



# Arsenic Removal by $\alpha$ , $\beta$ and $\gamma$ Cyclodextrin Polymers from Contaminated Water

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**Abstract:**  $\alpha$ ,  $\beta$  and  $\gamma$  cyclodextrin polymers (CDP) has been successfully tested for arsenic (As) removal from As contaminated water. Removal of As (III) was studied through batch adsorption experiment at pH 3.6 to 9.0 with different time ranges from 0.5 to 24 h.  $\alpha$ ,  $\beta$  and  $\gamma$ -CDP worked well at pH 6.8 but highest As removal (86.9%) was achieved from  $\gamma$ -CDP at pH 5.0 from the  $100 \mu\text{g L}^{-1}$  As solution after 24 hours incubation. Considering the time,  $\alpha$ -CDP has reached the maximum 86% As removal occurred at pH 6.8 within 30 minutes. But at highly acidic (pH 3.6) and basic medium (pH 9.0), all of these CDP did not performed well for As adsorption.  $\alpha$  and  $\beta$ -CDP has the capability to reduce As is less than  $20 \mu\text{g L}^{-1}$  at pH 6.8 and only  $\gamma$ -CDP has capable to achieve this limit at pH 5.0, which below the limit of As standard in Bangladesh ( $50 \mu\text{g L}^{-1}$ ). So, according to pH of water, this adsorbent might be used in different regions as and where is suitable.

**Keywords:** Adsorption, Arsenic, Contamination, Cyclodextrin, pH, Water

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## 1. Introduction

Arsenic (As) is a metalloid which is very toxic pollutant that adversely affects the health of millions of people at very low level [1]. The occurrence of As in the environment is mainly from minerals and geogenic sources, human activities such as mining, burning of fossil fuels, medicine, electronics, use of As-containing chemicals in agriculture and as wood preservatives [2]. Arsenic is a known carcinogen and mutagen and is detrimental to the immune system [3]. So, As in water has generally been a global concern. 18% of the wells of Bangladesh having As more than  $50 \mu\text{g L}^{-1}$  causes worst As poisoning in the world [4]. Approximately 59 districts from the total 64 are currently affected at various extents of As in Bangladesh [5]. Hence, there is a pressing demand for more innovation to maintain As at the safe levels in water. There are a number of As removal methods, which include coagulation followed by precipitation, membrane separation, ion exchange, phytoremediation and adsorption, etc. [6–9]. Adsorption is the most demanding one which has

favorable economics, low installation and maintenance cost. Arsenic sorption is commonly studied in terms of sorption capacity, ionic strength, and the effects of pH etc. [10]. Cyclodextrins are useful molecular chelating agents. They possess a cage-like supramolecular structure (figure. 1), which is the same as the structures formed from cryptands, calixarenes, cyclophanes, spherands and crown ethers [11]. Removal of heavy metals by  $\alpha$ ,  $\beta$  and  $\gamma$  cyclodextrin polymers (CDP) have been used extensively in the last few years' modification with epichlorohydrin, nano zero valent iron, chitosan and others [12–14]. Sikder *et al.*, [13] found that epichlorohydrin cross-linked  $\alpha$ ,  $\beta$ , and  $\gamma$ - CDP can remove 99% cadmium ions from solution. But very few researches held on As removal using these polymers in home and abroad. So the current study has been designed using unmodified  $\alpha$ ,  $\beta$ , and  $\gamma$ - CDP for removal of most toxic and carcinogenic As from the water environment.

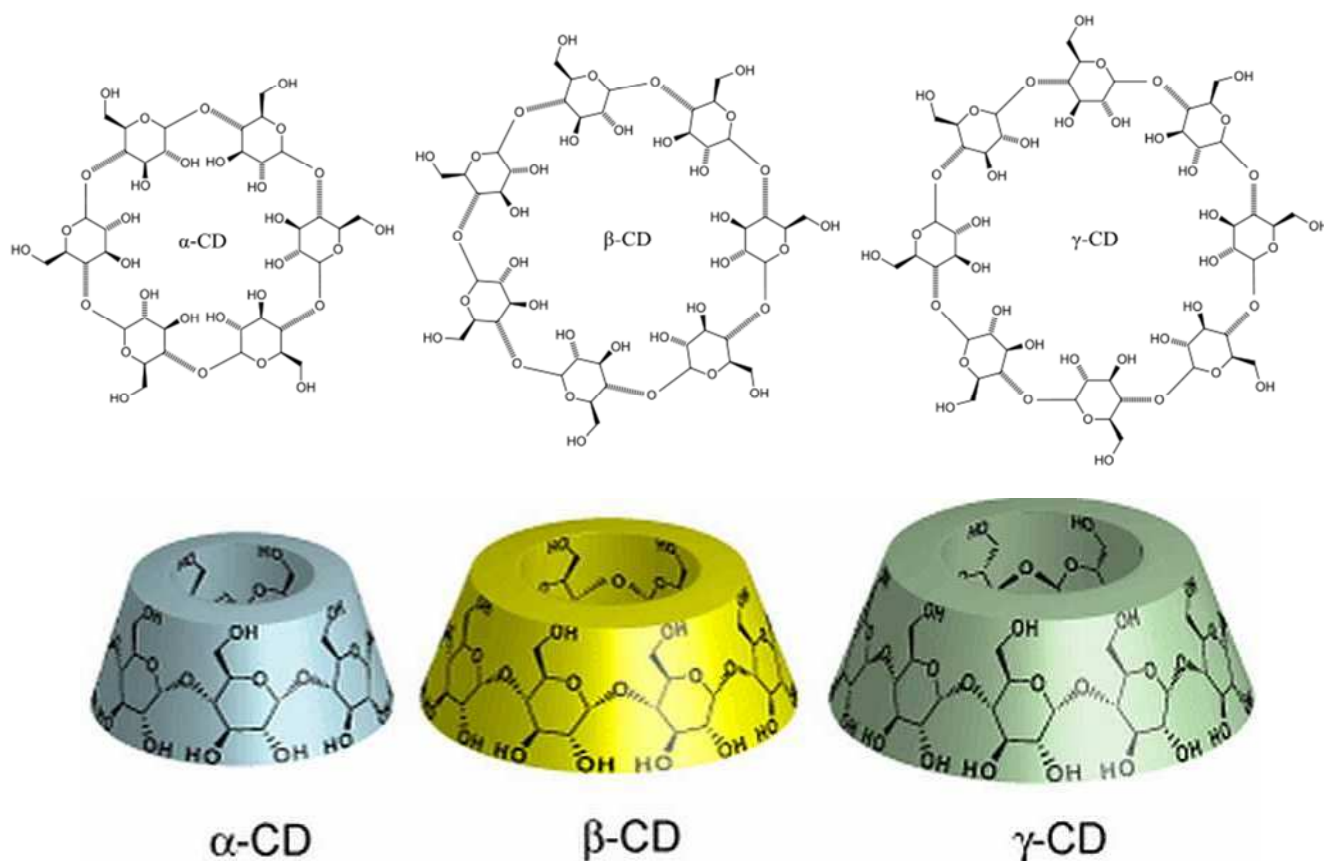


Figure 1. Cage-like structure of  $\alpha$ ,  $\beta$ , and  $\gamma$ -Cyclodextrin [15, 16].

## 2. Materials and Methods

$\alpha$ ,  $\beta$ , and  $\gamma$ -CDP are composed of six, seven and eight  $\alpha$ -(1,4) linked glycosyl units, respectively (figure. 1). The main properties of those cyclodextrins are given in Table 1 [11]. The adsorption of As (III) by  $\alpha$ ,  $\beta$ , and  $\gamma$ -CDP was examined using a batch equilibrium technique in aqueous solutions at pH 3.6, 5.0 6.8 and 9.0 at room temperature (25°C). In general, 30 mL of buffer solutions (100 mM phosphate buffer, pH 6.8 or 400 mM acetate buffer, pH 5.0 or 3.6) were prepared, and 100 mg of each adsorbent, along with 100  $\mu\text{g L}^{-1}$  of As (from sodium arsenite [ $\text{NaAsO}_2$ ]), were added into each buffer solution at different pH. The solution was then gently shaken with a constantly rotating stirrer from 0 to 24 hours (h) to attain equilibrium. The stirring period of 30 min to 24 h was chosen to determine the effect of contact time for the sorption of As (III). The adsorbents were removed by centrifugation at 2500 rpm for 5 min after the reaction. The obtained supernatant was filtered

by 0.45  $\mu\text{m}$  pore size millipore filters to remove the insoluble materials. The concentrations of As ions were measured using an atomic absorption spectrophotometer (AAS-Shimadzu AA 7000). All reagents were of analytical reagent-grade chemicals. Three replications were done throughout the study and statistical analysis was also done for different sorption data. The accumulated amount of metal ions onto CDP ( $q_t$ ) and percent (%) removal was calculated by the following numerical formula 1 and 2 [14]:

$$q_t = \frac{C_i - C}{W} \times V \quad (1)$$

$$\% \text{ Removal} = \frac{C_i - C}{C_i} \times 100 \quad (2)$$

where,  $q_t$  (mg/g) is the total adsorbed amount in time  $t$  (min),  $C_i$  and  $C$  are the initial and equilibrium concentrations (mg/L) of metal ion in the solution,  $V$  is the volume (mL), and  $W$  is the weight (g) of the adsorbent.

Table 1. Cyclodextrins properties.

Property	$\alpha$ -Cyclodextrin	$\beta$ -Cyclodextrin	$\gamma$ -Cyclodextrin
Number of glucopyranose units	6	7	8
Molecular weight (g/mol)	972	1135	1297
Solubility in water at 25°C (% w/v)	14.5	1.85	23.2
Outer diameter (Å)	14.6	15.4	17.5
Cavity diameter (Å)	4.7–5.3	6.0–6.5	7.5–8.3
Height of torus (Å)	7.9	7.9	7.9
Cavity volume (Å)	174	262	427

### 3. Results and Discussion

#### 3.1. Results

##### 3.1.1. Arsenic Adsorption Behavior of $\alpha$ , $\beta$ and $\gamma$ -CDPs at Acidic Medium

Arsenic adsorption efficiency (i.e., % removal) of  $\alpha$ ,  $\beta$  and  $\gamma$ -CDP at acidic medium (pH 3.6 and 5.0) were given in Table 2. At pH 5.0, As adsorption was gradually increased by  $\gamma$ -CDP and highest amount of As (86.9%) was adsorbed after 24 h shaken in a stirrer (Table 2). Arsenic adsorption was fluctuated at the same acidic medium in case of  $\alpha$ -CDP and  $\beta$ -CDP at different time intervals ranges from 42.5–58.9 and 63.3–76.2%, respectively. The lowest As adsorption occurred at acidic condition (pH 3.6) for all of the adsorbents ranges from 2.5–14.5, 7–17.5 and 6.5–19.9%, respectively, for  $\alpha$ ,  $\beta$  and  $\gamma$ -cyclodextrin polymers (Table 2). All of the CDPs adsorbed As at increasing trends with increasing stirring time. There were only 13, 23 and 41  $\mu\text{g L}^{-1}$  As present in the solution after treated with  $\gamma$ ,  $\beta$  and  $\alpha$ -cyclodextrin polymers, respectively at pH 5.0 (figure 2a).

##### 3.1.2. Arsenic Adsorption Efficiency of $\alpha$ , $\beta$ and $\gamma$ -CDPs at Neutral Water Environment

$\alpha$ ,  $\beta$  and  $\gamma$ -cyclodextrin polymers worked well at neutral water environment (pH 6.8) and maximum 86% of As adsorbed by  $\alpha$ -CDP within 30 minutes incubation from 100  $\mu\text{g L}^{-1}$  As concentration (Table 3). Though  $\beta$ -CDP adsorbed 83.2% As after 8 h stirring with the As tainted solution but  $\gamma$ -CDP removed almost similar amounts of As throughout the experimental period (Table 3). There were only 14  $\mu\text{g L}^{-1}$  As present in the solution from 100  $\mu\text{g L}^{-1}$  As (initial concentration) after treated with  $\alpha$ -CDP for 30 minutes and gradually desorbed with increasing time though  $\beta$  and  $\gamma$ -CDPs showed fluctuated behaviors for As adsorption at pH 6.8 (figure 2b).

##### 3.1.3. Arsenic Adsorption by $\alpha$ , $\beta$ and $\gamma$ -CDPs at Basic Medium

There were lowermost As adsorption occurred by  $\alpha$ ,  $\beta$  and

$\gamma$ -CDPs at basic water medium (pH 9.0) besides the acidic and neutral conditions. As removal rates were ranges from only 3.6–11.2, 8.5–14.4 and 5.1–13.1% for  $\alpha$ ,  $\beta$  and  $\gamma$ -CDPs, respectively at pH 9.0 (Table 3).

#### 3.2. Discussion

The present study showed the maximum removal efficiency of As (86.9%) happened by  $\gamma$ -CDP at pH 5.0. This is might be due to presence of high cavity volume of  $\gamma$ -CDP (Table 1) and have high chance of interaction with As. On the other hand, all of the CDP adsorbents performed very poor As adsorption at highly acidic (pH 3.6) or basic (pH 9.0) condition (Table 2 and 3). But average performance for As adsorption by  $\alpha$ ,  $\beta$  and  $\gamma$ -CDP was good at neutral condition (pH 6.8). So, the As adsorption behavior was totally dependent on pH and  $\alpha$ ,  $\beta$  and  $\gamma$ -CDP removed As in the order of pH 6.8 > 5.0 > 3.6. Chen *et al.* [17] and Ferna'ndez *et al.* [18] also pointed out that pH is the key controlling parameter in every adsorption process. The current findings is consistent with Sikder *et al.* [14] who found that the adsorption capacity of  $\beta$ -CDP increased with increasing the pH (3.0 to 9.0) in case of an initial concentration of 100 mg  $\text{L}^{-1}$   $\text{Cu}^{2+}$ . Ferna'ndez *et al.* [18] showed that desorption of solutes in basic medium was governed by diffusion, but at pH 1.2 the mechanism was more complex by using  $\beta$ -CDP. Sikder *et al.* [12] also experimented that these adsorbent have identical adsorption potential for both  $\text{Cd}^{2+}$  and  $\text{Cr}^{6+}$  and removal efficiency was 99% for cadmium and 40% for chromium at pH 6.5–7.5 and 3.6–6.5, respectively.

The uptake of As was fast at the early stages of the contact period and slow near the equilibrium at neutral condition (Table 3). This may be explained from the fact that repulsive forces between the solute molecules on the solid and bulk phases made it difficult to fill the surface sites with the solute [19]. The solution reached equilibrium at pH 6.8, and the sorption capacities significantly dropped at pH 3.6 (Table 2). It can be described as an insignificant competitive adsorption of hydrogen ions [20] with As.

**Table 2.** Arsenic adsorption efficiency (% removal) of  $\alpha$ ,  $\beta$  and  $\gamma$ -CDP at pH 3.6 and 5.0 from 100  $\mu\text{g L}^{-1}$  As containing solution.

Time (h)	% Removal of As (pH 3.6)			% Removal of As (pH 5.0)		
	$\alpha$ -CDP	$\beta$ -CDP	$\gamma$ -CDP	$\alpha$ -CDP	$\beta$ -CDP	$\gamma$ -CDP
0.5	2.5	7.0	6.5	58.9	63.5	45.1
1	7.1	9.7	9.2	56.3	70.8	46.3
2	9.4	10.9	14.3	52.3	64.3	50.0
4	14.7	15.1	17.3	42.5	63.3	72.4
8	12.3	16.3	19.9	46.2	73.9	82.4
24	14.5	17.5	19.3	58.2	76.2	86.9

**Table 3.** Arsenic adsorption efficiency (% removal) of  $\alpha$ ,  $\beta$  and  $\gamma$ -CDP at pH 6.8, and 9.0 from 100  $\mu\text{g L}^{-1}$  As containing solution.

Time (h)	% Removal of As (pH 6.8)			% Removal of As (pH 9.0)		
	$\alpha$ -CDP	$\beta$ -CDP	$\gamma$ -CDP	$\alpha$ -CDP	$\beta$ -CDP	$\gamma$ -CDP
0.5	86.0	74.9	74.9	3.6	8.5	5.1
1	79.2	72.2	73.6	4.1	10.6	7.5
2	74.9	72.0	72.3	4.9	12.1	10.2
4	73.8	71.5	74.0	8.3	12.9	10.7
8	78.6	83.2	75.7	9.0	14.4	12.8
24	75.3	74.3	70.3	11.2	13.1	13.1

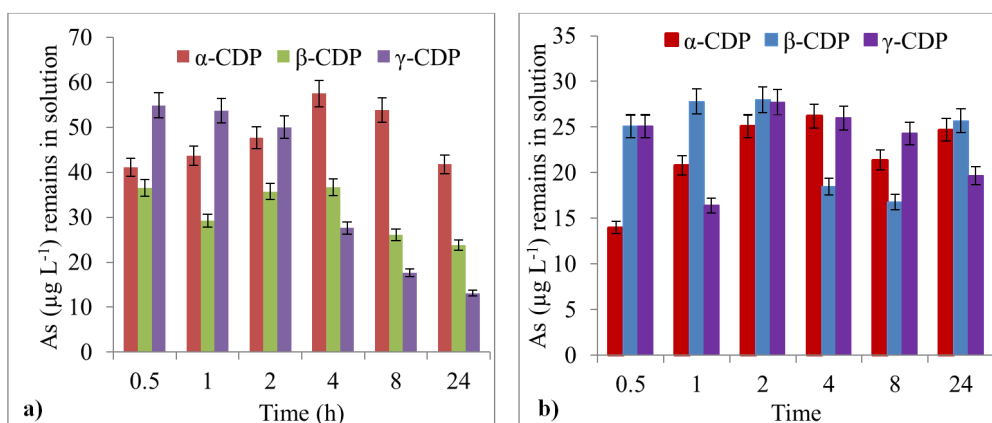


Figure 2. Arsenic ( $\mu\text{g L}^{-1}$ ) remains in solution after absorption of  $\alpha$ ,  $\beta$  and  $\gamma$ -CDP at pH 5.0 (a) and pH 6.8 (b) and initial As concentration was  $100 \mu\text{g L}^{-1}$ .

## 4. Conclusions

$\alpha$ ,  $\beta$  and  $\gamma$ -CDP worked well for As adsorption at pH 6.8 but not good at highly acidic or basic water environment. So, these adsorbent might be suitable to treat As in drinking water as pH of most of the underground and surface water are at neutral condition. Additionally due to negligible cytotoxic effects of CDPs, it will be an attractive adsorbent for environmental remediation. Detailed investigations are absolutely necessary to treat contaminated water, to understand the regeneration, and to reuse of these adsorbent in field level.

## References

- [1] Nriagu, E. (Ed.). 1994. Arsenic in the environment, Part 1. Cycling and characterization. Wiley, New York, USA.
- [2] Bissen M., Frimmel, F. H., 2003. Arsenic—a review. Part I: occurrence, toxicity, speciation, mobility. *Acta Hydrochimica et Hydrobiologica*, 31, 9–18.
- [3] NRC (National Research Council), 2001. Arsenic in drinking water. 2001 Update; National Academy Press: Washington, DC.
- [4] Chowdhury A. M., 2004. Arsenic crisis in Bangladesh *Sci Am.*, 291 (2): 86–91.
- [5] Karim M. M., 2000. Arsenic in groundwater and health problems in Bangladesh. *Water Resour* 34 (1): 304–310
- [6] Malik A. H., Khan Z. M., Mahmood Q., Nasreen S., Bhatti Z. A., 2009. Perspective of low cost arsenic remediation of drinking water in Pakistan and other countries. *J. Hazard. Mater.*, 168, 1–12.
- [7] Islam M. S., Ueno Y, Sikder M. T., Kurasaki M., 2013. Phytofiltration of Arsenic and Cadmium from the Water Environment Using *Micranthemum umbrosum* (J. F. Gmel) S. F. Blake as a Hyperaccumulator. *Int. J. Phytoremediation*, 15 (10): 1010–1021.
- [8] Islam M. S., Saito T., Kurasaki M., 2015. Phytofiltration of arsenic and cadmium using *Micranthemum umbrosum*: Phytotoxicity, uptake kinetics and mechanism. *Ecotoxicol. Environmen. Safety*, 112: 193–200.
- [9] Islam M. S., Sikder M. T., Kurasaki M., 2016. Potential of *Micranthemum umbrosum* for phytofiltration of organic arsenic species from oxic water environment. *Int J Environ. Sci. Technol.*, (in press) DOI: 10.1007/s13762-016-1142-9
- [10] Partey F., Norman D., Ndur S., Nartey R., 2008. Arsenic sorption onto laterite iron concretions: Temperature effect. *J. Colloid Interface Sci.*, 321 493–500.
- [11] Martin Del Valle E. M., 2004. Cyclodextrins and their uses: a review. *Process Biochem.* 39, 1033–1046.
- [12] Sikder M. T., Kikuchi T., Suzuki J., Kurasaki M., 2013. Removal of cadmium and chromium ions using modified  $\alpha$ ,  $\beta$ , and  $\gamma$ -cyclodextrin polymers. *Separation Sci. Technol.*, 48 (4): 587–597
- [13] Sikder M. T., Mihara Y., Islam M. S., Saito T., Tanaka S., Kurasaki M., 2014. Preparation and characterization of chitosan-carboxymethyl- $\beta$ -cyclodextrin entrapped nano zero-valent iron composite for Cu (II) and Cr (IV) removal from wastewater. *Chemical Eng. J.*, 236: 378–387.
- [14] Sikder M. T., Islam M. S., Kikuchi T., Suzuki J., Saito T., Kurasaki M., 2014. Removal of copper ions from water using epichlorohydrin cross-linked beta-cyclodextrin polymer. *Water Env. Res.*, 86 (4): 296–304.
- [15] Wikiwand, <http://www.wikiwand.com/en/Cyclodextrin> (accessed on 25/9/2016).
- [16] Ribeiro A. C. F., Valente A. J. M., Lobo V. M. M., 2008. Transport Properties of Cyclodextrins: Intermolecular Diffusion Coefficients. *J. Balkan Tribolog. Assoc.* 14 (3): 396–404.
- [17] Chen, H., Zhao, Y., Wang, A., 2007. Removal of Cu(II) from Aqueous Solution by Adsorption onto Acid-Activated Palygorskite. *J. Hazard. Mater.*, 149 (2), 346–354.
- [18] Ferná'ndez L., Machi'n R., Zornoza A., Ve'laz I., Marti'n C., Marti'nez-Oharriz M. C., 2011. Mechanism of sorption and release of a weak acid from b-cyclodextrin polymers. *J Incl Phenom Macrocycl Chem* 69: 411–415.
- [19] Shah B. A., Ajay V. S., Harendra D. P., 2011. Alkaline Hydrothermal Conversion of Agricultural Waste Bagasse Fly Ash into Zeolite: Utilisation in Dye Removal from Aqueous Solution. *Int. J. Environ. Waste Manage.* 7, 192–208.
- [20] Chen, H., Dai, G., Zhao, J., Zhong, A., Wu, J., Yan, H., 2010. Removal of Copper (II) Ions by a Biosorbent—*Cinnamomum camphora* Leaves Powder. *J. Hazard. Mater.*, 177 (1–3), 228–236.