

## Academic Conferences and Symposiums attended

1. **Gogoi, P.,** Thakur, A., Banerjee, S., Devi, R. R., Veer, V. and Maji, T. K. "Chitosan Based Nanoparticle for The Removal of Contaminants from Water", in the National conference Recent development in health and hygiene and environment held at defence Research Laboratory, Tezpur, Assam from 06-08<sup>th</sup> November, 2012 (Poster presented)
2. **Gogoi, P.,** Thakur, A., Banerjee, S., Devi, R. R., Veer, V. and Maji, T. K. "Moringa oleifera Seeds and Its Composite With Chitosan; Promising Materials for Defluoridation of Water", in the national seminar on Recent advances in chemical research held at Rajiv Gandhi University, Arunachal Pradesh, during 20-2<sup>th</sup> March, 2014. (poster presented)
3. **Gogoi, P.,** Thakur, A., Banerjee, S., Devi, R. R. and Maji, T. K. "Enhanced sorption of Arsenate ion from contaminated water by MMT clay incorporated chitosan nanoparticle", in the UGC-SAP National Conference on Contemporary Development in Chemical Sciences-2015 organized by Tezpur University during 23-24<sup>th</sup> November, 2015. (Oral Presentation)
4. **Gogoi, P.** Adhikari, P. and Maji, T. K. "Bioremediation of Arsenic from Water with Citric Acid Crosslinked Water Hyacinth (*E. crassipes*) root powder", in the international conference on Emerging trends in Nanomaterials Science and Technology, organized National Institute of Technology, Nagaland, during 4-6<sup>th</sup> January, 2017, (Poster presented)
5. **Gogoi, P.,** Dutta, D. and Maji T. K. "Starch immobilized TiO<sub>2</sub> nanoparticles in As(V) remediation from aqueous solution", in the International symposium on Sustainable Urban Environment (ISSUE 2017) held at Tezpur University on 23-24<sup>th</sup> June, 2017 (Oral Presentation)

# Equilibrium and kinetics study on removal of arsenate ions from aqueous solution by CTAB/TiO<sub>2</sub> and starch/CTAB/TiO<sub>2</sub> nanoparticles: a comparative study

Pankaj Gogoi, Debasish Dutta and Tarun Kr. Maji

## ABSTRACT

We present a comparative study on the efficacy of TiO<sub>2</sub> nanoparticles for arsenate ion removal after modification with CTAB (N-cetyl-N,N,N-trimethyl ammonium bromide) followed by coating with starch biopolymer. The prepared nanoparticles were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffractometry (XRD), thermogravimetry, scanning electron microscopy (SEM) and electron dispersive X-ray analysis (EDX). The removal efficiency was studied as a function of contact time, material dose and initial As(V) concentration. CTAB-modified TiO<sub>2</sub> showed the highest arsenate ion removal rate (~99% from 400 µg/L). Starch-coated CTAB-modified TiO<sub>2</sub> was found to be best for regeneration. For a targeted solution of 400 µg/L, a material dose of 2 g/L was found to be sufficient to reduce the As(V) concentration below 10 µg/L. Equilibrium was established within 90 minutes of treatment. The sorption pattern followed a Langmuir monolayer pattern, and the maximum sorption capacity was found to be 1.024 mg/g and 1.423 mg/g after starch coating and after CTAB modification, respectively. The sorption mechanisms were governed by pseudo second order kinetics.

**Key words** | CTAB modification, kinetics, regeneration, sorption capacity, starch coating

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## ABBREVIATIONS

ATC arsenic-treated SPC  
CMT CTAB-modified TiO<sub>2</sub>  
CTAB N-cetyl-N,N,N-trimethyl ammonium bromide  
SPC starch-coated CMT  
UTi unmodified TiO<sub>2</sub>

## INTRODUCTION

TiO<sub>2</sub> is currently considered as the most versatile nanomaterial. It has a wide range of applications in different fields (Xiaobo & Samuel 2007). These are attributed to its low cost, low toxicity, photostability in solution, redox selectivity and strong oxidizing power of holes. The application of TiO<sub>2</sub> at the nanoscale further

improves efficiency due to the high surface area, large pore volume and presence of high affinity surface hydroxyl groups (Daimei *et al.* 2006; Gupta *et al.* 2012). TiO<sub>2</sub> and its different modified forms have also drawn the attention of researchers in the field of the removal of contaminants from water. It is capable of removing heavy metals as well as arsenite and arsenate from contaminated water (Gautham *et al.* 2010).

Gupta & Tripathi (2011) reviewed the use of TiO<sub>2</sub> for environmental clean-up of organic pollutants through photo-oxidation. Xu *et al.* (2007) studied the photocatalytic degradation of organic arsenic to inorganic form by TiO<sub>2</sub> and successful sorption on its surface.

Debnath & Ghosh (2009) applied nanostructured hydrous titanium oxide to adsorb Ni(II) from natural and



# A comparative study on sorption of arsenate ions from Water by crosslinked chitosan and crosslinked Chitosan/MMT nanocomposite



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## ARTICLE INFO

Received 8 June 2016

Revised 15 September 2016

Accepted 17 September 2016

Available online 19 September 2016

### Key words:

Arsenate

crosslinked chitosan

montmorillonite

## ABSTRACT

Montmorillonite (MMT) clay incorporated chitosan (CT) nanocomposite was prepared by simplified ionic gelation method. Different characterization techniques were performed to investigate the binding and structural properties of prepared materials. It was found that incorporation of clay into chitosan followed by crosslinking with glutaraldehyde (GLU) enhances the arsenate sorption rate and better stability was observed on cyclic run compared to glutaraldehyde crosslinked chitosan (Ct/GLU). The sorption process attained equilibrium within 90 minutes of treatment time and a dose of 2g/L of crosslinked chitosan/MMT (MMT/Ct/GLU) was sufficient to bring down the arsenate concentration below 0.01mg/L. Increase in initial ion concentration of arsenate ions decreases the sorption rate, but the ion uptake capacity increases. The sorption was reasonably explained with Langmuir ( $R_L \sim 0.995$  &  $0.996$  for MMT/Ct/GLU & Ct/GLU) and Freundlich isotherms ( $n \sim 2.75$  &  $3.12$  for MMT/Ct/GLU & Ct/GLU). The  $R^2$  values indicated a monolayer type of chemisorption pattern. The sorption process was found to be governed by pseudo second order kinetics.

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## 1. Introduction

The acute toxicity of arsenic at high concentrations as well as at low concentration (when exposed for long term) is well known to all. Drinking water is the major source of human intake of arsenic in its most toxic (inorganic) form. appearance of the contaminated water. It is quite difficult to detect arsenic in drinking water without complex analytical techniques [1]. World Health Organization (WHO) recommends a guideline value for arsenic in drinking water as 0.01 mg/L [2-4]. Arsenic can't be predicted by any physical means like taste, odor or From

many decades researchers are engaged for developing methods to remove arsenic from contaminated water with minimum cost. Chemical precipitation, membrane separation, ion exchange, electrochemical methods, adsorption etc. are some of the reported methods for removal of arsenic [5,6]. Adsorption has many advantages over the other methods when arsenic is present in low concentrations. These include low cost, easy operation and least use of chemical additives [7,8].

Use of different adsorbing materials like activated carbon, clay, metal oxides, various synthetic and natural polymers etc. have already been reported [9,10]. These materials either possess high surface area, pore on its surface or contain different functional moiety. Materials with nano dimension like metal, metal oxide, clay etc. have advantages over other adsorbing materials as they possess high surface area [11]. They are also accompanied by least waste generation after the treatment as nearly all adsorbent molecules or atoms on large surfaces are actively utilized for adsorption. Benavente extensively studied the equilibrium isotherms and the adsorption kinetics of heavy metals onto chitosan [12].

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# Bioremediation of arsenic from water with citric acid cross-linked water hyacinth (*E. crassipes*) root powder

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Received: 9 January 2017 / Accepted: 12 June 2017  
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**Abstract** A green and novel approach was demonstrated for successful remediation of arsenic from contaminated water by citric acid (CA) cross-linked water hyacinth root powder (RP). Different analytical techniques were used to investigate the binding and structural properties of prepared materials. Titanium dioxide played a significant role in the cross-linking process. Incorporation of CA into RP enhanced its integrity, and thus removal efficiency remained unaffected after several cyclic runs. Also the turbidity which formed due to treatment with uncross-linked RP was reduced to below the permissible limit. Effect of the amount of CA, material dose, treatment time, initial ion concentration, and pH were investigated. Use of 10% (w/w) CA was found to be sufficient to bring down the turbidity of the treated water below 2.5 nephelometric turbidity unit (NTU) without hampering the removal capacity/rate. A material dose of 5 g/L removed successfully total inorganic arsenic concentration to below 10 µg/L. The sorption process could be reasonably explained by Langmuir isotherm, and the maximum adsorption capacity was found to be 28 µg of arsenic/g. The material was found to be more efficient at acidic pH ( $\text{pH}_{\text{ZPC}} = 6.72$ ). The

sorption process was governed by a pseudo-second-order kinetic model.

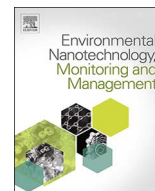
**Keywords** Water hyacinth root · Turbidity · Cyclic run · Isotherm · Pseudo second order

## Introduction

Phytoremediation of contaminated water by different aquatic plants is a very useful technique for waste treatment. It has much significance in the developing countries, as these plants are found abundantly in nature and can provide a simple, effective, and yet cheap method for removing heavy metals and other contaminants from water. Bioaccumulation of arsenic, phosphate, copper, cadmium, etc. by living *Hydrilla verticillata* has been well studied (Shaban et al. 2005; Srivastava et al. 2011; Wang et al. 2008; Xue et al. 2010; Bunluesin et al. 2007). *Lemna minor*, another aquatic plant, also can accumulate copper and cadmium from contaminated water (Hou et al. 2007). *L. minor* and algae ponds have been evaluated in post-treatment for textile wastewater which is a typical source of heavy metal pollution in aquatic ecosystems (Sekomo et al., 2012). Accumulation of Cd, Cu, Pb, Mn, etc. by different parts of *Phragmites australis* was analyzed by Laing et al. (2003) and Bonanno and Lo Giudice (2010). Another important aquatic plant used in this purpose is water hyacinth (*Eichhornia crassipes*). It is a fast growing, free-floating aquatic weed and contains mainly cellulose and lignin (Ibrahim et al. 2012). It has the capability of

**Electronic supplementary material** The online version of this article (doi:10.1007/s10661-017-6068-2) contains supplementary material, which is available to authorized users.

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## Research paper

## Adsorption of As(V) from contaminated water over chitosan coated magnetite nanoparticle: Equilibrium and kinetics study

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## ARTICLE INFO

## Keywords:

Magnetite  
Chitosan  
Competing ion  
Heterogeneity  
Kinetics

## ABSTRACT

The efficacy of chitosan/magnetite nanocomposite (CTN) for remediation of arsenate ions [As(V)] from water was investigated. The prepared material could efficiently perform several cyclic runs with high As(V) removal efficiency and has the advantages over many established method. Different characterization techniques were performed to investigate the binding and structural properties of prepared materials. The study also focused on the effect of competing ions viz. phosphate and chloride on removal efficiency. The initial As(V) concentration (0.6 mg/L) was found to decrease to less than 0.01 mg/L at a contact time of 120 min with an adsorbent dose of 1 g/L. Increase in initial ion concentration of arsenate ions decreased the sorption rate, but the ion uptake capacity was increased. The sorption was reasonably explained with Langmuir ( $R_L \sim 0.9851$ ) and Freundlich isotherm models ( $n \sim 1.78$ ). At low concentrations Langmuir monolayer sorption was followed but heterogeneity appeared at higher arsenate concentrations. The maximum adsorption capacity ( $Q_m$ ) calculated from Langmuir isotherm was found to be 10.81 mg As(V)/g at room temperature and neutral pH. The sorption process was found to be governed by pseudo second order kinetics.

## 1. Introduction

Arsenic is a toxic element which causes several hazards to human (Sacco and Masotti, 2010). It is a global health problem which is affecting millions of people daily (Ratnaik 2003). The maximum permissible limit for arsenic in drinking water as suggested by world health organization (WHO) is 10 µg/L (Lenoble et al., 2003; Karim 2000). According to International Agency for Research on Cancer, it is grouped among the most carcinogenic substances (Chakravarty et al., 2002). Researchers are engaged for developing methods to remove arsenic from contaminated water. Some of the reported methods are chemical precipitation, membrane separation, ion exchange, electrochemical methods, adsorption etc. (Bordoloi et al., 2013; Kadirvelu and Namasivayam 2003; Choong et al., 2007). Among these, adsorption is considered as the most preferred method especially at low concentrations as it is associated with low cost, easy operation and trivial use of chemical additives (Akin et al., 2012; Thakur et al., 2013).

In this regard, different materials like activated carbon, clay, metal oxides, various synthetic and natural polymers etc. have already been established as good adsorbing materials (Mohan and Pitterman Jr, 2007). Recently nano sized metal oxides have drawn the attention of scientists due to their high surface areas. But the separation of the

nanomaterial from water after treatment is a major concern. These nanomaterials could be tailored by using polymers. Chitosan bio polymer represents an attractive alternative as adsorbents. It is largely available in nature, bio-compatible, non-toxic and bio-degradable as compared to the synthetic polymers (Yanfang et al., 2014). Arida et al. investigated the removal of As(V) from groundwater using Chitosan coated bentonite in a fixed-bed system and cited the advantages of using chitosan being economically viable, safe in disposal and high metal uptaking material (Arida et al., 2015).

Several reports addressed the use of iron oxide nanoparticles for removal of contaminants in water. Khodabakhshi et al. have studied the efficiency of magnetic iron oxide nanoparticles ( $Fe_3O_4$ ) in the removal of As (III) from industrial waste water (Khodabakhshi et al., 2011). Gupta et al. have reported the efficacy of chitosan zerovalent iron nanoparticles towards arsenic removal (Gupta et al., 2012). They successfully stabilized Fe(0) nano particles within chitosan bio polymer matrix which could be used repeatedly. Chang and Chen have studied the adsorption properties of monodisperse chitosan bound  $Fe_3O_4$  magnetic nanoparticles for the removal of Cu(II) ions (Chang and Chen, 2005). Liu et al. have prepared a magnetic chitosan nanocomposite and successfully utilized it as a useful recyclable tool for removal of  $Pb^{2+}$ ,  $Cd^{2+}$  and  $Cu^{2+}$  ions (Liu et al., 2009).

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## Chitosan: A Promising Biopolymer in Drug Delivery Applications

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Received date: August 19, 2015, Accepted date: October 06, 2015, Published date: October 13, 2015

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### Abstract

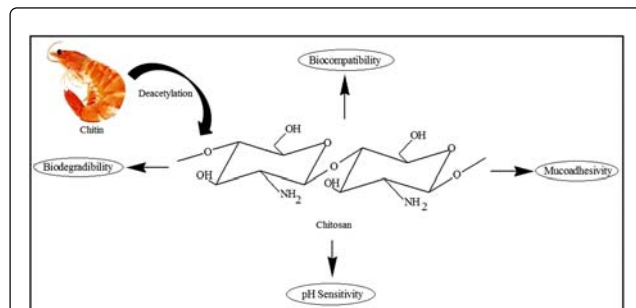
Drug delivery system with controlled release technology has emerged as a powerful tool for the treatment of various diseases. The therapeutic index of the active agent can be enhanced by increasing its stability, solubility and bioavailability, along with specific site delivery. Polymers have been playing an integral role as carrier in formulating an efficient drug delivery system by their stability, drug loading capacity and tunable properties. 'Chitosan' the natural cationic polymer derived from chitin has received growing attention mainly due to their biodegradable, biocompatible, non-toxic, mucoadhesive and ability to target specific delivery properties. Chitosan has itself many medicinal properties like antimicrobial, antioxidant, low immunogenicity etc. which enhance its potential in different biomedical applications. The various techniques for preparation of chitosan micro/nano particles are discussed in this review. Various types of chitosan based drug delivery systems are surveyed to elucidate its role in different biomedical applications.

**Keywords:** Drug delivery; Controlled release; Micro/nano particles; Biomedical applications

### Introduction

#### Origin, history and chemical structure of chitosan

Chitosan is a cationic linear copolymer polysaccharide made up of random distribution of  $\beta$  (1 $\rightarrow$ 4) linked 2- amino- 2- deoxy- D- glucose (D-glucosamine) and 2- acetamido- 2- deoxy- D- glucose (N- acetyl- D- glucosamine) units. The structure is shown in Figure 1 and it is very similar to cellulose, in which the C-2 hydroxyl groups are replaced by acetamido residue. However owing to the presence of large percentage of nitrogen (6.89%), chitosan shows much commercial interest than synthetically substituted cellulose (1.2%). This provides chitosan chelating properties. Chitosan is typically obtained by extensive deacetylation of chitin, an abundant polysaccharide found in crustacean shells.



**Figure 1:** Structure of Chitosan along with its characteristics properties.

Chitin was first identified by Henri Braconnot, Director of botanical garden in Nancy, France in 1811 [1]. He used the name 'fungine' as a component of mushroom cell. Odier introduced the name 'chitin' in 1823. It was derived from the Greek word 'chiton' which means 'covering', 'tunic' or 'envelop'. The structure was solved by Albert Hofmann in 1929 [2]. It is present in many natural resources viz. in cell walls of fungi, in exoskeletons of arthropods mainly in crustaceans (e.g. crabs, lobster and shrimps), insects, radulae of molluscs and in beaks and internal shells of cephalopods (e.g. octopus and squid). Depending upon the source, chitin occurs in three different crystalline forms i. e.  $\alpha$ ,  $\beta$  and  $\gamma$ - form [3]. However  $\gamma$ - chitin is nothing but a variant of  $\alpha$ - chitin [4].

For industrial preparation, the major source for chitin is still the crustacean shells. The source is cheap as crab and shrimp shells can be obtained from the sea food industries as waste or by products. These shells contain 20- 40% of chitin along with proteins, calcium and small amount of pigments. But this type of supplies are limited to fishing industry site and available only in particular season. This problem can be solved by the waste mycelium obtained from industries of fungal products like antibiotics, enzyme or citric acid. It has been reported that annual world production of citric acid estimated at around 400,000 tons resulting into approx. 80,000 tons of waste mycelium of *Aspergillus niger* [5]. Moreover, this type of source contains lower percentage of inorganic materials in comparison to crustacean shells, due to which demineralization is not needed during processing.

Deacetylation process of synthesis of chitosan from chitin is generally done by hydrolysis under alkali condition at high temperature. There are four steps in the preparation method i. e. deproteinization, demineralization, decoloration and deacetylation [6]. Deproteinization involves overnight alkaline treatment with 3- 5% aqueous NaOH (w/v) solution at room temperature. The inorganic ingredients are then removed by treating with 3- 5% aqueous HCl (w/v) solution at room temperature for 5 h. After that, crude chitosan is obtained, which is then purified by precipitating the chitosan from its acetic acid solution by NaOH and washing with distilled water till