Low-Cost Carbon-Based Materials for Selective Removal of As(III) from Waste Waters

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ABSTRACT

A low-cost carbon-based material from pyrolytic carbon from recycled tyres (PCrt) has been developed for selective removal of lead or arsenite from waste waters. The PCrt material has been characterized with X-Ray Fluorescence, XRD, And FTIR spectroscopies. Arsenite and Pb uptake was studied at the ppb level by Cathodic and Anodic Stripping Voltammetry (CSV). Adsorption isotherms, kinetic and pH-edge data show that PCrt can bind arsenite at a wide pH range from 4 to 9. More specifically, PCrt after mild treatment with HNO_3 and calcination at 500°C can adsorb 8.8 mg of As (III) and 27,7 mg Pb(II) per gram of material. PCrt can selectively uptake arsenite vs. lead when the two metals are present simultaneously in the aqueous solution. Importantly, when Pb is first adsorbed by PCrt, this forms PbS sites that act as additional arsenite binding sites. This is a unique example where one toxic metal, Pb(II), acts synergistically for adsorption of another toxic, As(III) on the appropriate matrix.

Keywords: low-cost, pyrolytic carbon, selective, Pb(II), As(III), metal uptake

INTRODUCTION

Disposal of waste tyres has become a serious source of environmental pollution [1]. More of 330 million waste tyres are discarded each year [2]. Tyre rubbers consist mainly of synthetic and natural rubber, tyre rubber additives i.e. like carbon black, sulphur and zinc oxide [1, 3]. A feasible solution for an environmentally friendly treatment of waste tyres would be to recycle them to valuable products that can be used in various applications.

Pyrolysis is an established process, which involves thermal decomposition of waste tyres at high temperatures (450-900 °C) under oxygen-free atmosphere, transforming them into useful products [3-4]. Tyre rubber pyrolysis results in the production of an oil- and a gas- fraction, plus the carbonized solid residue, the Pyrolytic Char from recycled tyres (PCrt) [3]. Pyrolytic oil and gas can be used as a source of chemical feedstock or a fuel with high calorific value for in-process, on-site or off-side applications [5]. PCrt may be used as carbon black filler for the tyre and printing-ink industries or as a precursor to manufacture low-cost adsorbent materials because of its high carbon content [4].

Arsenic may present in two main redox states Arsenites (As $^{3+}$) and Arsenate (As $^{5+}$) in natural waters, changes in solubility and mobility therefore occur as a function of redox potential and pH conditions in the environment and also are common in natural waters.[6] The World Health Organization (WHO) provisional guideline of 10 ppb (0.01 mg L^{-1}) have be adopted as the drinking water standard also U.S. Environmental Protection Agency (U.S EPA) required public drinking water to 10 ppb (0.01 mg L^{-1}). Arsenic is mobilized by natural weathering reactions, biological activity, geochemical reactions, volcanic emissions and other anthropogenic activities. Most environmental arsenic problems are the result of mobilization under natural conditions. However, mining activities, combustion of fossil fuels, use of arsenic pesticides, herbicides, and crop desiccants and use of arsenic additives to livestock feed create additional impacts.[7]. Pb (II) dominates in acid while $PbOH^+$ predominates in most environment pHs. The drinking water guideline recommended by WHO is 0.05 mg L^{-1}. The maximum allowable lead in drinking water has been set at a concentration of 15 ppb by U.S. EPA. Lead is widely used in processing industries such as electroplating, paint and dyes, explosive manufacturing, and lead batteries and in lakes and streams by acid. Also leads emitted into the atmosphere by combustion of fossil fuels and the smelting of sulfide ores.[8]. Also historic mining and industrial have produced numerous sites containing high concentration levels of As, Pb, Zn and Cd. Remediation of the contaminated sites is necessary because unthreaded effluent may have an adverse impact for the protection of the environment and public health.[9]. In the present study, priority heavy metal Pb (II) and metalloid As (III) were used as representative adsorbates which were removed from aqueous solutions by PCrt. Batch experiments were conducted to investigated kinetics and isotherms characteristic of arsenite and lead adsorption onto Pc. Finally we test the competitive adsorption of arsenite and lead onto PCrt.

METHODOLOGY

Preparation of tyre rubber pyrolytic char: The char was derived from the pyrolysis of used rubber tyres at 450°C in oxygen-free atmosphere under vacuum for 4 hours. For the purification of as-received pyrolytic tyre char 2 gr of as received pyrolytic char suspended onto 2M HNO_3 for 2 hr . At the end of 2 hr suspension the material was collect and washed with deionized water for 6 times to final pH =7 and solid was finally dried at room temperature. After room temperature drying, solid was calcinated at 500 °C under inert condition (N_2) for 1 hr.

Chemicals: Sodium meta-arsenite $NaAsO_2$ was obtained from Sigma-Aldrich, while HCl, NaOH and KNO_3. $Cu(NO_3)\cdot 3H_2O$, $Pb(NO_3)_2$ and HNO_3 were obtain from Merck. 2-(N-Morpholino) ethanesulfonic acid hydrate, 4-Morpholineethanesulfonic acid MES hydrate & 4-(2-Hydroxyethyl) piperazine-1-ethanesulfonic acid, N-(2-Hydroxyethyl) piperazine-N-(2-ethanesulfonic acid) HEPES used for pH buffering were obtained from Sigma-Aldrich. Ultrapure water was produced by a Milli-Q Academic system, Millipore. All solutions were prepared with analytical grade chemicals and ultrapure Milli-Q water with a conductivity of 18.2 $\mu S\ cm^{-1}$

Characterization of pyrolytic chars: The X-Ray powder Diffraction (XRD) patterns for the as received PCrt, char purified and $char_{500}$, were recorded by a Brüker Advance D8 instrument using Cu K_a radiation (λ = 1.5418 Å) in the 2θ range from 10° to $80^{\circ}$with a 2θ resolution of 0.02°. N_2 adsorption–desorption isotherms were obtained at 77 K using a Tristar Micrometrics Instruments and the specific surface area (S_{BET}) of the $Char_{500}$ was calculated using the Brünauer–Emmett–Teller (BET) method based on the adsorption data. The carbon, hydrogen, nitrogen and oxygen (CHNO) contents of the tyre - derived chars were determined using an elemental analyzer Perkin Elmer (2400 Series II) at 1.100 ^{o}C. Oxygen content was determined by mass difference. The ash content was determined by calcination of 1g of chars in a muffle furnace (800 ^{o}C, 4 h).

Analytical determination of As (III) and Pb (II): The concentration of metals in the aqueous solution was determined by Cathodic Stripping Voltammetry (CSV) using a Trace Master5-MD150 polarograph by Radiometer Analytica. An Ag/AgCl electrode with a double liquid junction was used as the reference electrode whilst a Pt electrode. Importantly, samples were not purged with N_2 gas in order to avoid loss of As(III) [10]. During the stripping step the solution was stirred at 525 rpm. For the measurements we used aliquots of 8.3 mL adjusted at pH 0.5 by HCl [11]. Then 8 ppm Cu^{2+} was added and the pH was readjusted if necessary to pH 0.5. In the following, As (III) was determined by square-wave CSV (SW-CSV) with accumulation potential E = -400 mV and accumulation time 60 s. As (III) was quantified by its signal at $E_{1/2}$ = -670 mV. The concentrations of Lead in the aqueous phase were determined by Anodic Stripping Voltammetry (ASV) .[12]

As (III) and Pb (II) sorption experiments: As (III) and Pb (II) uptake from aqueous solutions were studied in batch experiments. Adsorption kinetics of arsenite and lead onto PCrt, were screened for contact times ranging between 0 and 240 min at pH 7, $NaAsO_2$ = 3 mg L^{-1}, PCrt = 0.1 g L^{-1} and $Pb(NO)_3$=3 mg L^{-1} , PCrt= 0.1 g L^{-1} . In each experiment the supernatant was collected by centrifugation and then analyzed for arsenite and lead. Adsorption isotherms were recorded at pH 7 in the presence of $NaAsO_2$ and $Pb(NO)_3$ at concentrations between 10 to 50 mg gr $^{-1}$ and 10 to 60 mg gr $^{-1}$ respectively for 0.1 g L^{-1} of PCrt suspended in 50 mL buffer solution in polypropylene tubes.

Comparative adsorption were recorded at pH 7 in presence $NaAsO_2$ = 3 mg L^{-1} $Pb(NO)_3$=3 mg L^{-1} , PCrt = 0.1 g L^{-1} in 50 mL buffer for 120 min equilibrium time. Control experiments (without PCrt) showed no loss of initial As (III). The initial pH values of buffers were adjusted using small volumes of 2.5 M HCl or 2.5 M NaOH to the desired value. After metals addition, the suspension was allowed to equilibrate for 120 min at room temperature (25 ˚C ± 0.2) for arsenite and lead respectively while agitated in a magnetic stirrer. After completion of the equilibration, the suspension was centrifuged at 5000 rpm for 10 min the As (III) concentration of the supernatant solution was analyzed by Cathodic Stripping Voltammetry (CSV) and the Pb (II) concentration of the supernatant solution was analyzed by Square Wave Anodic Stripping Voltammetry (SW-ASV) as described above.

RESULTS AND DISCUSSION

Characterization of the materials: The X-Ray Diffraction patterns of as receive PCrt, acid- treated PCrt, PCrt calcinated at 500 °C after acid- treatment, are presented in Figure 1. The XRD patterns show a typical peak of graphitic carbon 25° [13](Fig. 1). The peaks at 27°, 47° and 57° are characteristic of zinc sulfide (ZnS) [14]. On the other hand, the peak at 43° relates to iron carbides (Fe_3C).[14-15]

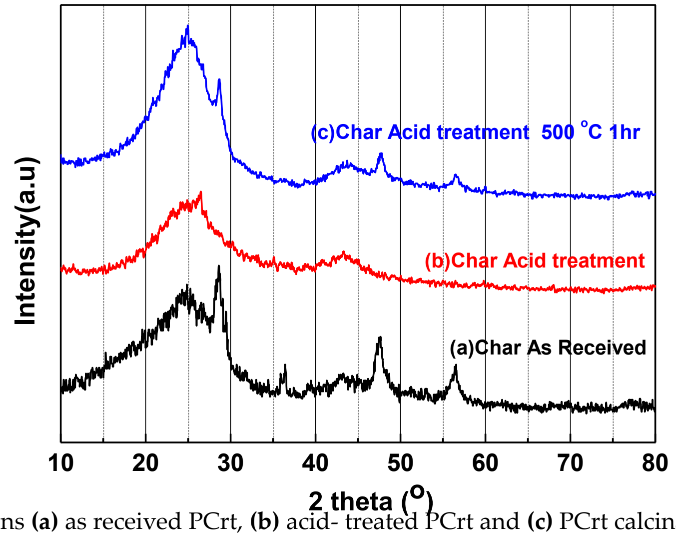

Figure 1 XRDs patterns **(a)** as received PCrt, **(b)** acid- treated PCrt and **(c)** PCrt calcinated at 500 °C after acid- treatment.

The IR spectra of the materials are shown in Fig. 2. The absorption peaks at 3400, 2380, 1600 cm^{-1} can be assigned to the =C-H, C-H and C=C stretching modes and shown in all materials [16]. The band at 1060 cm^{-1} is due to S=O stretching and appears in all materials [16]. The weak peak at 500 cm^{-1} indicates the existence S-S bonds and appears to as received char and char calcinated at 500 °C for 1 hour [16]. The band at 722 cm^{-1} is due to ZnS and shows up only at char calcinated at 500 °C for 1 hour[17]

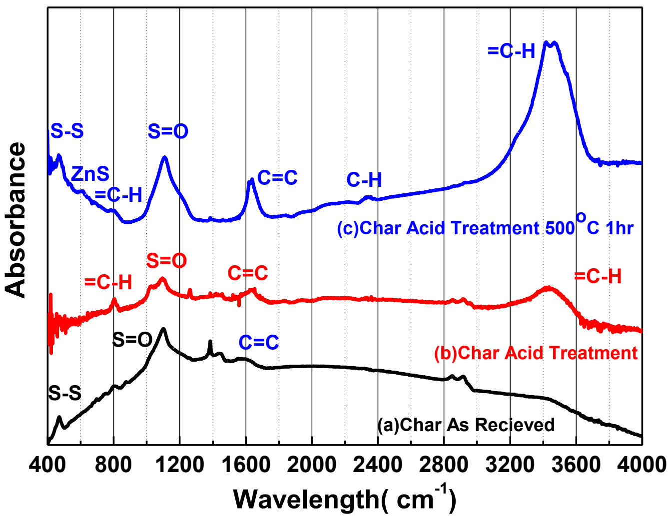

Figure 2 FTIR patterns **(a)** as received PCrt, **(b)** acid- treated PCrt and **(c)** PCrt calcinated at 500 °C after acid- treatment.

Arsenite and Lead adsorption: Adsorption kinetic data of arsenite onto PCrt in contact times ranging between 0 and 240 min (4 h). Arsenite uptake is accomplished after 120 min (data not shown). The maximum As (III) uptake capacity for the PCrt was evaluated at room temperature by fitting the experimental data with the Langmuir adsorption isotherm

$$q_e = \frac{q_m * K * C_e}{1 + K * C_e} \qquad \text{(Eq.1)}$$

Where q_e is the surface concentration or the surface density in mg g^{-1}. C_e has units of either mol L^{-1} or mg L^{-1}. The maximum q_m adsorption derived from the fit, listed in Table 1 is found 8,8 mg gr^{-1} of As(III) per gram at pH=7 (Fig. 3a).

Adsorption kinetic data of lead onto PCrt in contact times ranging between 0 and 240 min (4 h). Lead uptake is accomplished in the first 120 min (data not shown). The maximum Pb(II) uptake capacity for the PCrt was evaluated at room temperature by fitting the experimental data (see Table 1) with the Langmuir adsorption isotherm with equation 1 as describe above and was found 27.7 mg gr^{-1} of Pb(II) per gram at pH=7 (Fig. 3b)

Table 1 Langmuir Isotherm Constants at pH 7.0

Materials	Adsorbed	q_m (mg gr^{-1})	K_l	R^2
PCrt _acid_500^{0}C	As(III)	8,8	0,084	0,991
PCrt _acid_500^{0}C	Pb(II)	27,7	0,087	0,979
[[PCrt _acid_500^{0}C]- Pb(II)]	As(III)	31	0,69	0,989

For comparison, adsorption experiments with as received char and wash and char calcinated at 500 °C without acid-treatment show 1.8 mg gr^{-1} of arsenite at pH 7. This demonstrates that acid-treatment before the calcination step is essential for optimizing the PCrt surface for metal uptake.

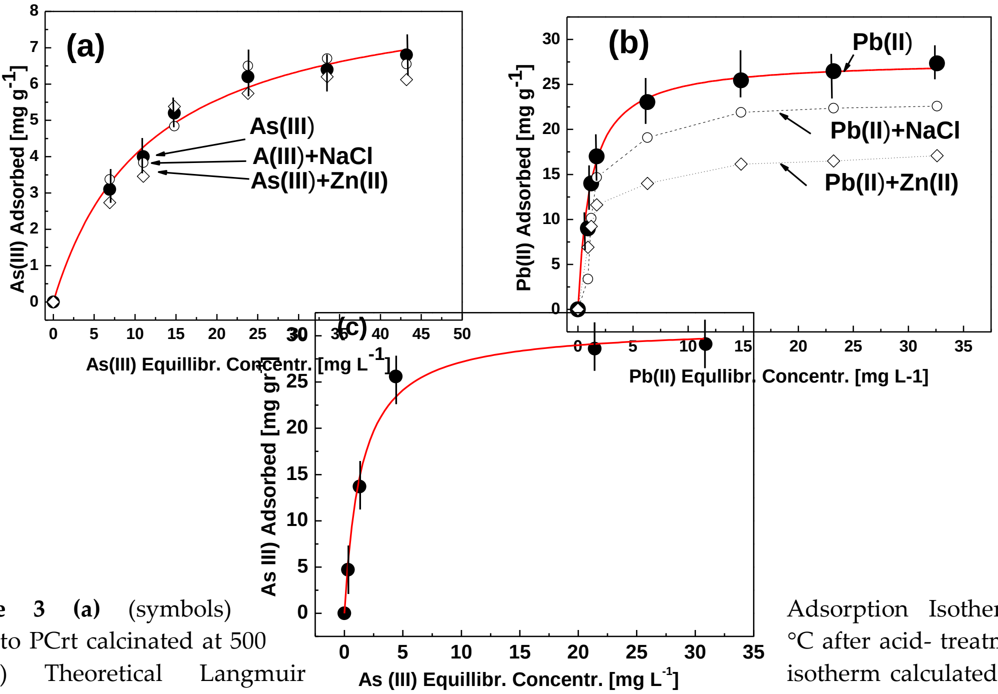

Figure 3 **(a)** (symbols) Adsorption Isotherm of As (III) onto PCrt calcinated at 500 °C after acid- treatment. (red line) Theoretical Langmuir isotherm calculated using the parameters listed in Table 1. Open symbls: As(III) uptake isotherms in the presence of 100mM NaCl, or 3mg/L Zn(II). **(b)** (symbols) Adsorption Isotherm of Pb (II) onto PCrt calcinated at 500 °C after acid- treatment. Open symbls: Pb(II) uptake isotherms in the presence of 100mM NaCl, or 3mg/L Zn(II) (red line) Theoretical Langmuir isotherm calculated using the parameters listed in Table 1, **(c)** (symbols) Adsorption Isotherm of As (III) onto [[PCrt _acid_500^{0}C]-Pb(II)]. (red line) Theoretical Langmuir isotherm calculated using the parameters listed in Table 1.

Selectivity of As(III) Uptake:

(a) Pb(II) enhances As(III) Uptake: Comparative adsorption Pb (II) and As (III) onto PCrt reveal an interesting phenomenon. When simultaneously present in the initial solution, 3 mg L^{-1} $NaAsO_2$ and 3 mg L^{-1} $Pb(NO)_3$ with 0.1 g L^{-1} PCrt, the adsorption of arsenite is strongly increased to 22.5 mg gr^{-1} and adsorption of lead show decrease to 16.9 mg gr^{-1}. This indicates that Pb (II) results in an –at first glance unexpected- enhancement of As (III) uptake. To further prove this we have performed an adsorption experiment where [i] first 27,7 mg gr^{-1} Pb (II) was allowed to be adsorbed on PCrt

_acid_500^{0}C for 2 hours, [ii] then As(III) adsorption was studied on the so-formed [[PCrt _acid_500^{0}C]- Pb(II)] material. The data reveal a significant boost of the As (III) uptake to 31 mg gr^{-1} after 30 min equilibrium time (Fig. 3c).This clearly demonstrates a novel phenomenon that can be explained if we consider the formation of PbS sites i.e. from adsorbed Pb (II) ions on S-sites that exist in the PCrt structure. In crystalline form, PbS has strong affinity for As (III) Bostick et al. [18] and Piquette et al. [19] that show arsenites adsorption onto PbS (galena). In the present case we consider that PbS sites are formed during lead adsorption, and these act as additional As (III) adsorption sites.

(b) Effect of electrolyte ions Na$^+$, Cl$^-$: Common electrolyte ions i.e. such as Na$^+$ and Cl$^-$ have different effect on As(III) vs. Pb(II) uptake (compare open circles in Fig 3(a) vs. 3(b)). In the case of As(III) electrolyte ions at 100mM concentration have practically no effect, while Pb(II) uptake is inhbited by ~15%. This phenomenon can be explained as follows: at any pH<9 As(III) is in its neutral form H_3AsO_3 [6, 18] thus it is adsorbed preferentially on neutral sites of the adsorbing materials [6, 12,13b 18]. In contrast, Pb(II) cations are preferentially uptaken by anionic surface sites [12, 13b]. Thus electrolyte ions –which act via electrostatic forces in the electrostatic double layer at the interface- have no effect on the <H_3AsO_2-[neutral surface sites]> interaction whilst they do affect the <Pd(2+)-[surface anionic sites]> interaction.

(c) Effect of Zn(II): analogously, the presence of 3mg/L Zn(II) ions has negligible effect on As(III) uptake, see Figure 3a, while they severely compete for Pb(II) binding i.e. since both Pb(II) and Zn(II) cations compete for binding at the same anionic surface sites of PCrt.

Thus the present data reveal a selective As(III) uptake by the PCrt metarial that is not impaired by other common cations or anions.

Comparison with analogous As(III) sorbents: Low-cost Granular Activated Carbon, (GAC) and Fe-loaded GAC were reported to achieve an uptake of 0.4 mg As/g (GAC) and 3 mg/gr (GAC)-Fe respectively [20]. Other methods such as co-precipitation e.g. with Al or Fe hydroxides require significantly longer timescales i.e. days [6], *vs.* a max time of 120 minutes in the present systems. Moreover, the so formed precipitates have to be deposited on a low-cost substrate such as sand, Al_2O_3 or a carbon matrix [6, 21] in order to be usable in leaching-free column applications. For example Fe-hydroxide coated Al_2O_3 was shown to achieve As(III) uptake 7.6mg/g [6]. Our present approach suggests that PCrt-Pb outperforms these materials. When compared with more expensive materials prepared in our lab [12, 13d] the low-cost PCrt can be considered as a promising material on a performance/ cost basis.

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ΕΥΡΩΠΑΪΚΗ ΕΝΩΣΗ

ΑΝΤΑΓΩΝΙΣΤΙΚΟΤΗΤΑ ΕΠΙΧΕΙΡΗΜΑΤΙΚΟΤΗΤΑ

ΕΠΑΝ ΙΙ

η περιφέρεια στο επίκεντρο της ανάπτυξης

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