporous silica) phases with organic groups. This process is carried out primarily by reaction of organosilane of the type $(R'O_3)_3SiR$, or less frequently chlorosilanes $ClSiR_3$ or silazanes HN $(SiR_3)_3$, with the free silanol groups of the pore surfaces (Figure 2.5). Principally, functionalization with a variety of organic groups can be realized in this way by variation of the organic residue R (Hoffmann et al., 2006).

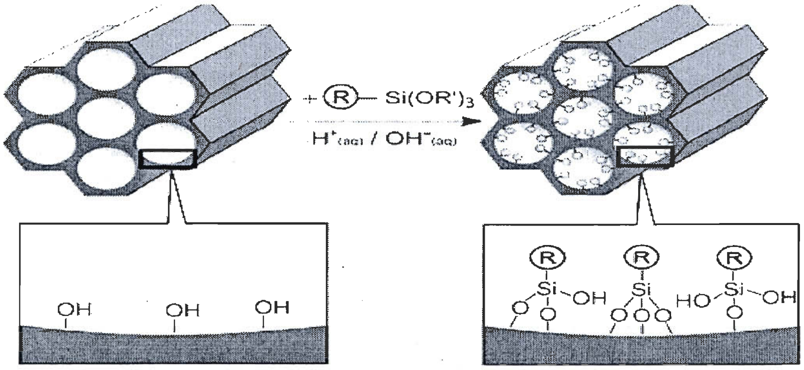

Figure 2.5. Grafting (post-synthetic functionalization) for organic modification of mesoporous silica phases with terminal organosilanes (Hoffman et al., 2006).

The post synthetic functionalization of the mesoporous silica phases (grafting) is also used for the development of adsorbents. Amine, thiol carboxylate, chloride, alkyl, vinyl, and phenyl are among the most commonly included groups into silicas. As a result, the ability of a surface to interact by hydrogen bonds or Van der Waals forces, electrostatic or covalent bonds can be used for adsorption applications. For instance, Mercier et al., (1998) showed that thiol-functionalized MCM-41 demonstrated high affinity for mercury (Hg^{2+}) cations in solution, while Liu et al., (2000) reported that amine-functionalized SBA-15 exhibited preferential adsorption properties to Cu^{2+}, Zn^{2+}, Cr^{3+}, and Ni^{2+}. As for Yoshitake et al. (2002), they showed that acidified amine-functionalized MCM-41 and SBA-1 sample is suitable for the removal of toxic oxyanions such as arsenate and chromate from contaminated effluent.

2.4.2.2. Co-condensation «direct synthesis»

Also called one-pot synthesis, in which mesoporous silicas could be synthesized and functionalized in a single step. Its is possible to prepare ordered mesoporous silica phases by the co-condensation of tetraalkoxysilanes [$(RO)_4$ Si (TEOS or TMOS)] with terminal trialkoxyorganosilanes of the type $(R'O)_3$ SiR in the presence of structure-directing agents leading to materials with organic moieties anchored covalently to the pore walls (Figure 2. 6) (Hoffmann et al., 2006).

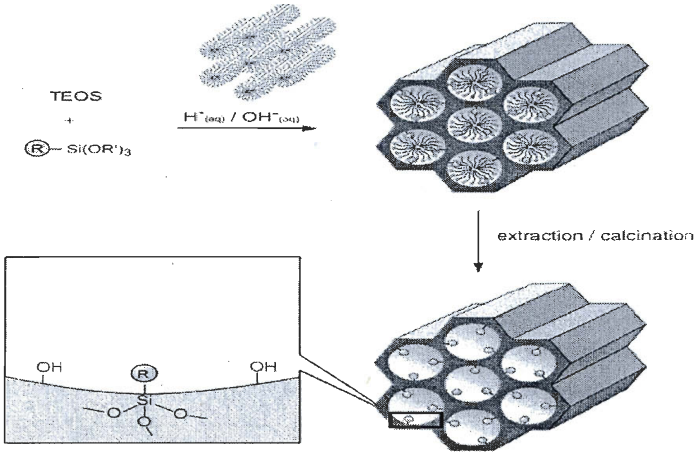

Figure 2.6. Co-condensation method (direct synthesis) for the organic modification of mesoporous pure silica phases. R= organic functional group (Hoffman et al., 2006).

2.4.3. Periodic mesoporous organosilicas «PMOs»

In contrast to the organically functionalized silica phases, which are obtained by post-synthetic or direct synthesis, the organic unit in this case are incorporated in network structure of the silica matrix through covalent bonds and thus distributed totally homogenously in the pore walls. These materials, which are obtained as porous aero-and xerogels, can have large inner surface areas of up to 1800 $m^2 g^{-1}$ as well as high thermal stability but generally exhibit completely disordered pore system with a relatively wide distribution of pore radii (Figure 2. 7) (Hoffman et al., 2006)

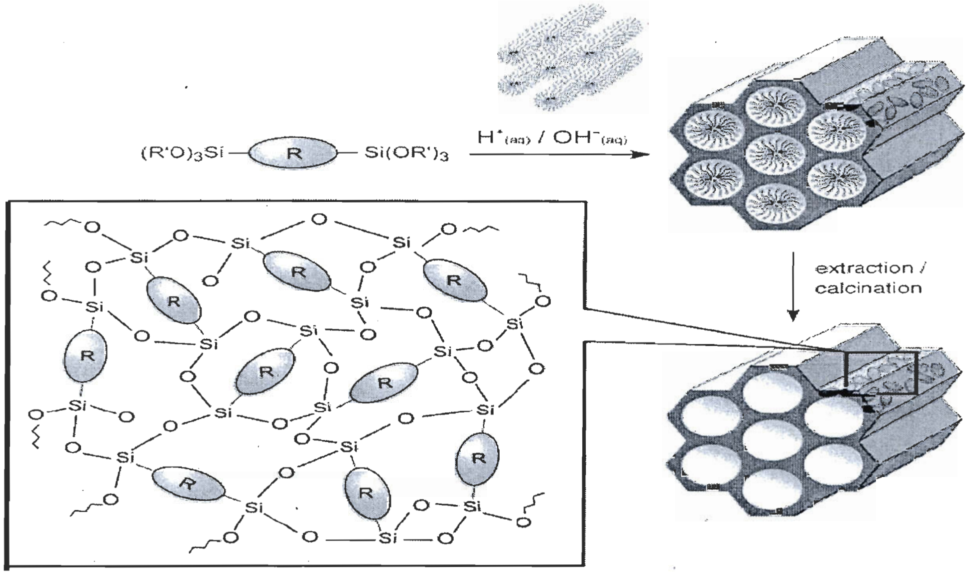

Figure 2.7. General synthetic pathway to PMOs.

2.5. Environmental applications of functionalized mesoporous materials in water treatment

The most important applications of functionalized mesoporous silica reported in the literature were in the field of catalysis and environmental remediation (Sayari and Hamoudi, 2001). Within the framework of the present project, we are interested in the environmental applications of mesoporous silicas as adsorbents. Functionalized mesoporous materials have great potential for environmental applications due to their high surface area and tailored porosity.

The functionalization of MCM-41 with mercaptopropyl group has been studied to adsorb the mercury with 421 mg/g adsorption capacity (Liu et al., 1998). Mercier et al. (1998) reported the high affinity of mercury (ii) for thiol-functionalized MCM-41 phases. The adsorption capacity was 501 mg/g in the case of using the same functional group for mercury adsorption on MSU (Brown et al., 2000). Yoshitake et al. (2003) studied the removal of chromate and arsenate by using MCM-48 functionalized with mono, di and tri amino-silanes with 160 and 182 mg/g adsorption capacity for chromate and arsenate, respectively. In another study Yoshitake et al. (2002) showed that mono, di- and triamino ligands fixed on SBA-1 mesoporous silica were found to have high adsorption capacities for chromate and arsenate.

Kang et al. (2004) reported that imidazole- and thiolfunctionalized SBA-15 phases show high selective affinity for Pd^{2+} and Pt^{2+} in the presence of other cations (Ni^{2+}, Cu^{2+}, Cd^{2+}).

In other study Liu et al. (2000) have been employed Thiol- and amino-functionalized SBA-15 silicas for removing heavy metal ions from waste water, they found that the thiolated SBA-15 adsorbent exhibited a higher complexation affinity for Hg2+, while the other metal ions (Cu^{2+}, Zn^{2+}, Cr^{3+} and Ni^{2+}) showed exceptional binding ability with its aminated analogue. Showkat et al.(2007) found that amine functionalized MCM-41 prepared with ETAB (eicosane trimethyl ammonium bromide) showed higher adsorption capacity for Cr (VI), As (V), Pb (II) and Hg (II) ions in comparison to MCM-41 prepared with CTAB (cetyl trimethyl ammonium bromide) and DTAB (dodecyl trimethyl ammonium bromide).

Recently, Saad et al. (2007) obtained 46 and 43 mg/g adsorption capacity when using ammonium functionalized MCM-48 for phosphate and nitrate ions removal, respectively.

2.6. Adsorption modeling

Adsorption isotherms are used to describe the experimental adsorbed amount q_e (mg/g) as a function of the equilibrium concentration C_e (mg/L) of the adsorbing molecule at constant temperature. Several equilibrium models are used to describe the adsorption process. The Freundlich equation, Langmuir equation, BET, Henry and Temkin are commonly used. However, the Langmuir, Freundlich and Temkin equations are three of the most widely used and are incorporated in the following sections. These models allow us to summarize and compare adsorption data.

2.6.1. Langmuir equation

The Langmuir equation was derived using the following assumptions:

- The surface of the adsorbent has a fixed number of identical sites which can each retain one molecule, resulting in adsorption monolayer coverage.
- Adsorption is also reversible.
- The molecules do not move laterally along the surface of the substrate.
- The adsorbate molecules do not react with each other and the adsorption energy for all sites is identical, regardless of surface coverage (Sparks 1995).

The isotherm is mathematically described as:

$$qe = k_L .\ qm.\ Ce / (1 + k.\ Ce) \qquad (2.1)$$

The Langmuir linear form described as:

$$Ce\ /\ qe = Ce\ /qm + 1/\ k_L.qm \qquad (2.2)$$

Where ***qe*** (mg/g) is the amount of adsorbed species per unit weight of adsorbent and ***Ce*** (mg/L) is unadsorbed concentration in solution at equilibrium. k_L (mg/L) is the Langmuir equilibrium constant and ***qm*** (mg/g) the maximum adsorption capacity.

2.6.2. Freundlich equation

The Freundlich equation is an empirical model that was first used to describe gas and solute adsorption; it has also been used to describe ion retention by adsorption and precipitation processes. This model does not predict an adsorption maximum and implies that the adsorption energy of a surface varies with surface coverage (Sparks, 1995). The Freundlich model is given by the following linearized equation:

$$\mathrm{Log}\ (x/m) = (1/n)\ \log C_e + \log K_f \qquad (2.3)$$

Where K_f is the distribution coefficient, C_e is the equilibrium concentration, ***x/m*** is mass phosphate adsorbed/mass adsorbent, and ***n*** is a correction factor.

2.6.3. Temkin equation

Temkin isotherm equation is derived from the Langmuir adsorption isotherm by inserting the condition that the heat of adsorption decreases linearly with surface coverage. Temkin model is given as (Temkin and Pyzhev., 1940):

$$q\mathrm{e} = RT / b \ \mathrm{ln}\ (K_{\mathrm{te}}.C\mathrm{e}) \qquad (2.4)$$

The linear presentation of this model is expressed by the following equation:

$$q\mathrm{e} = (RT/b)\mathrm{Ln}\ K_{\mathrm{te}} + (RT/b)\ \mathrm{Ln}\ C\mathrm{e} \qquad (2.5)$$

Where qe (mg/g) is the amount of adsorbed species per unit weight of adsorbent and Ce (mg/L) is unadsorbed concentration in solution at equilibrium. K_{te} and B are the Temkin constants.

CHAPTER 3: HYPOTHESIS AND OBJECTIVES

3. 1. Hypothesis

Despite efforts to remove phosphorus from aqueous solutions, there are many unanswered questions and issues that arise and stand around materials under development from the viewpoint of their efficiency and costs. Currently, the advent of mesoporous materials has opened up the door to several sorts of manipulative usage of such materials in catalysis and environmental applications for pollutants removal.

We hypothesized that mesoporous silicas with their large specific surface area, large pore sizes and a high number of accessible pores functionalized with ammonium groups represent an excellent and alternative adsorbent for phosphate removal from aqueous solutions. Additionally, the adsorption is a reversible process permitting use to reuse the SBA-15, and phosphate anions.

3. 2. Objectives

The overall aim of this study is to assess and evaluate the feasibility of synthesis and functionalization of mesostructured silica material with desired characteristics bearing in mind the prospective environmental applications of such materials. For phosphate removal from wastewater, SBA-15 mesoporous silica has been synthesized and functionalized with ammonium groups. In order to attain this goal, the following specific objectives have been drawn:

1. Synthesis and functionalization of SBA-15 mesoporous silica materials with organic ammonium groups.
2. Physicochemical characterization of ammonium-functionalized silicas using two techniques: N_2 adsorption-desorption isotherms (BET) and X-ray diffraction.
3. Optimization of operating conditions such as initial phosphate concentration, adsorption temperature, pH, adsorbent dose, the presence of competing species, and stirring speed controlling phosphate adsorption process.
4. Study of the optimal regeneration conditions of mesoporous silicas and their efficiency upon multiple adsorptions-desorption cycles.

CHAPTER 4: MATERIALS AND METHODS

4.1. Chemicals

In this study, the following chemicals were used:

- Surfactant Triblock co-polymer P123 (EO20PO70EO20) (BASF);
- Tetraethylorthosilicate (TEOS; purity >98%) (Sigma Aldrich);
- 3-aminopropyltriethoxysilane (APTES; purity >99%) (Sigma Aldrich);
- N- [3-(trimethoxysilyl)-propyl] ethylene diamine (TPED; purity > 97%) (Sigma.Aldrich);
- N-[3-(trimethoxysilyl)-propyl] diethylene triamine (TPDT) (Sigma Aldrich);
- Concentrated hydrochloric acid 35% (HCl) (Fisher Chem.);
- Potassium dihydrogen orthophosphate (KH_2 PO_4; purity > 98-101%) (BDH);
- Toluene (Fisher Chem.);
- Iso Propanol (Fisher Chem.).

All chemicals were used as received without any further purification treatment.

4.2. Equipment

- Magnetic hot-plate, Fisher;
- Diffractometer with focusing beam monochromated Cu *Ka* radiation, Ultima III Rigaku, Japan (Figure 4.1);
- Volumetric adsorption analyzer, Quantachrome Instruments, Boyton Beach, Florida (Figure 4.2);
- HPLC ICS-2500 Dioncx, USA (Figure 4.3) equipped with:
  - Column IonPac AS18 (4 × 250 mm), Dionex, USA;
- Digital temperature path controller, Poly science, U.S.A;
- Isotemp oven, Fisher scientific, USA;
- VULCAN furnace 3-550 PD NEY, USA (Figure 4. 4);
- Glass condensers.

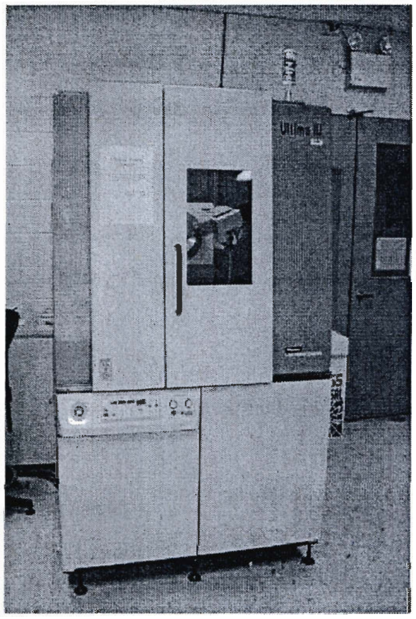

Figure 4.1. Diffractometer (Ultima III Rigaku)

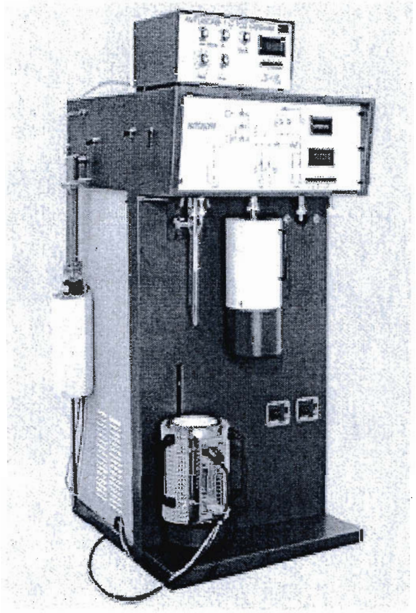

Figure 4.2. Volumetric adsorption analyzer

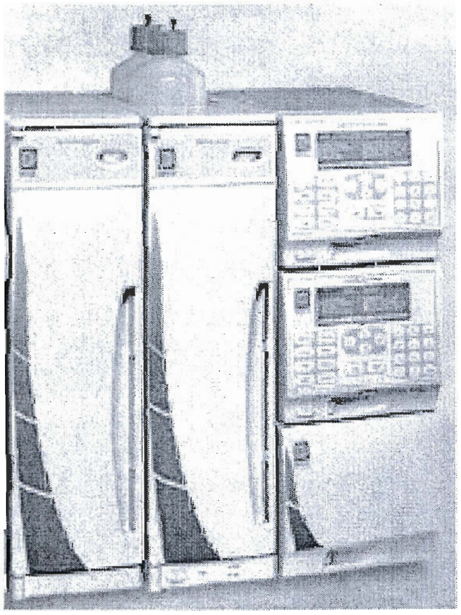

Figure 4.3. HPLC (ICS-2500 Dionex)

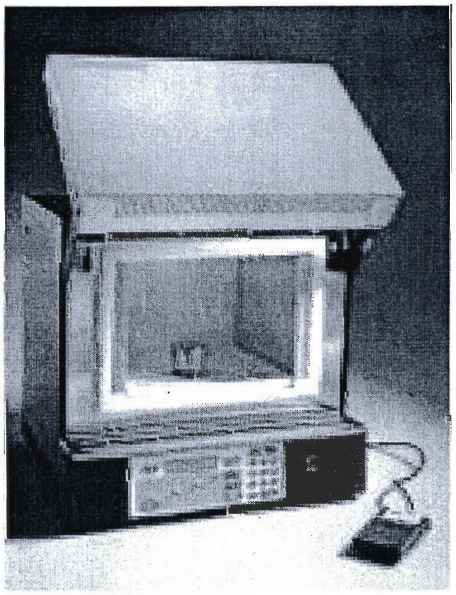

Figure 4.4. VULCAN furnace

4.3. Methods

4. 3. 1. Synthesis of SBA-15

4. 3. 1. 1. Synthesis of pure SBA-15

Pure SBA-15 was synthesized in acidic condition by using pluronics P123 as a structure-directing agent and TEOS as a silica source according to Zhao et al. (1998). The molar composition of the mixture was TEOS: 6.1 HCl: 0.017 P123: 165 H_2O.

A typical synthesis of SBA-15 material was carried out using the following procedure. Pluronic P123 (4 g) was dissolved in 120 g of 2N HCl solution and 30 g of water in a 500 mL beaker with stirring. After dissolution of the surfactant at room-temperature, the homogeneous solution was heated to 40°C before adding drop wise 8.5 g tetraethylorthosilicate, TEOS (Aldrich) under stirring. The resulting gel was aged at 40 °C for 24 h and finally transferred into a 1000 ml Pyrex bottle then aged at 100 °C for 24 h under static conditions. The solid product was filtered, washed 5 times at least with deionized water until no detection of chloride ions in filtrate using silver nitrate. The obtained solid precipitate was dried at room temperature overnight.

To remove surfactant, the obtained solid was calcined in a programmable VULCAN furnace 3-550 PD NEY from room temperature to 540 °C with a heating rate of 3 °C/min. Then the temperature was held constant at 540 °C for 5 h.

4.3.1.2. Functionalization of SBA-15 mesoporous silicas

Once the SBA-15 was obtained, the grafting technique was applied for the functionalization of SBA-15 with amine groups (monoamino, diamino and triamino) in the presence of toluene according to Yokoi et al. (2004).

3-aminopropyltriethoxysilane (APTES), N-[3-(trimethoxysilyl)-propylethylene] diamine (TPED) or trimethoxysilyl propyl diethylenetriamine (TPDT) are used as sources of single-, double- and tri-amine groups, respectively. Different percentages of the three amine sources were explored to study the effect of amine source and loading on the phosphate adsorption process.

3-aminopropyltriethoxysilane (APTES) (Figure 4.5) as a source of mono-amine was introduced to calcined SBA-15. In a typical functionalization (0.186, 0.3712, 0.5568, 0.7424 or 1.4848) g of APTES was added to 1g of calcined SBA-15 and 25 ml of dried Toluene (Fisher chem.) to have a load of (5, 10, 15, 20, and 40 %) on a molar basis respectively. The mixture was reacted in 250 ml round bottom flask which was attached with glass condenser under vigorous stirring at 110 °C for 10 h. The final solid product was filtered, washed with isopropanol and dried at room temperature.

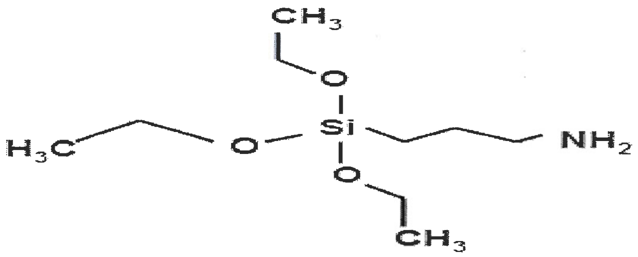

Figure 4. 5. The molecular structure of 3-aminopropyltriethoxysilane(APTES).

In the cases of SBA-15 functionalized with double amine groups, 0.38, 0.76, 1.52 g of N-[3-(trimethoxysilyl)-propylethylene] diamine (TPED) (Figure 4.6) was added to 1g of calcined SBA-15 and 25 ml of dried Toluene (Fisher chem.) to have a load percent of 10, 20, 40 % di amine respectively. Functionalization was conducted under similar conditions to the the mono amine –functionalized SBA-15.

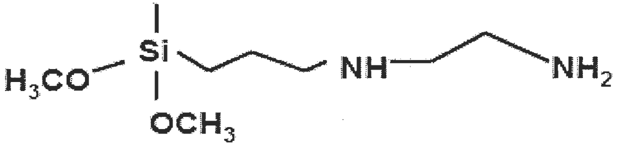

Figure 4. 6. The molecular structure of N-[3-(trimethoxysilyl)-propylethylene] diamine.

Finally, for the functionalization with tri amine, 0.44, 0.88, 1.76 g of trimethoxysilylpropyl diethylenetriamine (TPDT) was refluxed in the presence of 1 g of calcined SBA-15 and 25 ml of dried toluene to have a load percent of 10, 20, 40 % tri-amine respectively. The mixture was reacted under the same conditions of mono amine synthesis.

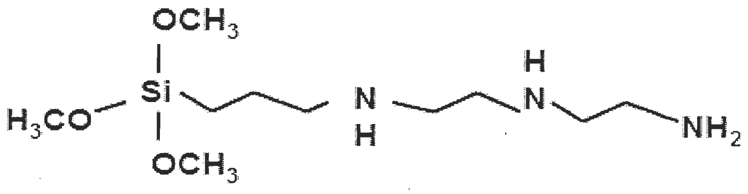

Figure 4.7. The molecular structure of trimethoxysilyl propyl diethylenetriamine.

4.3.1.3. Acidification of functionalized SBA-15

After the functionalization of SBA-15 by amino groups, the materials were then acidified in HCl solution in order to convert amino groups to positively charged ammonium bearing moieties suitable for phosphate adsorption. Indeed, 1g of functionalized SBA-15 was stirred in 1 L of 0.1 M HCl for 1h at room temperature, followed by simple filtration and dried at room temperature before its use as an adsorbent.

Figure 4.8 summarize the steps of SBA-15-$NH_3^+Cl^-$ (adsorbent) functionalization and acidification in the case of monoamine-functionalized SBA-15.

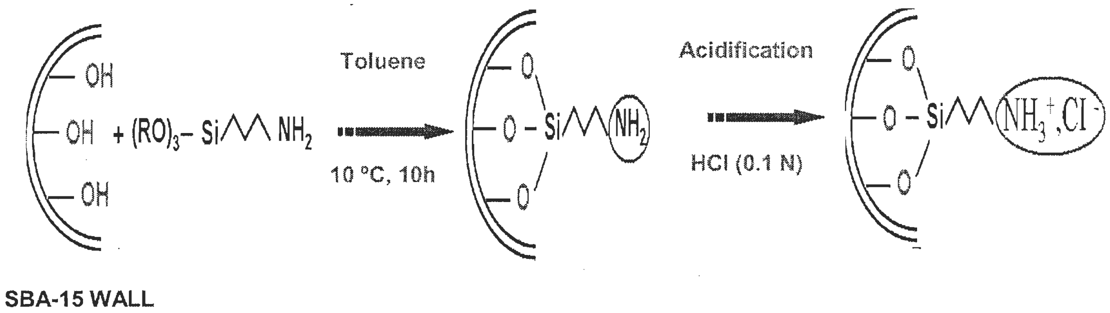

Figure 4.8. Functionalization of SBA-15 with mono-amine groups and acidification.

4.3.2. Characterization of SBA-15

4.3.2.1. Nitrogen adsorption analysis

Nitrogen adsorption-desorption technique is a method for the determination of textural properties of porous solids, such as the specific surface area, the pore size distributions, and the total pore volume.

Nitrogen adsorption-desorption measurements were performed at 77 K using a Quantachrome Autosorb 1 volumetric analyzer. Before analysis, the materials were degassed under vacuum (in order to assure removal of physically adsorbed species) until a residual pressure of 10^{-5} mbar was reached at 200 °C for 4 h for the pure silica materials and 120 °C for 12 h for the functionalized materials.

The specific surface area of the SBA-15 was calculated using the Brunaeur-Emmet-Teller (BET) method, the BET method assumed that the first layer of gas molecules is adsorbed more strongly than the subsequent layer, and that the heat of adsorption of subsequent layers is constant. They also assumed the absence of lateral interaction between adsorbed molecules (Brunauer et al., 1938). The specific surface area, *S*BET (m^2/ g), was determined from the linear part of the BET plot ($P/P_0 = 0.05–0.20$) using the BET equation:

$$\frac{P/P_0}{n.(1-P/P_0)} = \frac{1}{n_m.C} + \frac{(C-1)}{n_m.C}.(P/P_0) \qquad \textbf{(4.1)}$$

Where n is the weight of gas adsorbed at a relative pressure, P/Po, and n_m is the weight of adsorbate constituting a monolayer of surface coverage. The C constant of BET is related to the energy of adsorption in the first adsorbed layer and consequently its value is an indication of the magnitude of the adsorbent/adsorbate interactions.

The pore size distributions were calculated from the desorption branch using the Barrett–Joyner–Hallenda and the Horvath–Kawazoe methods for the mesoporous (pore size > 2.0 nm) and microporous (pore size < 2.0 nm) materials, respectively.

The Barrett-Joyner-Halenda (BJH) method for calculating pore size distributions is based on a model of the adsorbent as a collection of cylindrical pores. The theory accounts for capillary condensation in the pores using the classical Kelvin equation, which in turn assumes a hemispherical liquid-vapor meniscus and a well-defined surface tension.

The total pore volume was evaluated from the adsorbed amount of N at a relative pressure *P/Po* of about 0.99.

4.3.2.2. X-ray powder diffraction

X-ray powder diffraction method is applied to determine the crystal structure symmetry of the ordered silica frameworks before and after functionalization. X-ray diffraction data of the synthesized materials was carried out using a Rigaku D-Max-Ultima III diffractometer with nickel-filtered Cu$K\alpha$ radiation of wavelength 1.5406 Å. Powder diffraction patterns were obtained between 0.75° and 5° with a scan speed of 1°/min.

4.3.3. Adsorption tests

The following adsorption tests were conducted in order to evaluate the phosphate removal using ammonium functionalized SBA-15:

- Effect of time
- Effect of stirrer speed
- Effect of initial phosphate concentration and adsorbent loading
- Effect of pH
- Effect of temperature (adsorption isotherms)
- Effect of ion adsorption competitivity
- Effect of amine type and concentration
- Regeneration of SBA-15

Adsorption experiments were conducted batchwise in flasks containing phosphate solutions. Phosphate stock solution was prepared by dissolving potassium dihydrogen orthophosphate (KH_2PO_4) in deionized water.

For all the adsorption tests presented hereafter, the sub-sample of the solution was collected into the syringe and filtered with 0.2 μm filter disk into a sample tube properly. Then phosphate concentration of the filtered solutions was analyzed using an ion chromatograph ICS 2500 from Dionex equipped with an electrochemical detector and an IonPac AS18 (4 × 250 mm) column. The adsorption experiments were performed in duplicate or triplicate and analyzed twice.

Phosphate removal **(R)** was defined as:

$$(\mathrm{R})\ \% = 100 \times ((C\mathrm{i}-Ce)/C\mathrm{i}) \qquad (4.2)$$

The amount of anions retained on the sorbent phase (mg/g) was calculated as

$$qe = (C\mathrm{i} - Ce) \times (\mathrm{V/m}) \qquad (4.3)$$

Where qe is the amount adsorbed at equilibrium (mg P/g adsorbent), *C*i and *C*e are the initial and final concentrations of the anion in solution (mg/L), V is the solution volume (L), and m is the mass of adsorbent (g).

4.3.3.1. Effect of time

The effect of contact time 5, 10, 15, 60, 120, 180 min for phosphate removal was investigated; the initial phosphate concentration was 300 ppm while the adsorbent dose was 2g/L. In this test, 50 ml of phosphate was added to 0.1 g of ammonium functionalized SBA-15 under stirring at 400rpm for different contact time at room temperature.

4.3.3.2. Effect of stirrer speed

The effect of agitation on phosphate removal was studied for stirrer speed of 100, 200, 300, 400, 600 and 800 rpm. The experiments were conducted with 50ml of 300 ppm phosphate initial concentration, and 0.1 g (2g/L) ammonium functionalized SBA-15 at room temperature for 60 min.

4.3.3.3. Effect of initial phosphate concentration and adsorbent loading

The effect of varying initial concentration (50-100-200-300mg/L) on phosphate removal by various masses (2-5-7-10) g of ammonium functionalized SBA-15 was studied, the experiments were carried out at ambient temperature for a contact period of 60 min and 400 rpm stirring speed.

4.3.3.4. Effect of pH on phosphate removal

The effect of pH on phosphate removal was investigated at 2, 4, 5, 6, 8 and 10 pH. The pH of the solutions was adjusted by addition of 0.01 M solution of HCl or NaOH with using Accumet pH meter (Fisher Scientific). The total volume added for pH adjustment never exceeded 1% of the total volume.

The tests were carried out at 400 rpm with 50 ml of 300 ppm phosphate solution and 0.1 g of ammonium functionalized SBA-15 for 60 min at room temperature.

4.3.3.5. Effect of temperature (adsorption isotherms)

The adsorption isotherms experiments were realized to study the effect of temperature on phosphate removal by using ammonium functionalized SBA-15 and to determine the maximum adsorption capacities. The tests were carried out at different temperatures 5, 10, 15, 25, 35 and 45 °C using phosphate solution having concentrations of 50, 100, 150, 200, 250 and 300 ppm P. The temperature was controlled using temperature controlled water bath. Adsorption isotherms were performed under constant agitation rate (400 rpm) and at constant adsorbent loading (2g/L).

Duplicates 0.1g of ammonium functionalized SBA-15 were placed in flasks containing 50mL of different phosphate concentrations at 5 °C for 60 min. After 60 min of agitation insuring equilibrium (based on preliminary tests which indicated that the equilibrium was reached within 10 min of contact time), each flask was filtered and 1ml of solution was taken for analysis using the HPLC. The forward steps comprise the first temperature (5 °C), which was repeated by five other temperatures (10, 15, 25, 35 and 45 °C) under identical conditions.

4.3.3.6. Effect of ion adsorption competitivity

In the present study all tests were carried out with synthetic phosphate solutions. However, in real systems several other ions, which can compete with phosphate, will possibly be present and interfere with phosphate removal upon adsorption. To assess the competing effect of other anions on phosphate removal by SBA-15, phosphate batch adsorption tests were carried out by equal concentration addition of other anions such as sulfate, chloride, carbonate, nitrate, calcium, magnesium, and ammonium.

300 ppm solutions of $CaCl_2$, $MgCl_2$, Na_2SO_4, KNO_3, NH_4Cl, $CaCO_3$, $CaCl_2$ and KH_2PO_4 were prepared as sources of calcium Ca^{2+}, magnesium Mg^{2+}, sulfate SO_4^{2-},, nitrate NO_3^-, ammonium NH_4^+, carbonate CO_3^{2-}, chloride Cl^-, and phosphate $H_2PO_4^-$, respectively.

In a beaker of 100 ml, 15 ml (300 ppm) of each anion or cation separately was added to 15 ml of phosphate (300 ppm) solution and it was completed to 50 ml with 20 ml of de-ionized water, then 0.1g of ammonium functionalized SBA-15 was added to the mixture.

The mixture was stirred at 400 rpm for 60 min at room temperature, then it was filtered and the filtrate was taken and analyzed using the HPLC as mentioned above (4. 2. 3).

4.3.3.7. Effect of amine type and concentration

The effect of amine type and concentration on phosphate removal was investigated using the mono (N), di (NN), tri (NNN) ammonium functionalized SBA-15 which were functionalized and acidified as described previously in sections (4.3.1.2) and (4.3.1.3), respectively.

The effect of mono ammonium functionalized SBA-15 concentration on phosphate adsorption was studied using different molar concentrations (5, 10, 15, 20 and 40%) of mono amine functionalized SBA-15, the initial phosphate concentrations were 50, 100, 150, 200, 250 and 300 ppm under constant agitation rate (400 rpm) and adsorbent load (2g/L) at room temperature. Duplicate 0.1 g of mono ammonium functionalized SBA-15 was placed in flasks containing 50 ml phosphate solutions at different concentrations (50, 100, 150, 200, 250 or

300 ppm) under stirring for 60 min. The solutions were then filtered and 1mL of the filtrate was taken for HPLC analyses.

Effect of di- and tri- ammonium functionalized SBA-15 on phosphate adsorption was investigated at different molar concentration (10, 20 and 40%) and different initial phosphate concentration (50, 100, 150, 200, 250 and 300 ppm). The tests were carried out using the same method and conditions of mono ammonium functionalized SBA-15.

4.3.3.8. Regeneration of ammonium functionalized SBA-15

To investigate the regenerability of ammonium functionalized SBA-15, 0.1g of adsorbent was put on contact with 50 ml of different initial concentrations of phosphate 50, 100, 150, 200, 250 and 300 mg/L for 60 min at 25 °C and 400 rpm, the adsorbent then was separated by filtration then 1 ml of the precipitate was taken for the HPLC analyses. After filtration, the adsorbent was washed, dried at room temperature, and weighed. The anion loaded sample was stirred in 0.01 M NaOH solution for 60 min with a loading of 2 g adsorbent/L to strip the phosphate anion. After filtration and washing with deionized water, the solid was dried at room temperature and weighed. It was then acidified in HCl solution as described previously in section 4.3.1.3. The forward steps comprise the first adsorption–desorption cycle, which was repeated by four more cycles using the same adsorbent batch.

CHAPTER 5: RESULTS AND DISCUSSION

5. 1. Adsorbent characterization

5.1.1. X-Ray Diffraction

The XRD technique is conducted to determine the crystal structure symmetry of the adsorbent and the eventual changes in its structure upon functionalization. Figure 5.1, shows the XRD patterns of (A) fresh SBA-15, (B) functionalized SBA-15 with 10% amine molar ratio, and (C) ammonium functionalized SBA-15 (acidified). These samples exhibit well-ordered hexagonal structures as indicated by three diffraction peaks (100), (110), and (200) (Zhao et al., 1998). From this figure it is clear that the functionalization and the acidification did not affect the hexagonal structure of the SBA-15.

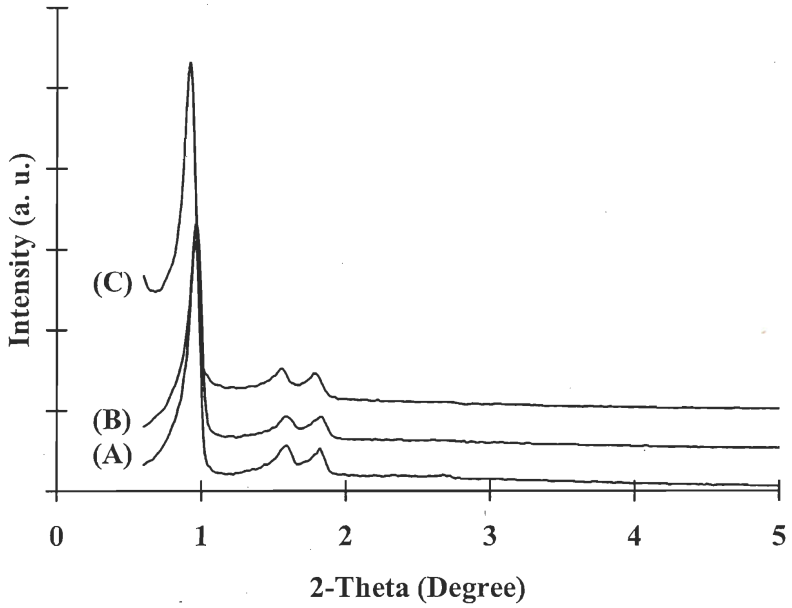

Figure 5.1. X-ray diffraction patterns of: (A) SBA-15, (B) 10% mono-amine SBA-15, and (C) 10% mono-ammonium SBA-15.

Figures from 5.2 to 5.9 show the XRD patterns of amine and ammonium functionalized SBA-15 materials which were functionalized with different molar ratios of amine (10, 20, and 40%) and with different sources of amine (mono, di, and tri-amine). In the case of SBA-15 functionalized with mono amine groups, with increasing the molar percentage of mono amine groups there is no drastic change found in the XRD pattern (Figures 5.1, 5.2 and 5.3). In the cases of SBA-15 functionalized with di-amine groups it was found that the molar ratio of 10%

did not change the SBA-15 structure. On the other hand above 10%, the XRD intensities decreased drastically (Figures 5.4, 5.5.5 and 5.6). The same observations were also found after attaching a tri amine functional group onto SBA-15 surface (Figures 5.7, 5.8 and 5.9). These results indicate that the amino and ammonium functionalized SBA-15 still have the original hexagonal structure, but have less ordered and smaller pore size doing to the surface modification.

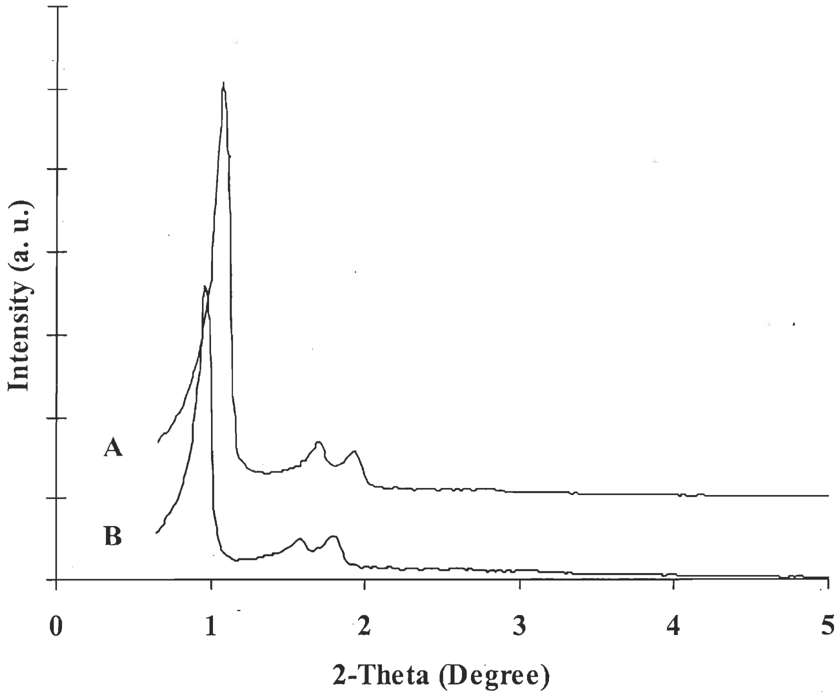

Figure 5.2. X-ray diffraction patterns of: (A) 20% mono-amine-SBA-15, and (B) 20% mono-ammonium-SBA-15.

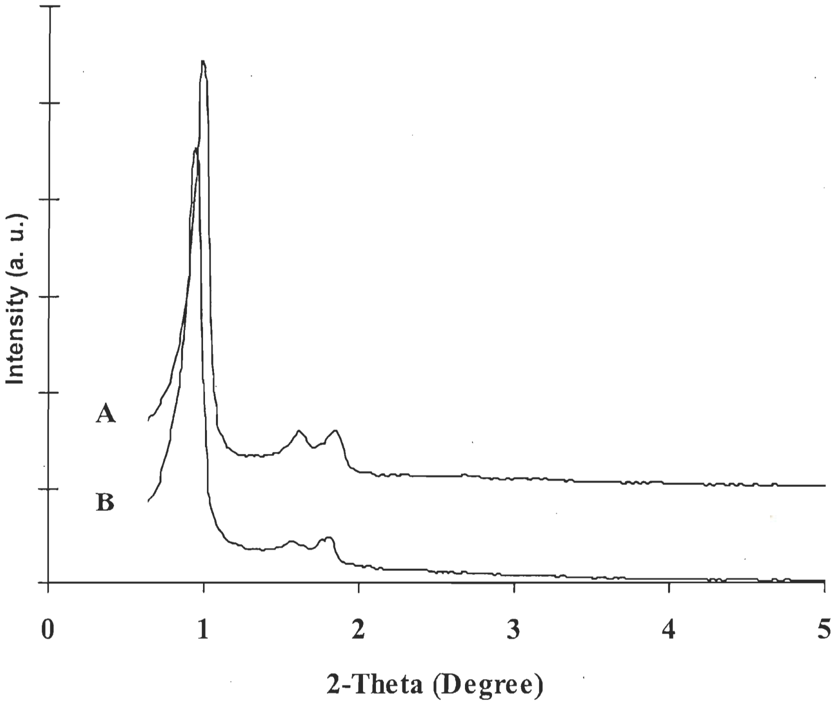

Figure 5. 3. X-ray diffraction patterns of: (A) 40% mono-amine SBA-15, and (B) 40% mono-ammonium SBA-15.

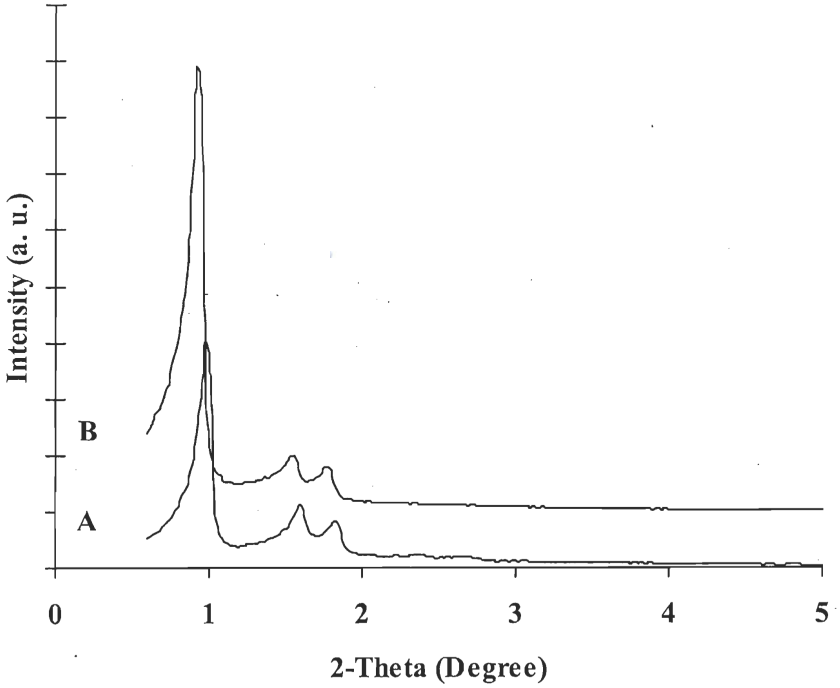

Figure 5.4. X-ray diffraction patterns of: (A) 10% di-amine-SBA-15, and (B) 10% di-ammonium- SBA-15.

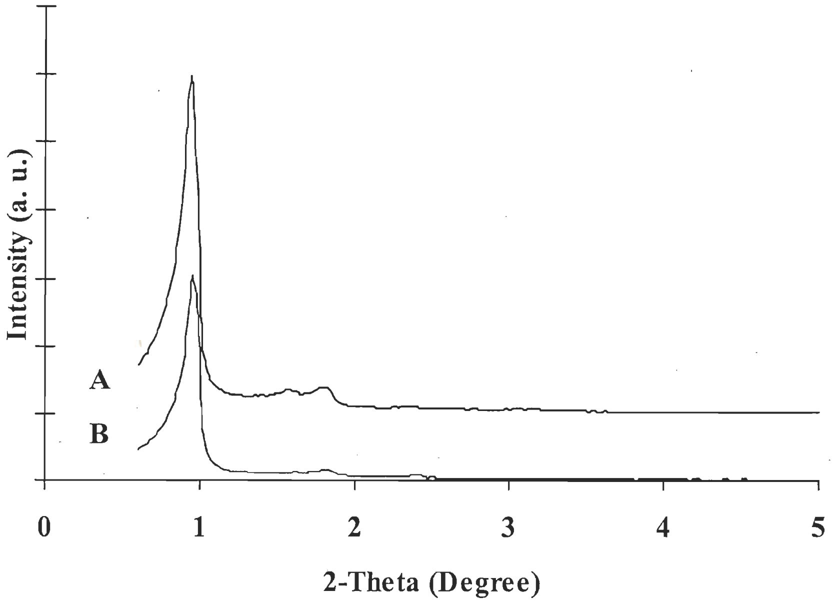

Figure 5.5. X-ray diffraction patterns of: (A) 20% di-amine SBA-15, and (B) 20% di-ammonium SBA-15.

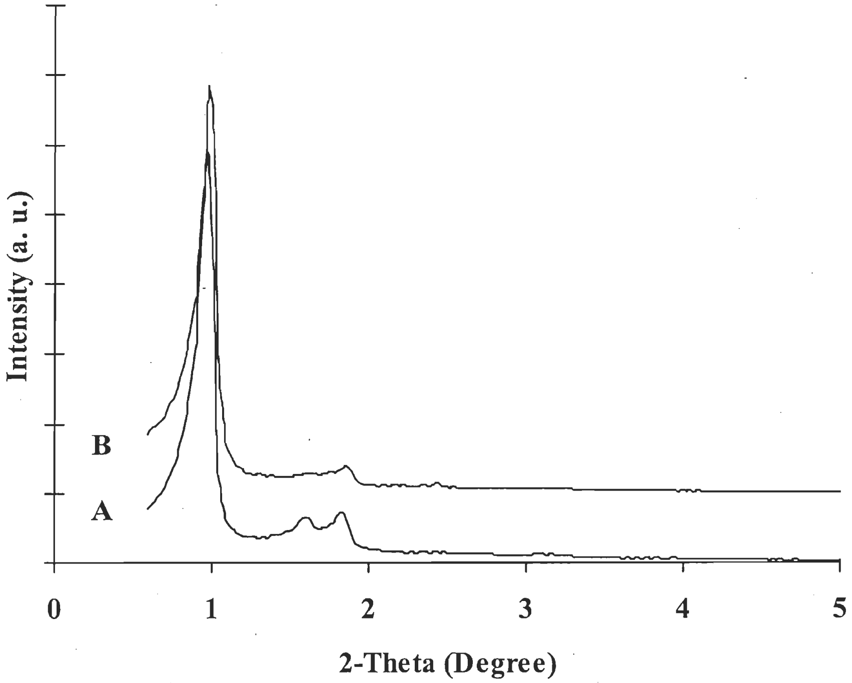

Figure 5.6. X-ray diffraction patterns of: (A) 40% di-amine SBA-15, and (B) 40% di-ammonium- SBA-15.

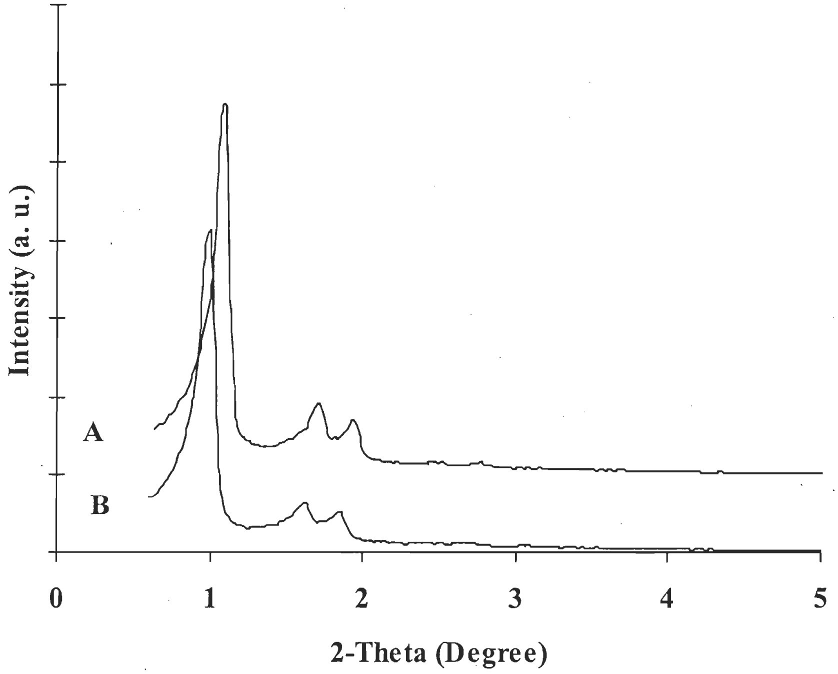

Figure 5.7. X-ray diffraction patterns of: (A) 10% tri-amine SBA-15, and (B) 10% tri-ammonium SBA-15.

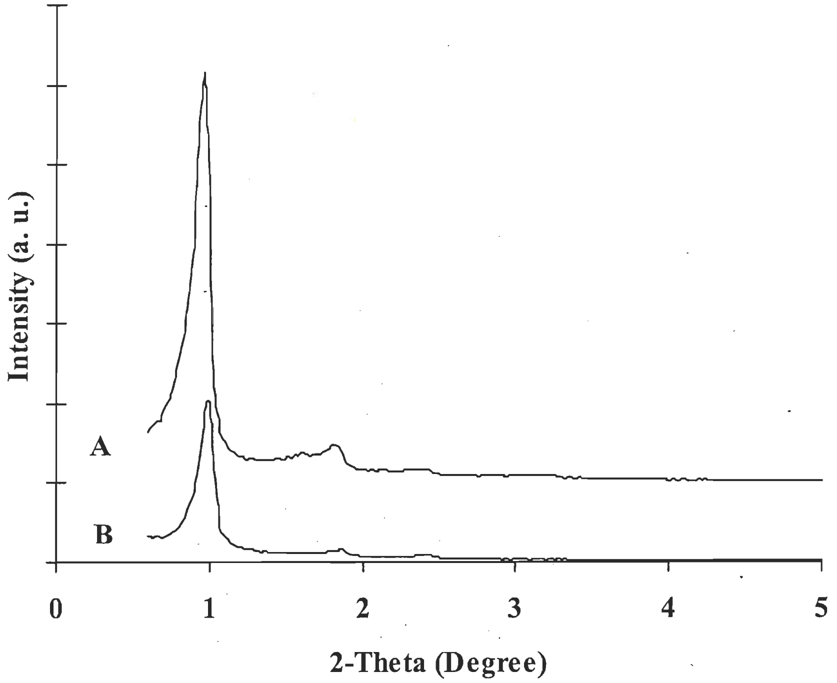

Figure 5.8. X-ray diffraction patterns of: (A) 20% tri-amine SBA-15, and (B) 20% tri-ammonium SBA-15.

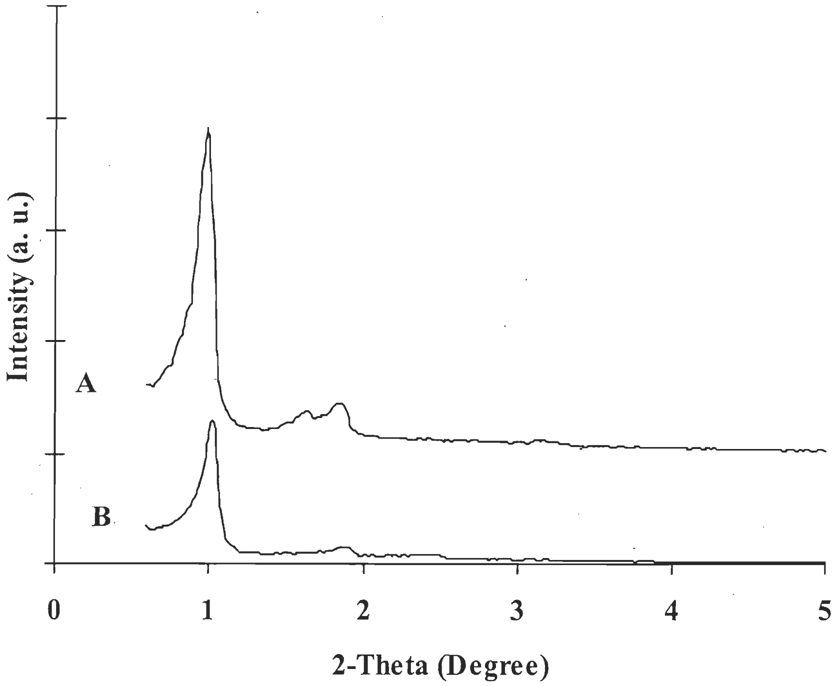

Figure 5.9. X-ray diffraction patterns of: (A) 40% tri-amine SBA-15, and (B) 40% tri-ammonium SBA-15.

5.1.2. Nitrogen adsorption-desorption isotherms

Figure 5.10 display the nitrogen adsorption isotherms for unfunctionalized, amino-functionalized and ammonium functionalized SBA-15 materials which exhibit hysteresis loops with sharp adsorption and desorption branches which are characteristic of well-defined SBA-15 materials (Zhao et al., 1998). On the other hand, the sharpness of the adsorption branches decreases with each of the functionalized and acidified SBA which could be owing to the surface modification with amino and ammonium groups. Other parameters were obtained from adsorption isotherms, such as specific surface area, pore size as well as pore volume, as shown in Table 5.1. It is noteworthy that the surface area, the total pore volume and the most frequent pore size decrease with each of the modification steps (functionalization and acidification) which are consistent with the presence of a significant amount of organic groups on the surface of adsorbent pore channels.

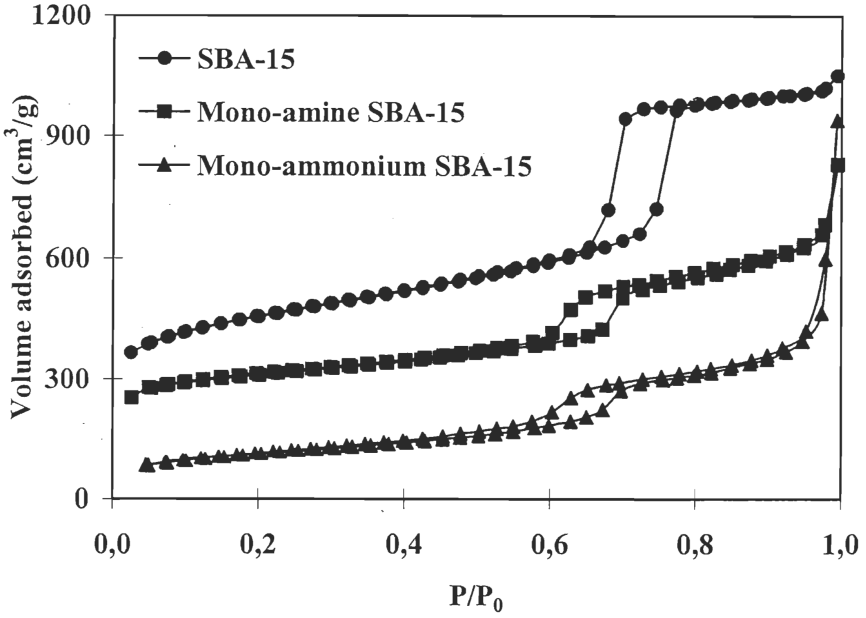

Figure 5.10. Nitrogen adsorption–desorption isotherms of SBA-15 materials.

Table 5. 1. Textural properties of synthesized SBA-15 mesoporous silica materials.

Materials	**Specific surface area (m^2/g)**	**Pore diameter (nm)**	**Total pore volume (cm^3/g)**
SBA-15	910	6.7	1.31
Mono-amine SBA-15	408	6.6	0.97
Mono-ammonium SBA-15	309	6.6	0.90

5.2. Effect of process variables on the phosphate adsorption

In the following section, phosphate concentration in the synthetic solutions used for the adsorption tests is expressed in terms of phosphorus (P) concentration.

5. 2.1. Effect of time

The effect of contact time of ammonium functionalized SBA-15 for phosphate removal was investigated. The experiments were performed at room temperature and 400 rpm. The load of adsorbent and the initial phosphate concentration was 2g/L, 300 ppm respectively. The results were shown in Figure 5.11. From this figure, it has been determined that 10 min of contact time is enough to reach the equilibrium and remove a considerable amount 34.36% (22.9 mg/g) and 36.80 % (24.54 mg/g) at 180 min of phosphate present in aqueous solution. Further increase in contact time does not seem to have any impact on the equilibrium concentration.

It is known that the time required to reach the equilibrium is short in the case of physical adsorption (Van den Boomgaard et al., 1987; Shulthess and Tokunaga, 1996; Gurses et al., 2003). The adsorption of phosphate into ammonium functionalized SBA-15 is a physical adsorption process occurring via electrostatic interactions between the positively charged surface ammonium groups and negatively charged phosphates anions in solution.

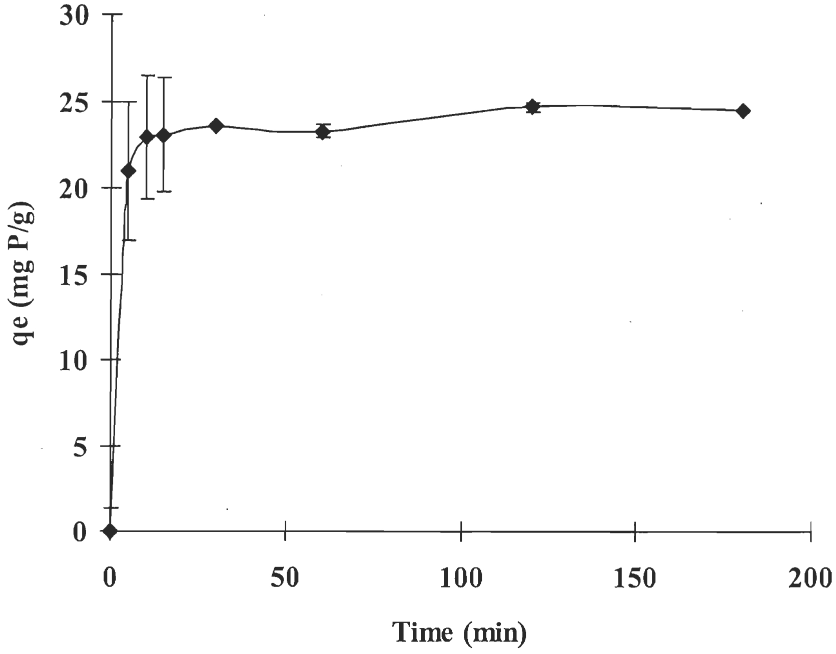

Figure 5.11. Adsorption of phosphate on mono-ammonium SBA-15 as a function of time.

When the ammonium functionalized SBA-15 surface (solid) is in contact with phosphate solution (liquid), the molecule of the liquid strikes the surface of the solid and the rate of adsorption is large as the whole surface is bare but as more and more of the system is covered, the available bare surface decreases and so does the rate of adsorption.

Das et al. (2006) studied phosphate adsorption on 1g/L adsorbent load of calcined layered double hydroxides and 500 ppm initial phosphate concentration and found that the time required to reach the equilibrium was 4h and attained phosphate removal of 42.4 mg/g. While in another study, adsorption on sludge from fuller's earth and at initial phosphate concentration of 30 ppm and adsorbent dose of 5g/L resulted in equilibrium in 9h representing a 95% removal (Moon et al., 2006). Karageogiou et al. (2006) studied the removal of PO_4^{3-} with 1 g of calcite and 20 ppm initial phosphate concentration, he found that 15 min is enough to reach the equilibrium with percentage removal of 88 and 99% at pH 8.5 and 10, respectively.

On the other hand, using natural and surface modified coir pith, Krishnan and Haridas (2007) found that the equilibrium was achieved at 12 h and 16 h in modified coir pith (CP-Fe)

(90%) and natural coir pith (CP) (20%), respectively. These findings were obtained under the following conditions: pH 3, 30°C, 2g/L adsorbent dose, and 50 ppm initial phosphate concentration. On the other hand, the equilibrium was reached after 24h and 5h for both commercial ZrO_2 and the synthesized ZrO_2 with a removal of 7% and 58.85% at an initial phosphate concentration of 300 ppm (Liu et al., 2007). These results indicate that the ammonium functionalized SBA-15 is a faster adsorbent for phosphate ions removal from wastewater in comparison with the other adsorbents currently used having a higher or lower adsorbent ratio depending on the mechanism of adsorption process.

5. 2. 2. Effect of initial phosphate concentration and adsorbent loading

The effect of varying initial concentration (50-100-200-300mg/L) on phosphate removal in the presence of (2-5-7-10) g/L of mono-ammonium SBA-15 was studied, the experiments were carried out at ambient temperature for a contact period of 60min and 400 rpm stirring speed.

The removal percentage of phosphate increased from 41.86 % (10.46 mg/g) to 82.84 % (4.14 mg/g) by increasing the adsorbent loading from 2g/L to 10 g/L at 50 ppm initial phosphate concentration. Using an initial phosphate concentration of 300 ppm, the removal percentage increased from 17.95 % (15.43 mg/g) to 47.04 % (14.11 mg/g) by increasing the adsorbent loading from 2 to 10 g/L.

The results are shown in Figure 5.12. From this figure, it can be seen that the removal of phosphate at different initial concentrations increased with increasing the adsorbent dose. This effect is due to the increase in the total available adsorbent surface area and adsorption sites with increasing adsorbent dose. This result is in agreement with the results of Golder et al., (2006) who have found that the percentage of adsorption increases with increasing amount of calcined metal hydroxides sludge waste. At an initial pH = 7 and 40 ppm initial phosphate concentration, the maximum percentage removal ($\approx$92%) was observed at an adsorbent dose of 0.8 g/L at 30 °C.

A dose of 0.4 g/L calcined LDH was reported to be sufficient to reach the maximum loading capacity of (44.3 mg/g) for 50 ppm initial phosphate concentration at pH 6 (Das et al., 2006).

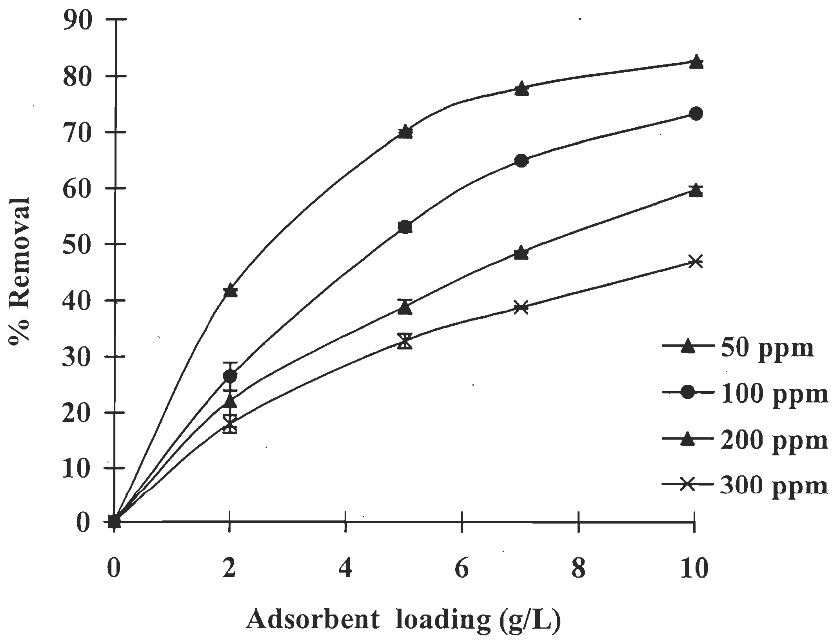

Figure 5.12. Effect of adsorbent loading and initial concentration on phosphate adsorptive removal at 25 °C.

Moreover, an increase in initial phosphate concentrations decreased the removal percentage of phosphate for the same adsorbent loading. This has been attributed to the higher initial concentration ratio of phosphate molecules to the available surface area; therefore adsorption is dependant on initial concentration. In other words, the pores of SBA-15-NH_3^+ were blocked because the $H_2PO_4^-$ was adsorbed by SBA-15-NH_3^+, which hindered more $H_2PO_4^-$ ions entering into the pores of SBA-15-NH_3^+.

Anirudhan et al., (2006) studied the phosphate removal using a weak anion exchanger prepared from lignocellulosic residue and found that with increasing the phosphate concentration from 10 to 75 ppm the amount adsorbed increased from 4.93 to 31.13 mg/g, this study was achieved at 30°C, 5 pH and 2 g/L of adsorbent.

Agyei et al., (2002) studied phosphate adsorption using 2g/L adsorbent loading of fly ash, slag, ordinary Portland cement and related blends at different initial phosphate concentrations (20, 40, 60, 80 ppm) and found that the adsorption of phosphate increased with increasing the initial phosphate concentration, this had been attributed to the chemisorptions which is a more significant phenomenon to phosphate removal than physical adsorption in his study. While in the present study, the adsorption on ammonium functionalized SBA-15 can be characterized as a physical process.

Chemisorption is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals (weak intermolecular) forces which cause physical sorption (Myers., 1999).

5. 2. 3. Effect of stirrer speed

The effect of stirrer speed on phosphate removal with mono-ammonium SBA-15 was studied at 100, 200, 300, 400, 600 and 800 rpm. The experiments were conducted with 300 mg/L phosphate initial concentration, and 2 g/L adsorbent at room temperature. The results are illustrated in Figure 5.13. The results show that upon increasing stirring speed, adsorption capacity of phosphate did not change after 300 rpm, which means that phosphate ions could be diffused easily and quickly from the solution to the surface of the adsorbent and into the pores without needing additional stirring. This result is in agreement with those obtained by Karaca et al., (2006).

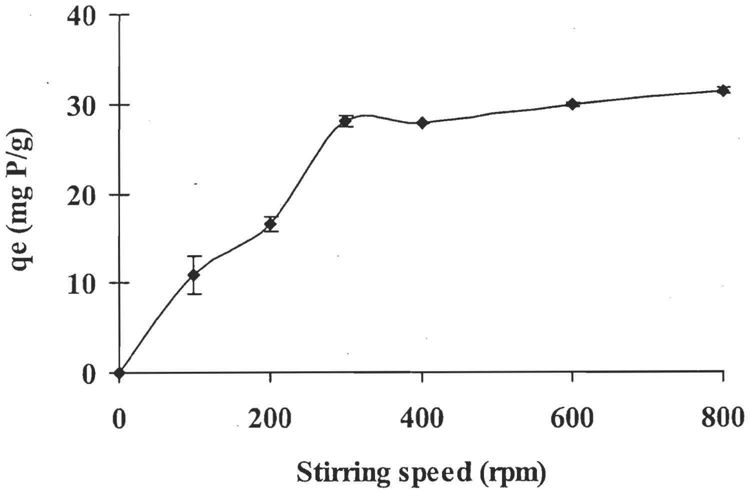

Figure 5.13. Effect of stirring speed on phosphate adsorption.

4. 2. 4. Effect of pH on phosphate removal

The effect of pH on phosphate removal was investigated at 2, 4, 5, 6, 8 and 10 pH, the tests were carried out at 400 rpm with 50 ml of 300 ppm phosphate solution and 0.1 g of mono-ammonium SBA-15 for 60 min at room temperature. The results are presented in Figure 5.14. It is observed that the maximum phosphate adsorption occurs at pH value 4 (31.5 mg/g), and then it decreases gradually from pH 4 to pH 8 and stabilizes from pH 8 to pH 12.

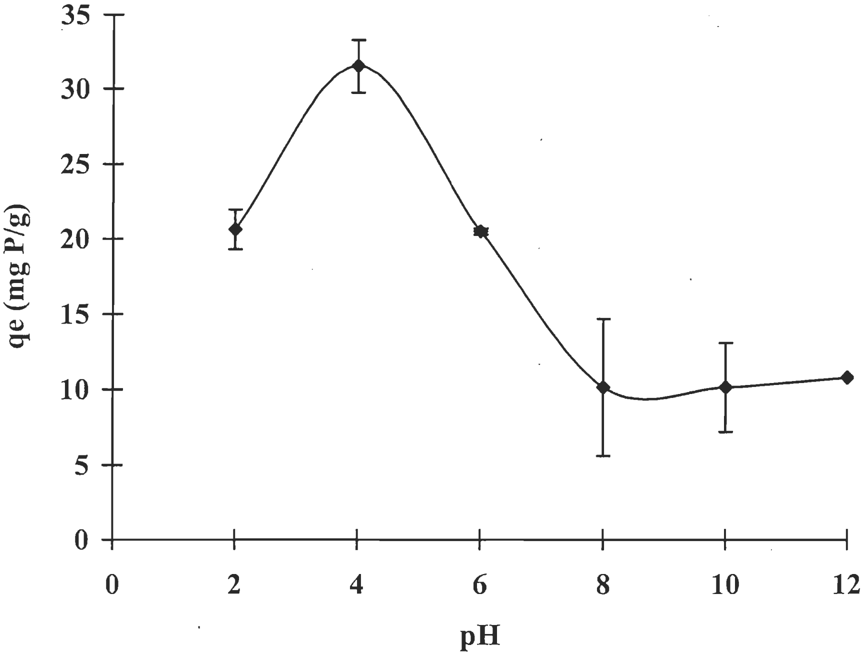

Figure 5.14. Influence of pH on phosphate adsorption.

There are three forms of phosphate: $H_2PO_4^{-}$ (dihydrogen phosphate anion), HPO_4^{2--} (hydrogen phosphate anion), or PO_4^{3-}(orthophosphate anion) (Figure 5.15), the form of phosphate in the solution is dependant on the pH as described in Figure 5.16 (Krishnan and Haridas, 2007) and equation 5.1, 5.2, 5.3 (Harris, 1987). $H_2PO_4^{-}$and HPO_4^{2-} species are present in the pH region between 4 and 10. The concentration of $H_2PO_4^{-}$ species is higher for pH below 7 while HPO_4^{2-} species prevail for pH between 7 and 10. For pH between 10 and 12 HPO_4^{2-} predominate over PO_4^{3-} species while, for pH higher than 12.5 the concentration of PO_4^{3-}species becomes significant. Moreover, the pK_a of propyl amine (grafted on SBA-15) is known to be 10.6 (Harris, 1987).

$$H_3PO_4 \leftrightarrow H_2PO_4^{-} + H^{+}, \qquad pK1 = 2.15 \qquad (5.1)$$

$$H_2PO_4^{-} \leftrightarrow HPO_4^{2-} + H^{+}, \qquad pK2 = 7.20 \qquad (5.2)$$

$$HPO_4^{2-} \leftrightarrow PO_4^{3-} + H^{+}, \qquad pK3 = 12.33 \qquad (5.3)$$

In this study, the higher removal of phosphate is expected at low pH values (corresponding to $H_2PO_4^{-}$) with increasing acidity of the solution pH < pK_a, the solution donates more protons than hydroxide groups (OH^{-}), and so the adsorbent surface is positively charged (attracting phosphate anions). Conversely, at higher pH > pK_a, the solution donates more hydroxide (OH^{-}), groups than H^{+} and then surface charge of ammonium functionalized SBA-15 become neutral and losing electrostatic attraction toward the occurring negatively charged phosphate anions HPO_4^{2-} and PO_4^{3-}.

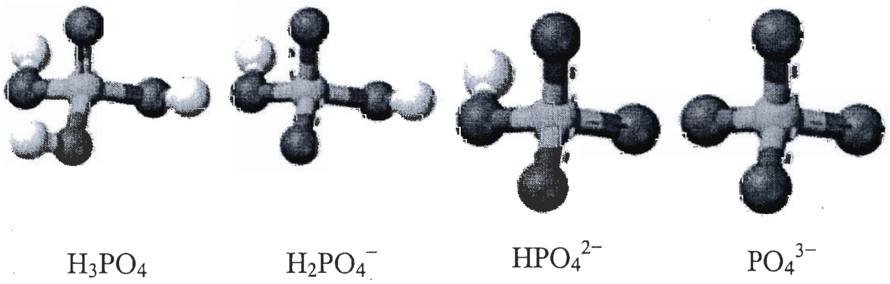

Figure 5.15. Forms of phosphate species in the solution.

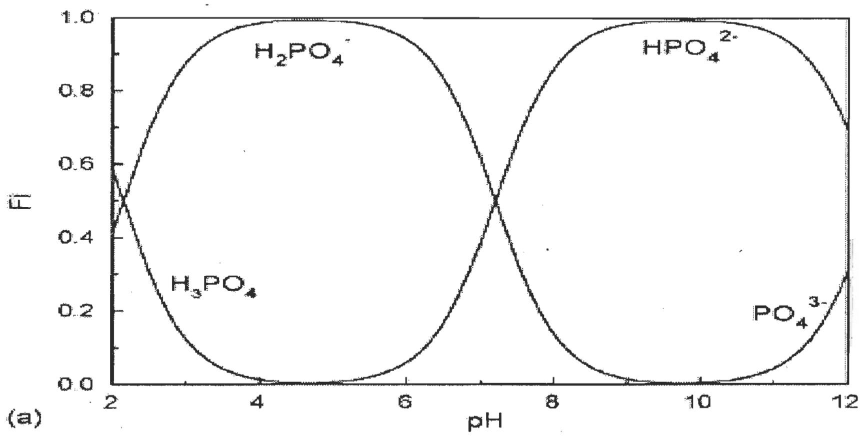

Figure 5.16. Distribution diagram for phosphate species as a function of pH (Xiaofang et al., 2007).

Namasivayam et al. (2004) studied the adsorption of phosphate onto $ZnCl_2$ activated coir pith carbon and found that the maximum adsorption removal occurred at pH of 3-10 because the forms of phosphate which exist in this range of pH are easy to be adsorbed.

Boujelben et al. (2007) found that the maximum removal capacity of PO_4^{3-} was observed at around pH 5 (0.25 mg/g) on iron coated natural and engineered sorbent. Similar observations have been made by Anirudhan et al. (2006), Das et al. (2006) and Saad et al. (2007) who found that the higher adsorption of phosphate ions occur in pH 5 with using the DMAHP (98.7%), LDH_S (91.7%) and ammonium functionalized MCM-48 (34 mg/g). In the case of iron coated natural, DMAHP and LDH_S, the higher pH value decreases the adsorption of phosphate due to the increasing of competitive effect of OH^- for adsorption on these adsorbents. While Saad et al. (2007) attributed the decreasing of phosphate adsorption into ammonium functionalized MCM-48 above the pH 8 to the neutral charge on the adsorbent which loses the electrostatic attraction toward the accruing negatively charged phosphate anions HPO_4^{2-} and PO_4^{3-} in the solution.

According to Zhang et al. (2004), the maximum adsorption of PO_4^{3-} on iron oxide tailings occurred at pH 3.2 (8.6 mg/g) due to the fact that the higher pH values cause more negative charge on the iron oxide surface thus repulsing the negatively charged PO_4^{3-} in the solution.

Opposite results were found by Bastin et al. (1999) who showed that the adsorption of phosphate on synthetic iron oxide-gypsum compound increased with increasing the pH and the maximum removal took place at pH 10 ($\approx$33 mg/g) because the higher pH value can lead to precipitate a significant amount of calcium phosphate. A good removal of 30–45 mg PO_4^{3-} /g-gel was found to be removed from aquaculture wastewater using polymeric hydrogels at pH 5-9 (Kioussis et al., 1999). The larger binding capacities were achieved at acidic pH, while in the basic pH (below pH 8) the amine groups lose a proton and occur in the NH_2 forms which cause the decreasing in phosphate binding into the polymer matrix.

5. 2. 5. Effect of ion adsorption competitivity

To assess the competing effect of other ions on phosphate removal by SBA-15, phosphate batch adsorption tests were carried out by addition of other ions such as sulfate, chloride, carbonate, nitrate, calcium, magnesium, and ammonium. The experiments were carried out at room temperature, 400 rpm, and 2g/L adsorbent. The results are depicted in Table 5.2.

Table 5.2. Effect of competing ions on phosphate amount adsorbed by mono-ammonium SBA-15

Existing ions	**Amount adsorbed (mg P/g)**
$H_2PO_4^-$ alone	36.7 ± 0.07
$H_2PO_4^- + Cl^-$	34.48 ± 0.3
$H_2PO_4^- + SO_4^{-2}$	11.77 ± 0.05
$H_2PO_4^- + HCO^-_3$	30.64 ± 1.15
$H_2PO_4^- + Ca^{2+}$	30.77 ± 0.18
$H_2PO_4^- + Mg^{2+}$	27.2 ± 0.7
$H_2PO_4^- + NO_3^-$	30.25 ± 0.1
$H_2PO_4^- + NH_4^+$	24.94 ± 3.86

As shown in Table 5.2, the effect of competing ions on phosphate adsorption by mono-ammonium SBA-15 was found to follow this order $Cl^- < Ca^{2+} < HCO^-_3 < NO_3^- < Mg^{2+} < NH_4^+ < SO_4^{-2}$.

The divalent SO_4^{-2} was found to affect the adsorption of phosphate ions largely. This can be attributed to the ionic exchange between SO_4^{-2} and two cations of NH_3^+ grafted in the surface of SBA-15 which decreases the adsorption capacity towards phosphate anions.

The adsorption behaviour of PO_4^{3-} in the presence of various competing anions has been studied (Das et al., 2006) on LDH_s. The divalent anions were shown to have a profound interfering effect compared to the monovalent anions. Moreover, the effect of competing anions and cations on phosphate adsorption by ammonium functionalized MCM-48 were reported to follow the order $HCO^-_3 < Ca^{2+} < Cl^- < Mg^{2+} < SO_4^{2-}$ (Saad et al., 2007).

On the other hand, Georgantas et al. (2007) studied the effect of competing anions and cations such as (Ca^{2+}, Cl^-, NH_4^+, Mg^{2+}, SO_4^{-2}, Ca^{2+}) on the orthophosphate and metaphosphate ions removal using alum and aluminum hydroxide and found that the presence of these ions did not influence the adsorption of orthophosphate and metaphosphate.

5. 2. 6. The regeneration study

The regenerability of ammonium functionalized SBA-15 was studied at different initial concentrations of phosphate 50,100, 150, 200, 250 and 300 mg/L for 60 min at 25 °C and 400 rpm for 5 cycles. The results are shown in Figure 5.17.

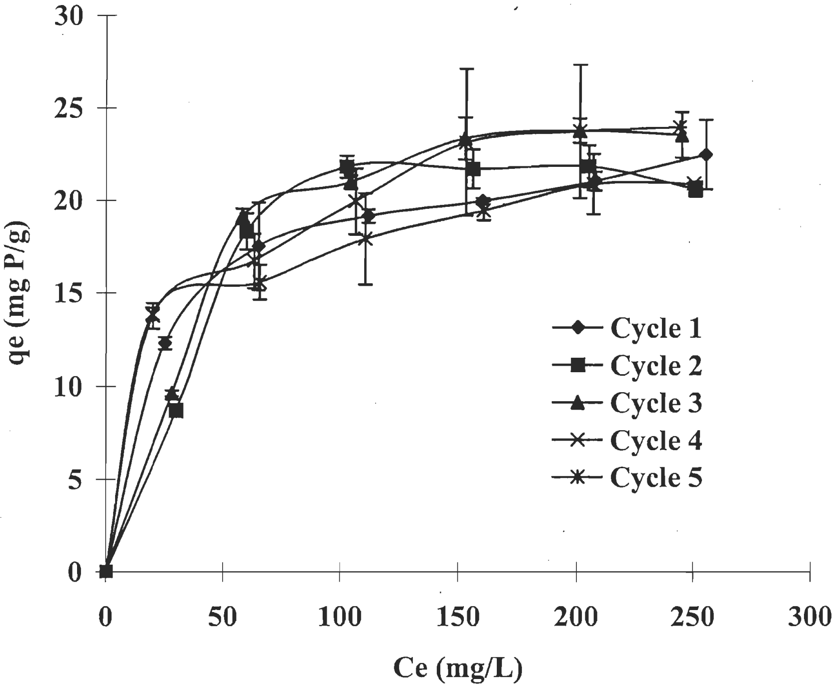

Figure 5.17. The effect of regeneration of mono-ammonium SBA-15.

From this figure, it was observed that the adsorption capacity of the ammonium functionalized SBA-15 did not decrease after 5 cycles of regeneration with adsorption capacity of (22.5, 20.6, 23.56, 20.9, 23.98 mg/g) for the cycle 1 to 5 at 300ppm initial phosphate concentration, respectively.

Saad et al., (2007) reported that the ammonium functionalized MCM-48 was effectively regenerated for 5 cycles. While Kuzawa et al., (2006) showed that the PO_4^{3-} which loaded LDHs were regenerated for 10 cycles and the capacity after 10 regenerations was 60% of the initial one. Blaney, et al., (2007) while using hybrid anion exchanger for trace phosphate removal, showed that 95% of phosphate was successively regenerated for three cycles in 12 beds.

Successful regeneration of PO_4 has been demonstrated by Kioussis et al. (1999) on polymeric hydrogels who concluded that the binding capacity of the gels increases by as much as 15% after being reused for 5 cycles.

5. 2. 7. Effect of amine type and concentration

Ammonium functionalized SBA-15 materials with different amine types (mono, di, and tri) at different molar ratios were synthesized and acidified as described previously in sections (4.3.1.2) and (4.3.1.3) respectively.

The effect of organic functional group concentration in the silica framework for mono-ammonium SBA-15 concentration on phosphate adsorption was studied using different molar concentrations (5. 10, 15, 20 and 40%) of the organosilane (APTES) in the silica framework. The initial phosphate concentrations were 50, 100, 150, 200, 250 and 300 ppm under constant agitation rate (400 rpm) and adsorbent load (2g/L) at room temperature.

The same effect was investigated for di- and tri- ammonium functionalized SBA-15 using molar concentrations (10, 20 and 40%) under otherwise identical conditions of phosphate concentrations, adsorbent loading, agitation speed and temperature.

The results are presented in Figures 5.18, 5.19 and 5.20. It is clearly demonstrated in Figure 5.18 that the amount adsorbed of phosphate increased with increasing the molar percentages of ammonium functionalized SBA-15 from 5 (14.73 mg/g) to 40 % (31.18 mg/g) at 300 ppm initial phosphate concentration. This effect could be attributed to the increasing of ammonium groups on the surface of SBA-15 which are responsible of the phosphate adsorption process.

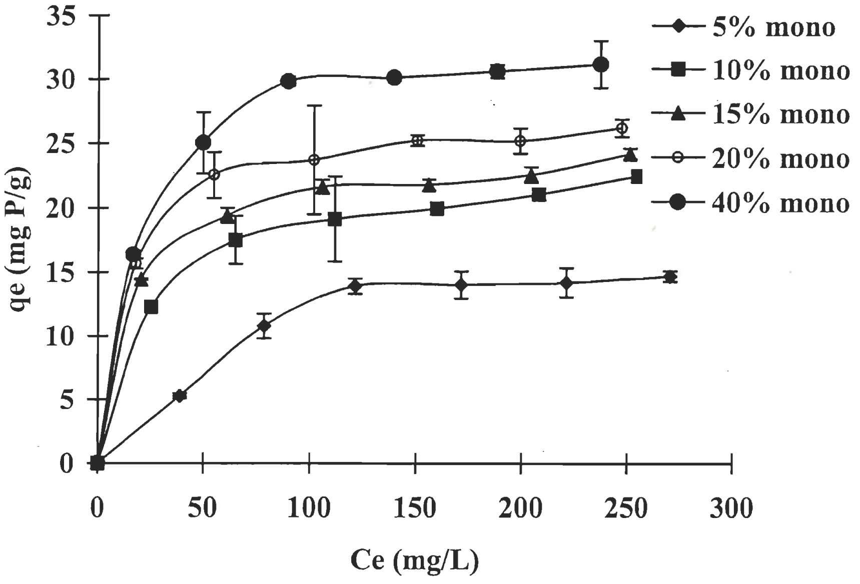

Figure 5.18. Effect of organosilane concentration for mono-ammonium SBA-15 on phosphate adsorption.

In the cases of di- and tri-ammonium functionalized SBA-15, the amount adsorbed of phosphate was doubled with increasing the percentage of amine from 10 % to 20 % at 300 ppm initial phosphate concentration, respectively. However, the amount adsorbed of phosphate did not increase at 40% in the two cases (di- and tri-ammonium functionalized SBA-15) as shown in Figure 5.19 and 5.20. These results can be explained as follows.

With increasing the percentage of amine, the grafted quantity will increase and so the amount adsorbed of phosphate increased until reaching the saturation of the surface of SBA-15. After saturation, the increasing of amine percentage will not have any effect on the grafted quantity. Consequently, the amount adsorbed of phosphate will be limited by the number of amine groups present on the surface of SBA-15. Also, the multi-amino silane groups occupy larger spaces in the pore channels because of theirs higher density and longer chains leading to pore blockage and decreasing the amount adsorbed of phosphate.

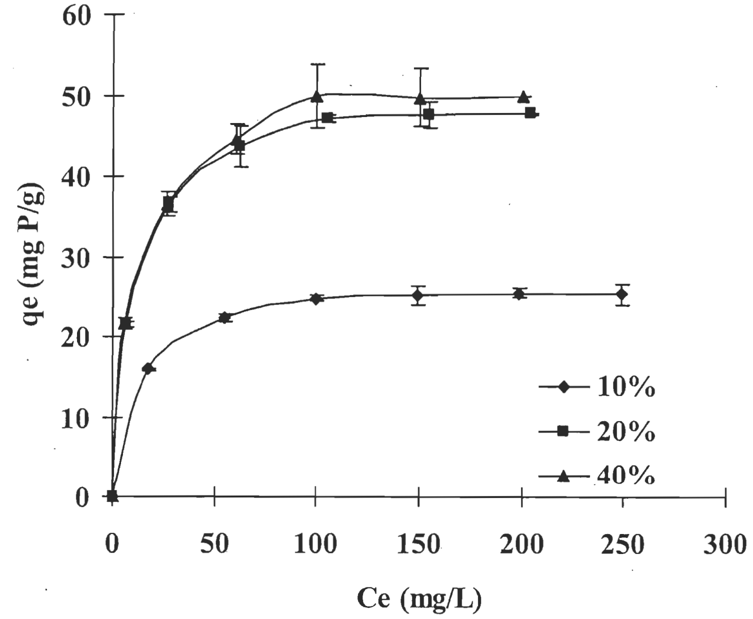

Figure 5.19. Effect organosilane concentration for di-ammonium functionalized SBA-15 on phosphate adsorption.

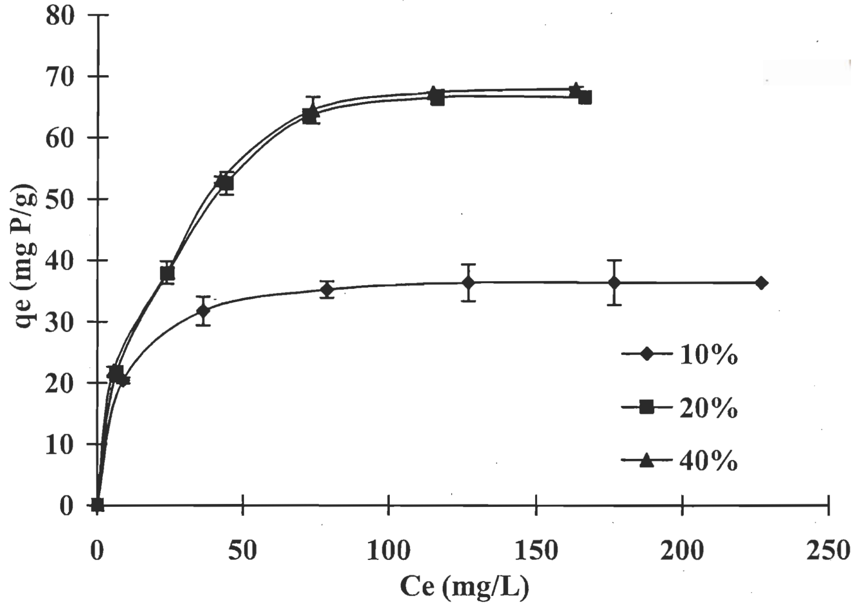

Figure 5.20. Effect of organosilane concentration for tri-ammonium functionalized SBA-15 on phosphate adsorption.

Figures 5.21, 5.22, 5.23 depict the effect of amine type on the amount adsorbed of phosphate with the same concentration. From these figures, it is clear that the amount of phosphate adsorbed increased with changing the amine type. The changing of amine type from mono, di and tri leads to increasing the number of adsorption sites on the surface of ammonium functionalized SBA-15 resulting in an increase in the amount adsorbed of phosphate.

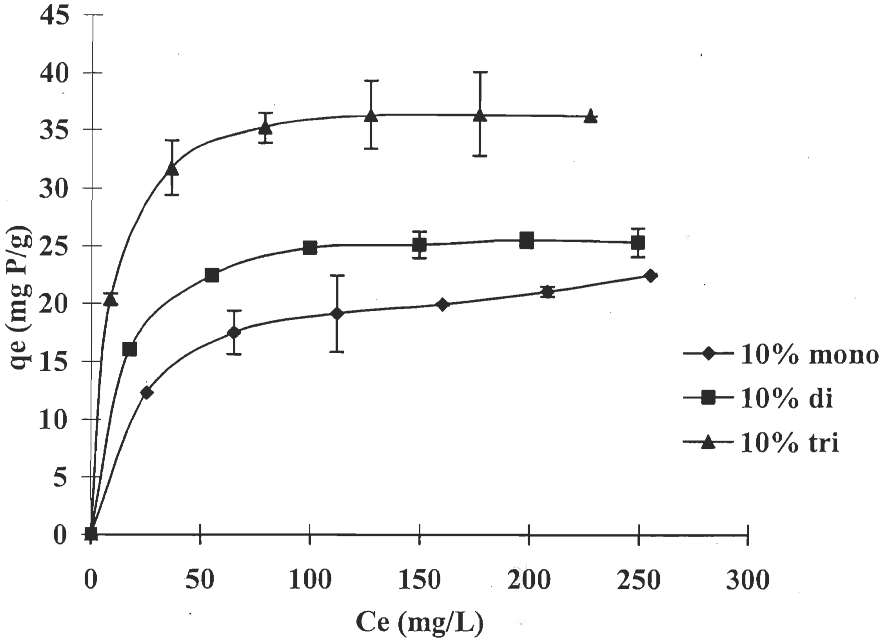

Figure 5.21. Effect of amine type on phosphate adsorbed amount at 10% organosilane concentration.

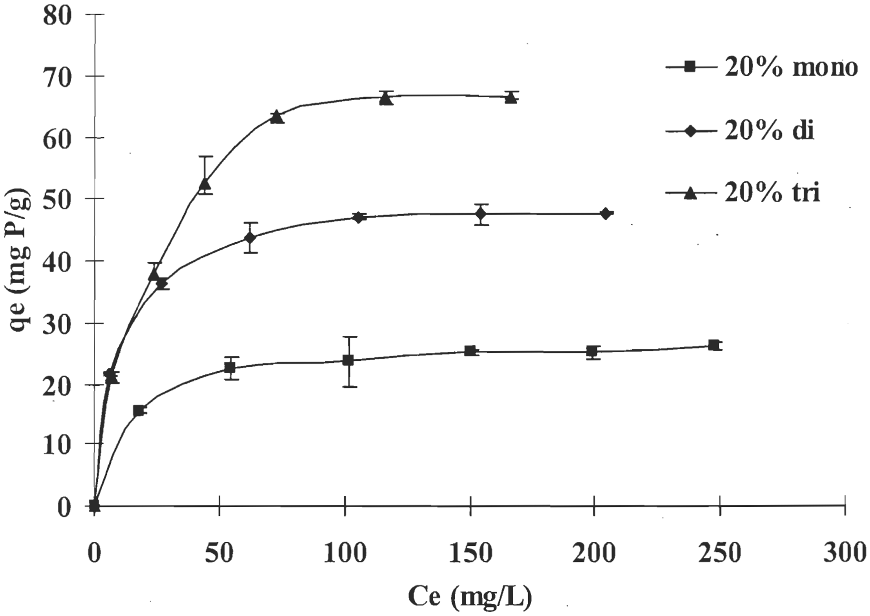

Figure 5.22. Effect of amine type on phosphate adsorbed amount at 20% organosilane concentration.

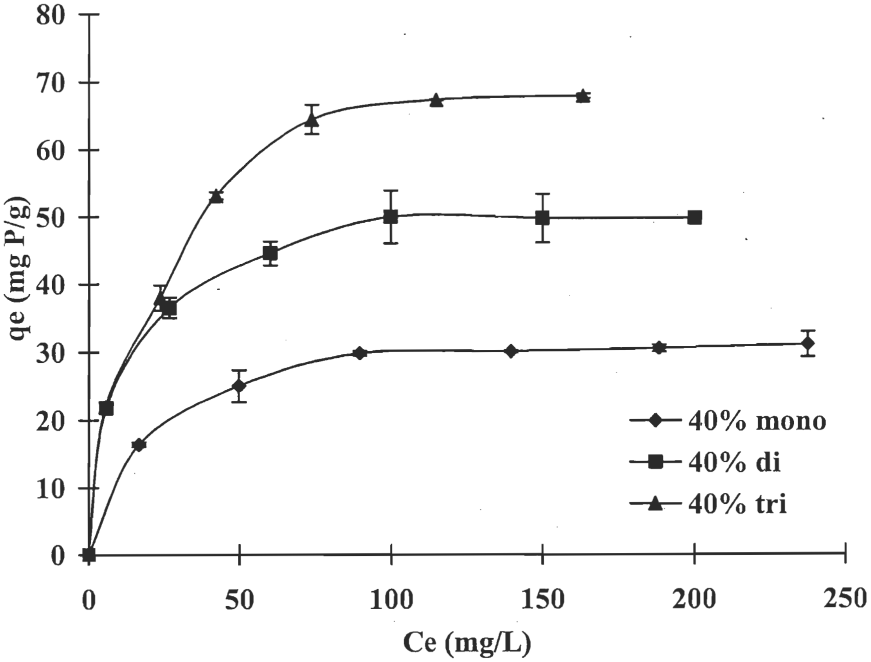

Figure 5.23. Effect of amine type on phosphate adsorbed amount at 40% organosilane concentration.

5. 2. 8. Effect of temperature

The adsorption isotherms experiments were realized to study the effect of temperature on phosphate removal using mono-ammonium functionalized SBA-15. The tests were carried out at different temperatures 5, 10, 15, 25, 35 and 45 °C using phosphate solution having initial concentrations of 50, 100, 150, 200, 250 and 300 ppm. Adsorption isotherms were performed under constant agitation rate (400 rpm) and at constant adsorbent loading (2g/L).

The results are depicted in Figure 5.24. As seen, it was found that 5 °C is the best temperature for phosphate adsorption using ammonium functionalized SBA-15 with 27.7 mg/g adsorbed amount compared to 15.08 mg/g at 45 °C for phosphate initial concentration of 300 ppm.

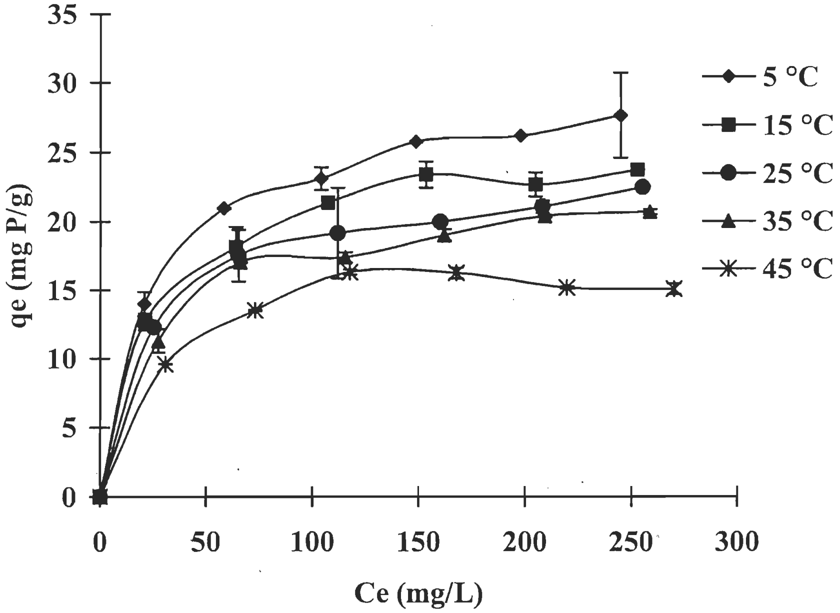

Figure 5.24. Phosphate adsorption isotherms at different temperatures.

CHAPTER 6: CONCLUSION AND SUGGESTIONS FOR FUTURE WORK

6.1. Conclusion

The main objective of this study was to synthesize and functionalize the SBA-15 mesoporous silica with ammonium groups in order to evaluate its capacity for removing the phosphate from aqueous solutions. The adsorption performances of the ammonium functionalized SBA-15 mesoporous silica have been tested under different experimental conditions such as the equilibrium time, pH, temperature, adsorbent loading, ammonium groups loading and type, stirring speed, phosphate concentration. Also, the presence of different ions and cations and the regeneration of the adsorbent were extensively studied in this work.

Major conclusions derived from this study are summarized as follows:

- The time necessary to attain the equilibrium is 10 min.
- Maximum phosphate removal (31.5 mg P/g) occurs at acidic pH values (around pH 4).
- A maximum capacity of 27.7 mg P/g was obtained at 5°C.
- Adsorption percentage increase with increasing the adsorbent loading.
- The adsorbed phosphate increased with increasing the concentration of mono-, di-and tri-ammonium until 40%.
- The adsorbed amount decreased with increasing phosphate concentration.
- Competitive ions were found to influence phosphate adsorption in the order $Cl^- < Ca^{2+} < HCO^-_3 < NO_3^- < Mg^{2+} < NH_4^+ < SO_4^{-2}$.
- The adsorption performances did not change after five cycles of adsorption-desorption.

Therefore, it can be concluded that the ammonium SBA-15 proved to be an interesting adsorbent for the removal of phosphate from aqueous solutions.

6.2. Suggestions for future work

In this study, we studied the adsorption of phosphate using the ammonium functionalized SBA-15 as adsorbent. This work may now be extended to cover other ions such as nitrate and ammonia as target pollutants well as other types of functionalized mesostrcutured silica materials as adsorbents. Also, it is recommended to analyze the kinetic data of phosphate adsorption onto ammonium functionalized SBA-15 as well as the determination of the thermodynamic parameters.

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