

Adsorption of lead, ethylenediaminetetraacetic acid and lead-ethylenediaminetetraacetic acid complex onto granular activated carbon

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ABSTRACT: This study investigated simultaneous removal of lead and ethylenediaminetetraacetic acid from synthetic wastewater samples using granular activated carbon adsorption. Data from a 1×10^{-4} M lead-ethylenediaminetetraacetic acid adsorption isotherm study fitted well to Freundlich isotherm. Furthermore, for the pH-dependent 1×10^{-4} M lead-ethylenediaminetetraacetic acid study both lead and ethylenediaminetetraacetic acid adsorptions increased reaching values of 82 % and 93 % respectively at pH 5.8. However, a further increase in pH resulted in decreasing but near equal lead and ethylenediaminetetraacetic acid removals. Results for the 2×10^{-4} M lead-ethylenediaminetetraacetic acid system showed a behavior that was qualitatively similar to the 1×10^{-4} M lead-ethylenediaminetetraacetic acid findings. However, the 1×10^{-3} M lead-ethylenediaminetetraacetic acid study showed only a decreasing adsorption trend. An increasing-decreasing type lead/ethylenediaminetetraacetic acid adsorption behavior was also noted for the 1×10^{-4} M lead/ 2×10^{-4} M ethylenediaminetetraacetic acid system. Nevertheless for the 2×10^{-4} M lead/ 1×10^{-4} M ethylenediaminetetraacetic acid system, lead removal at increased pH was comparatively higher. Furthermore, results from a continuous column study completed at 1×10^{-4} M lead and 0.75×10^{-4} M ethylenediaminetetraacetic acid showed high saturation times both for lead and ethylenediaminetetraacetic acid. Results from the present work show that a notable removal of aqueous phase lead and ethylenediaminetetraacetic acid could be achieved using activated carbon adsorption. The details related to the effect of pH and pollutants' concentration on the overall adsorption efficiency, as reported in the present work, would be of much use for an effective carbon adsorption process design for the treatment of respective wastewaters.

Keyword: Activated carbon; Adsorption; Ethylenediaminetetraacetic acid; Lead

INTRODUCTION

Presence of heavy metals such as lead and other pollutants in industrial wastewater from sources such as smelting, electroplating, metal finishing, metallurgy, chemical manufacturing, lead-batteries recycling, etc., remains a matter of serious concern because of related health issues (Palacios *et al.*, 2002; Abdel-Ghani and Elchaghaby, 2007; Abdel-Ghani *et al.*, 2009; Gaur and Dhankhar, 2009; Igbinsola and Okoh, 2009; Malakootian *et al.*, 2009; Shah *et al.*, 2009; Zvinowanda *et al.*, 2009). Additionally presence of extensively used chelating agent ethylenediaminetetraacetic acid (EDTA) in varying aqueous environments and its subsequent effect onto increased metal species bioavailability including lead, is gaining attention as well (Swanson, 1984, 1985; Riley *et al.*, 1992; Vohra and Davis, 1998;

Bargar *et al.*, 1999; Kim and Ong, 1999; Palacios *et al.*, 2002; Oviedo and Rodríguez, 2003; Xia *et al.*, 2009). Though free aqueous phase lead species can be conveniently removed using traditional techniques such as metal precipitation, however, the presence of EDTA renders such processes either partially or completely ineffective because of a strong metal-chelate complex formation (i.e., lead-EDTA). Considering this, several approaches have been proposed to remove lead that is complexed to EDTA including use of anion exchange resins (Dudzinska and Clifford, 1991, 1992; Kołodzińska *et al.*, 2009), cation-exchange membrane (Juang *et al.*, 1999), integrated cation-exchange membrane with electrokinetic extraction (Amrate *et al.*, 2006), a specific chemical process that includes EDTA recycling (Kim and Ong, 1999; Gaur and Dhamkhar, 2009) and advanced oxidation (Jiraroj *et al.*, 2006; Vohra and Davis, 2000).

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Furthermore, though several investigations do report lead removal using different carbon based adsorption materials, including the traditional activated carbon (Taylor and Kuennen, 1994; Zhang *et al.*, 2005; Issabayeva *et al.*, 2006; Giraldo and Moreno-Piraján, 2008; Aghamohammadi *et al.*, 2007), activated carbon cloths (Kadirvelu *et al.*, 2000; Faur-Brasquet *et al.*, 2002), carbon aerogel (Goel *et al.*, 2005) and carbon nanotubes (Li *et al.*, 2005) but studies reporting activated carbon initiated removal of lead in the presence of EDTA are few (Abdulkarim and Abu Al-Rub, 2004; Awwad *et al.*, 2008; Krishnan *et al.*, 2003; Reed and Arunachalam, 1994; Reed *et al.*, 1994). Furthermore, most of these lead/EDTA activated carbon adsorption studies have focused only on lead removal with no detailed mention of EDTA's fate. For example, Abdulkarim and Abu Al-Rub, (2004) reported significant decrease in lead uptake by activated carbon in the presence of EDTA. Similarly, Reed and Arunachalam (1994) found that the amount of aqueous phase lead that was not adsorbed was comparable to its complexed form (i.e., lead-EDTA) whereas Reed *et al.* (1994) noted that metal complexed to EDTA was not adsorbed on to activated carbon from the aqueous waste streams. Krishnan *et al.* (2003) report that lead adsorption in the presence of chelating agent was enhanced in pH range 2-5 but reduced in pH range 6-8. However a detailed study exploring the effect of both lead and EDTA on each other's adsorption on to activated carbon, at different stoichiometric ratios and pH values, has not been investigated to the best of found knowledge. Nevertheless a better understanding of such a simultaneous adsorption behavior is indeed needed to design effective granular activated carbon (GAC) systems for the treatment of respective waste streams. Hence the present study's main objective was to investigate the simultaneous adsorption behavior of both lead and EDTA on to GAC under varying mixed conditions. The obtained findings will be helpful to design efficient GAC systems for the removal both lead and EDTA species from respective co-polluted aqueous streams. All research work was performed in the Laboratory of Civil Engineering Department, King Fahd University of Petroleum and Minerals, during 2008 and 2009.

MATERIALS AND METHODS

All chemicals used for the present study were of high purity reagent grade quality. The major chemicals included Pb (NO₃)₂ [BDH], Na₂C₁₀H₁₄O₈N₂·2H₂O or Na₂EDTA [Fisher], FiltraSorb 400 granular activated

carbon or GAC [FiltraSorb F400], HClO₄ [BAKER], NaOH [FISHER] and pH calibration standards [FISHER]. For the 1 × 10⁻⁴ M lead-EDTA adsorption isotherm experiment, a set of ten clean glass bottles was first arranged and 100 mL of respective synthetic wastewater sample was then transferred into each bottle. The respective synthetic wastewater samples for this and all other adsorption experiments as reported in this work were prepared using high purity water (CORNING mega pure™ system) and stock solutions of respective chemicals. After this GAC quantities between 0.1 to 10.0 g/L were transferred to the individual glass bottles. A blank sample bottle without GAC was also always included to account for any pollutant loss because of reasons other than adsorption. The respective bottles were then appropriately sealed and transferred to the shaker. Samples for pollutant analysis were then collected at appropriate time intervals, till the adsorption equilibrium was noted, i.e., the 3rd day. The respective data, i.e., pollutant concentration remaining at equilibrium Vs amount of GAC, was recorded and then subjected to further analysis. As respective results showed near-complete EDTA removal at GAC amount ≥ 2 g/L at 3rd day, a lower GAC amount i.e., 1 g/L was subsequently used for all other experiments to avoid the masking effect resulting from high GAC amount and thus correctly quantifying the pollutant amount-adsorbed. The 1 × 10⁻⁴ M Pb-EDTA adsorption equilibrium data was fitted both to the Langmuir and Freundlich adsorption isotherms. However, the Freundlich adsorption isotherm comparatively provided a better fit both for lead and EDTA adsorption data. The Freundlich adsorption model is represented as:

$$q_e = [X/M] = [k (C_e^{1/n})]$$

Where,

X= Amount of pollutant adsorbed at equilibrium = C_o - C_e (mg/L)

C_o = Pollutant's initial concentration at time zero (mg/L)

C_e = Pollutant's aqueous phase concentration at equilibrium (mg/L)

M= GAC mass used (g/L)

q_e = [X/M] = (Amount of pollutant adsorbed at equilibrium) / (GAC mass used)

k= Empirical constant

n= Slope inverse constant

A 1 × 10⁻⁴ M lead-EDTA adsorption kinetics study was also completed at GAC amount of 1 g/L. For the respective experiment, 1 g of GAC was added to 1 L



batch of 1×10^{-4} M lead-EDTA synthetic wastewater along with vigorous mixing using a magnetic stirrer setup. Samples were then collected at several time intervals and the concentrations of both lead and EDTA were determined to realize the respective adsorption kinetic trend. The pH-dependent lead and EDTA adsorption isotherm studies were also conducted at 1 g/L GAC and aforementioned equilibrium time (use of respective GAC amount and time has been justified above). The respective EDTA-only adsorption studies were completed at 10^{-4} M and 10^{-3} M concentrations. The pH for these experiments was varied approximately between 2 and 9. Also the respective lead-EDTA adsorption studies were completed at the following varying ratios: 1×10^{-4} M Pb-EDTA, 2×10^{-4} M Pb-EDTA, 1×10^{-3} M Pb-EDTA, 1×10^{-4} M Pb and 2×10^{-4} M EDTA, 1×10^{-4} M Pb and 3×10^{-4} M EDTA, 2×10^{-4} M Pb and 1×10^{-4} M EDTA, 3×10^{-4} M Pb and 1×10^{-4} M EDTA. The pH for these experiments was varied approx. between 2 and 12. For each pH-dependent adsorption experiment, a set of clean glass bottles with each bottle containing 100 mL of respective synthetic wastewater sample and GAC amount equivalent to 1 g/L, was first arranged. A blank sample (without GAC and pH adjustment) was also retrieved. The initial pH of each 100 mL sample was then adjusted to the desired value using an appropriate acid and/or base solution. The respective sample bottles were then appropriately sealed, transferred to a shaker and allowed to equilibrate as per the equilibrium adsorption isotherm study procedure that is mentioned above. Each sample was then tested for the final pH value and analyzed for lead and EDTA species. The continuous column adsorption saturation study was completed using a down flow setup with following conditions: 1×10^{-4} M lead, 0.75×10^{-4} M EDTA, GAC amount 4 g, GAC bed inner diameter 1 cm, GAC bed length 7 cm and flow rate 3.4 mL/min.

The pH analyses were completed using a pH meter setup (ORION; U.S.A.) that was also regularly calibrated using the pH calibration standards. The aqueous EDTA concentration was indirectly monitored employing a standard TOC analyzer system (TOC-VCSN, SHIMADZU; Japan). The TOC system was calibrated employing the manufacturer-supplied standards. The lead species concentration was determined using a standard atomic absorption spectrophotometer setup (GBC; Australia) that was also regularly calibrated employing appropriate lead standards.

The lead and EDTA aqueous speciation was completed using MINTEQA2/PRODEFA2 software

from U.S. EPA (Allison *et al.*, 1991). Some important aqueous phase reactions used for the said speciation are provided in Table 1 and the respective details are given in Tables 2-5.

RESULTS AND DISCUSSION

First a 1×10^{-4} M lead-EDTA adsorption isotherm experiment was completed to estimate an appropriate GAC amount and equilibrium contact time that would be suitable for all pH-dependent adsorption isotherm studies. As results from the respective adsorption isotherm experiment showed near-complete EDTA removal at GAC amount ≥ 2 g/L at 3rd day, a lower GAC amount i.e., 1 g/L was subsequently used for all other experiments to avoid the masking effect resulting from high GAC amount and thus correctly quantifying the pollutant amount-adsorbed. The respective adsorption isotherm data for lead and EDTA was also fitted to the Freundlich and Langmuir isotherms. However the

Table 1: Reactions considered for lead and EDTA aqueous speciation (T = 25 °C)

No.	Reactions	Log K
1	$\text{EDTA}^{4-} + 5 \text{H}^+ \leftrightarrow \text{H}_5\text{EDTA}^+$	24.035
2	$\text{EDTA}^{4-} + 4 \text{H}^+ \leftrightarrow \text{H}_4\text{EDTA}$	22.499
3	$\text{EDTA}^{4-} + 3 \text{H}^+ \leftrightarrow \text{H}_3\text{EDTA}^-$	20.375
4	$\text{EDTA}^{4-} + 2 \text{H}^+ \leftrightarrow \text{H}_2\text{EDTA}^{2-}$	17.363
5	$\text{EDTA}^{4-} + \text{H}^+ \leftrightarrow \text{HEDTA}^{3-}$	11.267
6	$\text{Pb}^{2+} + \text{EDTA}^{4-} \leftrightarrow \text{PbEDTA}^{2-}$	19.942
7	$\text{Pb}^{2+} + \text{H}^+ + \text{EDTA}^{4-} \leftrightarrow \text{PbHEDTA}^-$	23.035
8	$\text{Pb}^{2+} + 2 \text{H}^+ + \text{EDTA}^{4-} \leftrightarrow \text{PbH}_2\text{EDTA}$	24.899
9	$\text{Pb}^{2+} + 2 \text{H}_2\text{O} \leftrightarrow \text{Pb}(\text{OH})_2\text{s} + 2 \text{H}^+$	-8.150
10	$\text{Pb}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{PbOH}^+ + \text{H}^+$	- 7.562
11	$\text{Pb}^{2+} + 2 \text{H}_2\text{O} \leftrightarrow \text{Pb}(\text{OH})_2 + 2 \text{H}^+$	-17.095
12	$\text{Pb}^{2+} + 3 \text{H}_2\text{O} \leftrightarrow \text{Pb}(\text{OH})_3^- + 3 \text{H}^+$	-28.056
13	$2 \text{Pb}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{Pb}_2(\text{OH})^{3+} + \text{H}^+$	- 6.078
14	$3 \text{Pb}^{2+} + 4 \text{H}_2\text{O} \leftrightarrow \text{Pb}_3(\text{OH})_4^{2+} + 4 \text{H}^+$	-23.746
15	$\text{Pb}^{2+} + 4 \text{H}_2\text{O} \leftrightarrow \text{Pb}(\text{OH})_4^{2-} + 4 \text{H}^+$	-39.557

Table 2: Aqueous speciation results for 10^{-4} M EDTA

pH	2	4	6	8	10
HEDTA ³⁻	---	---	37.0	98.2	88.0
H ₂ EDTA ²⁻	3.3	88.3	62.9	1.60	---
H ₃ EDTA ⁻	34.6	11.0	---	---	---
H ₄ EDTA	46.2	---	---	---	---
H ₅ EDTA ⁺	15.8	---	---	---	---
EDTA ⁴⁻	---	---	---	---	12.0

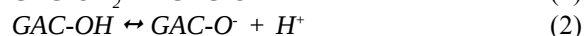
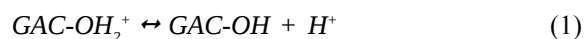
Table 3: Aqueous speciation results for 10^{-4} M Pb-EDTA

pH	2	4	6	8	10
Pb ²⁺	6.7	---	---	---	---
Pb-EDTAH ⁻	51.5	13.1	---	---	---
Pb-EDTAH ₂	37.7	---	---	---	---
Pb-EDTA ²⁻	4.1	86.8	99.8	100	100



Freundlich isotherm fitted better to the experimental adsorption findings. Freundlich isotherm for lead adsorption is thus given as $q_e = [X/M] = [k (C_e^{1/n})] = 3.0123 C_e^{1.1515}$ with R^2 of 0.9926. [Abdulkarim and Abu Al-Rub, \(2004\)](#) also reported that lead adsorption onto date-pits based activated carbon can be described by the Freundlich isotherm. Similarly the Freundlich adsorption isotherm for EDTA is given as $q_e = [X/M] = [k (C_e^{1/n})] = 9.5501 C_e^{0.4163}$ with R^2 of 0.9687. Furthermore, an adsorption kinetics study at 1×10^{-4} M lead-EDTA was also completed using GAC amount of 1 g/L. The respective results showed first order adsorption kinetics with 56 % lead and 59 % EDTA removal at time 140 min; however [Abdulkarim and Abu Al-Rub, \(2004\)](#) reported a pseudo second order kinetics for lead adsorption onto date-pits based activated carbon that could result from differences in the pore structure of the two activated carbon samples. This in conjunction with the adsorption isotherm results also supported use of above mentioned GAC amount (g/L) and equilibrium time (days), for all pH-dependent adsorption isotherm experiments, details of which are given below. [Figs. 1 and 2](#) provide the lead and EDTA adsorption results, respectively, for several equimolar Pb-EDTA systems. For the 1×10^{-4} M Pb-EDTA study an insignificant lead removal is noted at pH 2, but with an increase in pH both lead and EDTA adsorptions increase reaching values of ~82 % and ~93 %, respectively at pH 5.8. Similarly, [Krishnan et al. \(2003\)](#) also reported that lead adsorption in the presence of chelating agent was enhanced in pH range 2-5. However a further increase in pH results in decreasing but near equal lead and EDTA removals ([Figs. 1 and 2](#),

respectively). [Krishnan et al. \(2003\)](#) also reported that lead adsorption in the presence of chelating agent was reduced in pH range 6-8. Typically, the granular activated carbon surface is known to have several acidic functional groups including carboxylic, lactonic, hydroxyl, etc., which can be generalized by reaction 1 and reaction 2 as shown below ([Barton et al., 1997; Corapcioglu and Huang, 1987; Chen and Wu, 2004](#)):



Generally for lead-only systems a significant lead removal at higher pH will be expected because of a cationic type lead adsorption (i.e., $GAC-O-Pb^+$) and also metal precipitation ($Pb(OH)_2$). Nevertheless, as indicated by the respective aqueous speciation results for equimolar 1×10^{-4} M Pb-EDTA system ([Table 3](#)) that at higher pH most lead will remain complexed to the EDTA species and therefore the above mentioned free metal removal phenomena (i.e., cationic-adsorption and precipitation) that are specific to free lead species will not transpire. This is why we do not observe significant lead removal at higher pH values for the 1×10^{-4} M lead-EDTA system. Rather an anionic type adsorption behavior (i.e., $GAC-OH_2-EDTA-Pb^-$) is suggested to explain the decreasing and near equal lead and EDTA adsorption as noted at pH above 5.8 ([Fig. 1](#)). [Faur-Brasquet et al. \(2002\)](#) also suggested such a complex formation between the adsorbed benzoate and metals ions. [Kadirvelu et al. \(2000\)](#) who report copper, nickel and lead adsorption on to activated carbon cloths also suggested involvement of carboxylic groups at the surface of adsorbent. Hence

Table 4: Aqueous speciation results for Pb/EDTA systems (as % of total Pb/EDTA; Pb 10^{-4} M, EDTA $3 \times 10^{-4}/2 \times 10^{-4}$ M)

pH	2	4	6	8	10
EDTA $\rightarrow$	3×10^{-4}	2×10^{-4}	3×10^{-4}	2×10^{-4}	3×10^{-4}
Pb ²⁺	---	---	---	---	---
Pb-EDTAH ⁺	55.0/18.3*	54.9/27.4	12.7/4.2	12.9/6.4	---
Pb-EDTAH ₂	40.3/13.4	40.2/20.1	---	---	---
Pb-EDTA ²⁻	4.4/1.5	4.4/2.2	87.2/29.1	87.0/43.5	99.9/33.3
HEDTA ³⁻	---	---	---	---	---
H ₂ EDTA ²⁻	2.2	1.7	59.1	44.2	41.0
H ₃ EDTA ⁻	23.1	17.4	7.1	5.4	---
H ₄ EDTA	30.8	23.2	---	---	---
H ₅ EDTA ⁺	10.6	8.0	---	---	---
EDTA ⁴⁻	---	---	---	---	---

* % of total Pb concentration / % of total EDTA concentration



as with an increase in pH 1) the respective GAC cationic surface sites (i.e., GAC-OH_2^+) will decrease as indicated by reaction 1 and 2) the electrostatic conditions in the diffuse layer region of GAC particles will also become less conducive for the transport of dominant anionic Pb-EDTA^{2-} species (Table 3) to the GAC surface, a decrease in the respective anionic type adsorption would be expected (i.e., $\text{GAC-OH}_2\text{-EDTA-Pb}$) as noted in Fig. 1 and Fig. 2 as well. Reed and Arunachalam (1994) also found that the amount of aqueous phase lead that did not adsorb was comparable to its complexed form (i.e., lead-EDTA) whereas Reed *et al.* (1994) noted that metal complexed to EDTA was not adsorbed on to activated carbon from the aqueous waste streams. However as mentioned above the system pH seems to play a crucial role in this regard and hence should not be ignored.

To further clarify these trends, more equimolar lead-EDTA adsorption experiments were conducted with

pertinent lead and EDTA removal findings also summarized in Figs. 1 and 2, respectively. Results for the 2×10^{-4} M lead-EDTA system also show near equal lead and EDTA adsorption at pH above 4, a behavior that is qualitatively similar to the 1×10^{-4} M lead-EDTA findings and can be explained employing the previously suggested anionic type adsorption mechanism. Though different from the above mentioned findings the 1×10^{-3} M lead-EDTA study shows only a decreasing type adsorption trend, however for all three equimolar lead-EDTA systems obvious close lead and EDTA adsorption values after a specific pH that varies with the lead-EDTA initial concentration. Additionally, for all these systems comparatively higher EDTA adsorption (than lead) transpires at pH ~ 2 that indicates adsorption of both EDTA and lead-EDTA species. Abdulkarim and Abu Al-Rub, (2004) also reported significant decrease in lead uptake by activated carbon in the presence of EDTA.

Table 5: Aqueous speciation results for Pb/EDTA systems (as % of total Pb/EDTA; Pb $3 \times 10^{-4}/2 \times 10^{-4}$ M, EDTA 1×10^{-4} M)

pH	2	4	6	7	8
Pb $\rightarrow$	3×10^{-4}	2×10^{-4}	3×10^{-4}	2×10^{-4}	3×10^{-4}
Pb $^{2+}$	66.7	50.2	52.2	48.8	0.51
Pb-EDTAH $^+$	18.4/55.1*	27.5/54.9	4.2/12.7	6.4/12.8	---
Pb-EDTAH $_2$	13.4/40.3	20.1/40.2	---	---	---
Pb-EDTA $^{2-}$	1.5/4.4	2.2/4.4	29.1/87.2	43.5/87.1	33.33/99.9
PbOH $^+$	---	---	---	---	---
Pb(OH) $_{2s}$	---	---	---	---	---

* % of total Pb concentration / % of total EDTA concentration

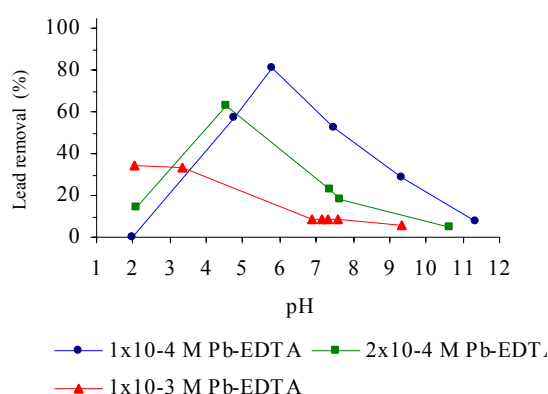


Fig. 1: Lead adsorption trends for the equimolar Pb-EDTA systems [1×10^{-4} M Pb-EDTA, 2×10^{-4} M Pb-EDTA, 1×10^{-3} M Pb-EDTA; GAC amount 1 g/L; equilibrium time up to 3 days]

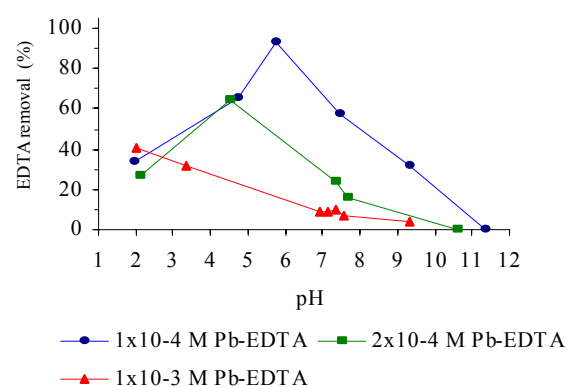


Fig. 2: EDTA adsorption trends for the equimolar Pb-EDTA systems [1×10^{-4} M Pb-EDTA, 2×10^{-4} M Pb-EDTA, 1×10^{-3} M Pb-EDTA; GAC amount 1 g/L; equilibrium time up to 3 days]



Furthermore, Fig. 1 also indicates that lead removal at pH ~ 2 tends to increase with an increase in the initial lead-EDTA concentration. In fact we note an increase both on *percent-basis* and *mass-basis*. Comparing the respective lead and EDTA adsorptions at pH ~ 2 for all equimolar systems also shows that the gap between the respective lead and EDTA adsorption values widens with a decrease in the lead-EDTA concentration. This tends to indicate that the portion of lead-EDTA complex species adsorption is higher at higher initial lead-EDTA amount. Adsorption of lead on to activated carbons produced from coconut and seed hull of palm tree has been investigated and also indicated increased lead adsorption on to respective activated carbon samples with an increase in lead concentration (Gueu *et al.*, 2007). To develop a better understanding of the above mentioned trends, some EDTA-only adsorption studies were conducted, as well. Fig. 3 provides the respective results. At 1×10^{-4} M EDTA, an increase followed by a decrease in EDTA adsorption with pH was noted. However, at 1×10^{-3} M EDTA, only an anionic type adsorption behavior transpires. Furthermore, though lower *percent-based* EDTA removal was observed at 1×10^{-3} M EDTA, however comparing the respective adsorption results on *mass-basis* leaves a different impression, e.g., at pH ~ 2 , nearly 0.23×10^{-3} and 0.035×10^{-3} M EDTA adsorptions transpire for the 1×10^{-3} and 1×10^{-4} M EDTA systems, respectively. For the latter system though up to 0.05×10^{-3} M adsorption does result at a higher pH value (Fig. 3), nevertheless it is still smaller than the above mentioned maximum for the 1×10^{-3} M EDTA system. The aforementioned GAC surface speciation (reactions 1 and 2) in addition to EDTA speciation as provided in Table 2 can provide some insight into the adsorption behavior as noted in Fig. 3. Table 2 shows the following dominant EDTA-species regions: H_4EDTA and H_3EDTA^- species at pH 2, H_2EDTA^{2-} at pH 4, H_2EDTA^{2-} and $HEDTA^{3-}$ at pH 6 and $HEDTA^{3-}$ at pH 8 and 10. Hence as the solution pH goes up the EDTA species would start to shift from a neutral to increasingly negatively charged species. Though initially such a change favors increased EDTA adsorption because of an anionic EDTA species and cationic GAC surface, however with a further increase in pH that is followed by an increase in EDTA negative charge and also a gradual loss of positively charged GAC surface sites, we do note a decrease in the EDTA adsorption as well (Fig. 3). Now comparing the 10^{-3} M

EDTA-only (Fig. 3) and 10^{-3} M lead-EDTA (Fig. 2) studies results, a significant increase is noted in EDTA removal at pH ~ 2 in the presence of lead, i.e., 25 % Vs 41 % respectively. Comparing the 10^{-4} M EDTA-only and 10^{-4} M lead-EDTA systems at pH 2 however shows insignificant difference if any in the EDTA removal, thus indicating a similar surface bonding mechanism; nevertheless, comparing the respective EDTA removal results in the pH 6 range, it is evident that higher EDTA adsorption transpires for the 1×10^{-4} M lead-EDTA system. Considering the EDTA-only and lead-EDTA aqueous speciation in the mentioned pH range (Tables 2 and 3, respectively), it can be suggested that a comparatively lower ionic charge on the $Pb-EDTA^{2-}$ species compared to $HEDTA^{3-}$ species will in turn require comparatively lesser amount of work to bring the former species close to the GAC surface, thus causing comparatively higher overall EDTA adsorption as noted in Fig. 2. The effect of EDTA concentration higher than lead on both lead and EDTA adsorption on to GAC was also investigated. Figs. 4 and 5 provide the respective details; results from the 1×10^{-4} M lead-EDTA system are included in these Figs. for a comparison purpose. Similar to the equimolar lead-EDTA studies, the EDTA adsorptions (for the EDTA > lead systems) at lower pH are also higher than the respective lead removals. This increase is both *percent* and *mass* based because of EDTA concentration being higher than lead. Nevertheless the respective lead removal results at lower pH also show an increase with an increase in EDTA concentration from 2×10^{-4} to 3×10^{-4} M, indicating that at higher EDTA amount the portion of lead-EDTA complex species adsorption is higher (Fig. 4). Amrate *et al.* (2006) who studied lead removal using integrated cation-exchange membrane with electrokinetic extraction also report enhanced removal of lead in the presence of EDTA. Similarly, Chen and Wang (2000) also report increased copper and zinc removal by activated carbon upon the addition of EDTA to the influent. Faur-Brasquet *et al.* (2002) who report copper and lead adsorption on to activated carbon cloths also indicate increased metal ion removal in the presence of benzoic acid because of a complex formation between the adsorbed benzoate and metals ions. Aroua *et al.* (2009) who studied the effect of polyethyleneimine (chelating polymer) impregnation of palm shell activated carbon on to lead adsorption also report higher metal uptake at higher chelating polymer concentration. Furthermore Zhu *et*



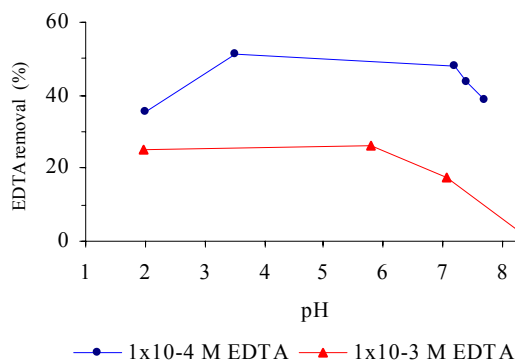


Fig. 3: Adsorption trends for EDTA-only systems [1×10^{-4} M EDTA, 1×10^{-3} M EDTA; GAC amount 1 g/L; equilibrium time up to 3 days]

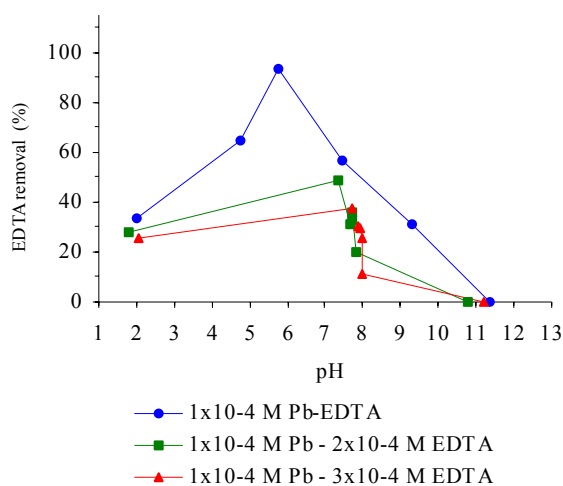


Fig. 5: EDTA adsorption trends for EDTA > Pb systems [1×10^{-4} M Pb-EDTA, 1×10^{-4} M Pb and 2×10^{-4} M EDTA, 1×10^{-4} M Pb and 3×10^{-4} M EDTA; GAC amount 1 g/L; equilibrium time up to 3 days]

al. (2009) also report that lead uptake by ethylenediamine modified activated carbon was comparatively faster with 62 % higher capacity as compared to the unmodified activated carbon. Sreejalekshmi *et al.* (2009) also reported higher lead uptake by sawdust activated carbon in the presence of citric acid. Additionally, comparing the respective EDTA removal results at lower pH shows that higher mass based removals result for the higher EDTA concentration system (Fig. 5). For the 1×10^{-4} M lead/ 2×10^{-4} M EDTA system, in addition to the above mentioned higher EDTA adsorption than lead at lower pH, an increasing-decreasing type lead and EDTA adsorption behavior was also noted. Both of these

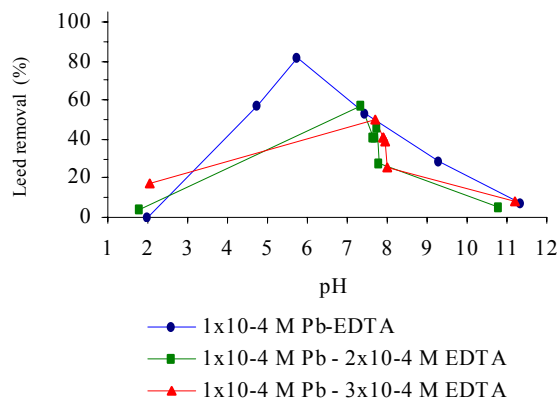


Fig. 4: Lead adsorption trends for EDTA > Pb systems [1×10^{-4} M Pb-EDTA, 1×10^{-4} M Pb and 2×10^{-4} M EDTA, 1×10^{-4} M Pb and 3×10^{-4} M EDTA; GAC amount 1 g/L; equilibrium time up to 3 days]

observations resemble to the previously mentioned equimolar 10^{-4} M lead-EDTA adsorption findings. However, a sudden drop in both lead and EDTA adsorption as noted in pH range 7~8 and shown in Figs. 4 and 5, respectively for 1×10^{-4} M lead/ 2×10^{-4} M EDTA system, is different from the 10^{-4} M lead-EDTA study. A similar cliff-type adsorption trend in pH range 7~8 is noted for 1×10^{-4} M lead/ 3×10^{-4} M EDTA system as well (Figs. 4 and 5). Though a competitive adsorption between the EDTA species and lead-EDTA complex (with EDTA > lead) may partially explain the noted trend however the question that remains is why both species show a similar trend? Table 4 that provides the respective aqueous speciation trends shows that between pH 6 and 8 a significant portion of uncomplexed-EDTA converts from H_2EDTA^{2-} to $HEDTA^{3-}$ species. However this change in EDTA speciation would only explain the aforementioned cliff-type trend for EDTA but not for lead as any significant change is not seen in the lead speciation between pH 6 and 8. Nevertheless, for the respective EDTA > lead systems a sizable lead and EDTA adsorption can still be achieved via a careful control of pH.

Adsorption experiments at lead concentration higher than EDTA were also conducted with Figs. 6 and 7 providing the respective findings; results from the 1×10^{-4} M lead-EDTA system are included in these Figs. for a comparison purpose. Comparing the EDTA removal results from Figs. 3 and 7 shows that generally the EDTA adsorption is higher for the latter system. It should also be noted that for the 2×10^{-4} M lead/ 1×10^{-4}



⁴ MEDTA system at pH ~ 2 insignificant lead but significant EDTA adsorption is noted. This trend is very similar to respective 1×10^{-4} M lead-EDTA and 1×10^{-4} lead/ 2×10^{-4} M EDTA trends. With an increase in lead to 3×10^{-4} M while keeping EDTA at 1×10^{-4} M, an insignificant lead removal was again noted at pH ~ 2 (Fig. 6). Comparing this to the 1×10^{-4} M lead/ 3×10^{-4} M EDTA findings (Fig. 4) it can be concluded that having EDTA higher than lead certainly increases latter's removal but vice versa does not yield a similar outcome. On the 2×10^{-4} M lead/ 1×10^{-4} M EDTA system, though an increasing-decreasing type adsorption trend is noted for the EDTA species (that is qualitatively similar to the previously mentioned equimolar lead-EDTA and EDTA > lead systems findings) however the overall decrease in lead removal at increased pH is not as significant compared to the other two lead/EDTA systems (Figs. 1 and 4). The most obvious reasoning is that though a small decrease in lead concentration does result at higher pH because of reduced lead-EDTA adsorption, but still the remaining free metal species (i.e., 1×10^{-4} M lead) will be partially removed both because of 1) precipitation ($\text{Pb}(\text{OH})_2$) and 2) adsorption (GAC-O-Pb^+). Abdel-Ghani *et al.* (2007) also report increased lead adsorption on to some low cost adsorbents, with an increase in pH. For example, for the 1×10^{-4} M lead-EDTA system at pH 7.5 approximately 53 % lead removal is noted that is equal to 5.3×10^{-5} M, whereas for the 2×10^{-4} M lead/ 1×10^{-4} M EDTA system we note 60 % lead removal that is equal to 1.2×10^{-4} M. Hence nearly 0.67×10^{-4} M additional lead removal that transpires for the latter system can partially be explained because of precipitation. Table 5

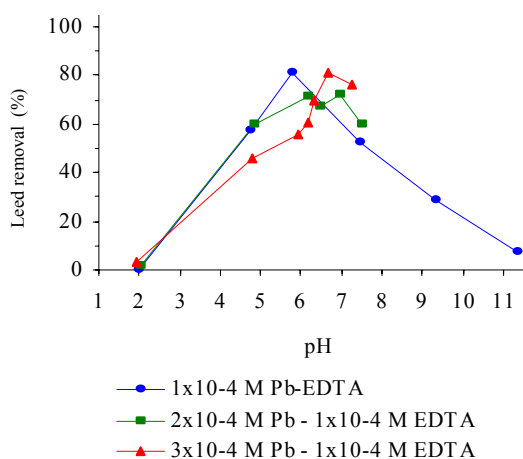


Fig. 6: Lead adsorption trends for Pb > EDTA systems [1×10^{-4} M Pb-EDTA, 2×10^{-4} M Pb and 1×10^{-4} M EDTA, 3×10^{-4} M Pb and 1×10^{-4} M EDTA; GAC amount 1 g/L; equilibrium time up to 3 days]

that provides the aqueous speciation trends for the lead > EDTA systems also shows nearly 50 % (1×10^{-4} M) lead precipitation for the 2×10^{-4} M lead/ 1×10^{-4} M EDTA system between pH 7-8. Overall, significant lead and EDTA removal can be achieved for the lead > EDTA systems as indicated by trends in Figs. 6 and 7.

Eventually a continuous column adsorption saturation study was also completed at 1×10^{-4} M lead and 0.75×10^{-4} M EDTA. The respective results as provided in Fig. 8 show high saturation times both for lead and EDTA. Hence placement of sufficient carbon adsorption columns in series would maximize the usage of

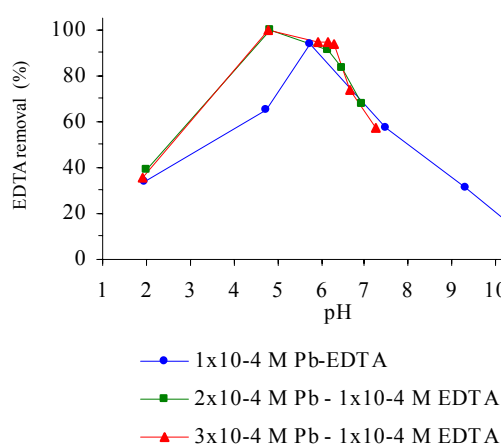


Fig. 7: EDTA adsorption trends for Pb < EDTA systems [1×10^{-4} M Pb-EDTA, 2×10^{-4} M Pb and 1×10^{-4} M EDTA, 3×10^{-4} M Pb and 1×10^{-4} M EDTA; GAC amount 1 g/L; equilibrium time up to 3 days]

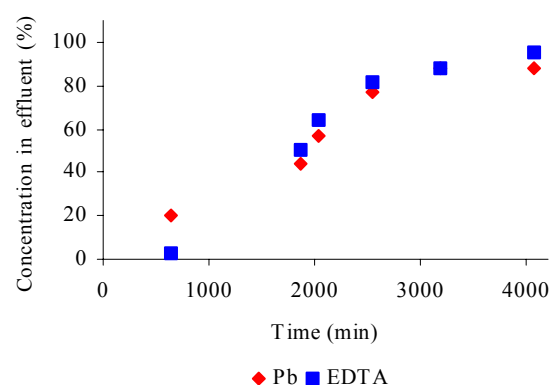


Fig. 8: Lead and EDTA adsorption trends from a continuous column adsorption saturation study [1×10^{-4} M lead and 0.75×10^{-4} M EDTA; GAC amount 4 g; GAC bed inner diameter 1 cm; GAC bed length 7 cm; Flow rate 3.4 mL/min]



respective GAC (in terms of pollutant removed from the aqueous phase per unit weight of GAC) while meeting effluent requirements for lead and EDTA.

CONCLUSION

The present study investigated simultaneous adsorption of lead and EDTA onto granular activated carbon under varying conditions. Data from a 1×10^{-4} M lead-EDTA adsorption isotherm study was noted to fit well to Freundlich adsorption isotherm both for lead and EDTA. The Freundlich adsorption isotherm for lead was noted to be $q_e = [X/M] = [k (C_e^{1/n})] = 3.0123 C_e^{1.1515}$ with R^2 of 0.9926. Similarly, the Freundlich adsorption isotherm for EDTA was noted to be $q_e = [X/M] = [k (C_e^{1/n})] = 9.5501 C_e^{0.4163}$ with R^2 of 0.9687. Furthermore an adsorption kinetics study at 1×10^{-4} M lead-EDTA and GAC amount of 1 g/L showed first order adsorption kinetics with 56 % lead and 59 % EDTA removal at time 140 min. For equimolar 1×10^{-4} M lead-EDTA pH-dependent adsorption study approximately 82 % and 93 % lead and EDTA adsorptions respectively were noted at pH 5.8. However, a further increase in pH resulted in decreasing but near equal lead and EDTA removals. Results for the 2×10^{-4} M lead-EDTA system showed a qualitatively similar behavior whereas the 1×10^{-3} M lead-EDTA study showed only a decreasing type adsorption trend with pH. Comparing the 10^{-3} M EDTA-only and 10^{-3} M lead-EDTA studies showed a significant increase in EDTA removal at pH ~ 2 in the presence of lead. An increasing-decreasing type lead/EDTA adsorption behavior was also noted for the 1×10^{-4} M lead/ 2×10^{-4} M EDTA and 1×10^{-4} M lead/ 3×10^{-4} M EDTA systems. For the 2×10^{-4} M lead/ 1×10^{-4} M EDTA system, though an increasing-decreasing type adsorption trend was noted for the EDTA species however the overall decrease in lead removal at increased pH was not as significant as compared to the other two lead/EDTA systems. In general, a sizable lead and EDTA removal was achieved for all studied lead-EDTA pH dependent adsorption isotherm studies. Furthermore, a continuous column adsorption saturation study was also completed at 1×10^{-4} M lead and 0.75×10^{-4} M EDTA. The respective results showed high saturation times both for lead and EDTA indicating that placement of carbon adsorption columns in series would maximize the usage of respective GAC while meeting effluent requirements for lead and EDTA.

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