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Treatment of contaminated soil leachate by precipitation, adsorption and ion exchange

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ABSTRACT

The alkaline washing of soil polluted by organic (pentachlorophenol (PCP) and polychlorinated dioxins and furans (DF)) and inorganic (As, Cr, and Cu) compounds generates large volumes of effluents with high concentrations of contaminants. The objective of the present study is the treatment of leachate produced by a soil decontamination process under alkaline conditions. The alkaline leachate (pH_0 13.1) initially contains $[As]_0 = 14.5\ mg\ L^{-1}$, $[Cr]_0 = 2.41\ mg\ L^{-1}$, $[Cu]_0 = 8.22\ mg\ L^{-1}$, $[PCP]_0 = 6.42\ mg\ L^{-1}$ and $[DF]_0 = 127$ ng TEF L^{-1}. Precipitation allows the reduction of the concentrations to below 5 mg/L for Cu and below 1 mg/L for PCP and As to comply with regulations for effluent discharge in sewer in Quebec City and Montreal. The concentration of Cr was taken into consideration in this study even if it is below the legal limit (5 mg/L) without any treatment. Precipitation is the most efficient technique investigated here for the simultaneous removal of metals and PCP but does not eliminate DF beyond 17%. None of the activated carbons and resins tested can effectively remove As and Cr in strong alkaline media. The anionic resin Lewatit SR7 developed for anion exchange in strong alkaline media is the most effective for the simultaneous removal of Cu, PCP and DF, with recovery yields of 83, 99 and 97%, respectively.

Introduction

In the last decades, several studies were carried out to remove inorganic and/or organic compounds from contaminated soil using physical, biological and/or chemical processes [1–5]. Among the chemical decontamination processes developed, the solubilization of As, Cr, Cu, PCP and DF using alkaline solutions and a biosurfactant seemed to be very promising in terms of contaminant removal efficiencies and operational costs. Indeed, Reynier et al. [6] highlighted that more than 60% of As, 32% of Cr, 77% of Cu and 87% of PCP can be removed from contaminated soils after 3 leaching steps of 2 h each carried out at 80 °C with a pulp density fixed at 10% in the presence of sodium hydroxide (0.5 M) and a surfactant ([BW] = 2%). For the DF, the removal yields ranged from 25 to 74% depending on the nature of the soil and the initial contaminant levels. According to the authors, the alkaline leaching process can be successfully used to remove inorganic and organic contaminants from polluted soils due to its efficiency and the low operating costs [6]. However, this leaching process generates large amounts of alkaline effluents with concentration of As, Cr, Cu, PCP and DF higher than the regulations for the discharge of effluents in sewers [7,8]. The present paper examines some potential technologies that can be used to efficiently treat alkaline effluents containing As, Cr, Cu, PCP and DF in order to remove these contaminants.

The most common techniques for the treatment of wastewater contaminated with metals are precipitation, coagulation, ion exchange and electrodeposition. For organic contaminants such as pentachlorophenol (PCP) and polychlorinated dioxins and furans (DF), the most common methods are adsorption onto various materials (e.g., activated carbon, chitosan), filtration, reverse osmosis and degradation by electrochemical treatment.

Many studies have shown that treatment by precipitation–coagulation is less expensive than adsorption, microfiltration or ion exchange [9–12]. Chemical coagulation allows the efficient treatment of wastewater polluted by metals as well as organic compounds, such as PCP. Several studies on the treatment of effluents contaminated with Cu, Cr, and As have shown that this technology has good potential for the recovery of these metals [13,14]. In most cases, the precipitation of metals is performed in the presence of alkaline agents ($Ca(OH)_2$, $Mg(OH)_2$ and NaOH) to form metal hydroxides. Studies have shown that the solubility of

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the metal hydroxides formed depends on the pH of the solution [15]. The effectiveness of wastewater treatment by coagulation–precipitation also depends on the oxidation state of the metal. Therefore, it is best to oxidize As(III) to As(V) before precipitation to obtain better removal rates as the solubility of As(V) is lower than the solubility of As(III). To enhance the removal of chromium from effluents, it is better to reduce Cr(VI) in Cr(III) as the solubility of Cr(III) is lower than the solubility of Cr(VI) [16,17]. However, As (V) and Cr(III) are the preponderant forms found in contaminated soils and the chemical leaching processes developed allowed the solubilization of As and Cr in their more easily forms to be precipitated without any oxidation or reduction. In alkaline solutions, As(V) is mainly found in its anionic form, AsO_4^{3-}, which is difficult to remove from effluents by precipitation. However, the removal of metals present in the effluent can be improved by adding a coagulant, especially for AsO_4^{3-} [18,19]. This study shows that the presence of ferric chloride facilitates the extraction of As by co-precipitation as $FeAsO_4$ or by adsorption on the hydroxides and the oxy-hydroxides ($Fe(OH)_3$ and FeOOH) formed. The method investigated by Janin et al. [18] allows the removal of 99% of the As, Cr and Cu originally present in the solution.

Ion exchange is a widely used technique for metal recovery. There are a wide variety of ion exchange resins. Strong and weak cationic resins often contain a sulfonic group (in the form of resin–SO_3/H^+) and carboxylic acid group (in the form of resin–CO_2/H^+), respectively, while the chelating resins can support bis–picolylamine groups or iminodiacetic groups [20]. Many studies on Cr, Cu or PCP recovery have been successfully conducted on Amberlite IRA 900, Amberlite IR 120, Dowex M4195, Amberlyst A21 and Amberlyst A21–XLT [13,21–23]. The removal of Cr and Cu using ion exchange resin is favorable, but As recovery is more difficult. Lewatit FO 36, a chelating resin with a FeOOH functional group, allows the selective extraction of As [24]. The removal of trivalent Cr using ion exchange resins has been widely studied. Some tests were performed by Rengaraj et al. [25,26] using synthetic solutions on strong cationic resins (Amberlite IR 1200, 1500 H, IRN97H, SKN-1, IRN 77). The adsorption of Cr on the iminodiacetic chelating resins Lewatit TP 207 and Chelex 100 was effective and optimal at pH 4.5 [27]. Lin et al. [28] tested the iminodiacetic resin Amberlite IRC 748 for the extraction of Cu and Ni in a synthetic solution. The extraction of Cu, Ni, Zn and Mn on the chelating resin Dowex M4195 was studied by Diniz et al. [20]. A method for the decontamination of effluents containing As, Cr, and Cu was established by Janin et al. [13]. This method allows the selective extraction of Cu and Cr by passage through a column containing Dowex M4195 chelating resin for the extraction of Cu followed by a column containing Amberlite IR120 resin for the extraction of Cr. These steps allow the fixation of 96% of the Cu and 68% of the Cr in the solution. To remove the remaining Cr and As, precipitation at pH 4 is performed. The complete leachate treatment process, involving ion exchange and precipitation, can extract 99% of the metals. The removal of perchlorate ions (ClO_4^-) on the Lewatit SR-7 resin was studied by Yoon et al. [29], yielding promising results.

The adsorption of contaminants by several types of natural or synthetic materials (activated carbon, chitosan, chitin, bentonite and kaolinite) is widely used for the removal of organic and inorganic contaminants present in wastewater. The recovery of organic contaminants such as PCP and DF by adsorption onto activated carbon media is an economic method of recovery [30]. The activated carbon has an excellent adsorption capacity for several types of contaminants. Activated carbon has a high adsorption surface area, usually varying between 850 and 1500 m^2/g. Fabre et al. [31] found that the effectiveness of PCP adsorption was 10–100 times greater on activated carbon than on bentonite or kaolinite. The adsorption of PCP occurs by complexation between the carboxyl group (—COOH) of the activated carbon and the aromatic ring of PCP (e^- acceptor) [32]. Desorption from the active carbon is affected by the presence of NaOH, which converts PCP into its sodium salt. Adsorption/desorption cycles performed by Anirudhan et al. [32] show a loss of efficiency of approximately 14% after four loops. The adsorption of DF on activated carbon is also favorable and depends strongly on the formulation of the activated carbon used and its functional groups.

The objective of the present study is the treatment of leachate produced from soil decontamination under alkaline conditions. The leachates contained various amount of metals (mainly As, Cr and Cu) and organics, such as PCP and DF. This study first investigated the treatment of this leachate by precipitation–coagulation using ferric sulfate and sulfuric acid for pH neutralization. Finally, adsorbents and ion exchange resins were tested to remove all of the contaminants without pH adjustment to allow effluent recirculation in the soil decontamination process.

Experimental

Soil leachate production

Three soils (S1, S2 and S3) contaminated by As, Cr, Cu, PCP and DF were used in this study. Soil decontamination in a 2-L beaker was performed on the 0–6 mm fraction of dry soil. Soils were screened using a sieve of 2- or 6-mm square aperture diagonal and allowed to dry overnight at room temperature. The decontamination process consists of three leaching steps followed by one rinsing step. The leaching steps were carried out by mixing 100 g soil samples with 1 L of alkaline solution (1 M NaOH). Leaching treatments were conducted over 2 h at 80 °C using a hot plate and in the presence of the amphoteric surfactant cocamidopropyl betaine (BW) at a concentration of 2% (v/w). Agitation was performed using an immersed axial impeller or by magnetic stirring and set at approximately 500 rpm. After each leaching step, the mixture was allowed to settle for at least 2 h, and the leachate was recovered. The solution was then allowed to settle overnight before being filtered with Whatman no. 4 membrane (porosity = 20–25 μm). The leachate treatments by precipitation, adsorption onto various adsorbent and ion exchange were performed at room temperature.

Leachate treatment by precipitation

The leachates obtained from the treatment of soils were highly contaminated with metals, PCP and DF. Precipitation tests were conducted to reduce the levels of contaminants to allow the recirculation of the effluent in the process or discharge to the sewer. Precipitation tests were performed on the leachate produced in the first leaching step (L1) of the decontamination process. First, a mixture (50/50) of the leachates produced from the decontamination of soil S2 (most heavily contaminated by metals) and soil S3 (most heavily contaminated by organics) was studied. Next, precipitation tests were performed on the L1 produced from the decontamination of each soil (S1, S2 and S3). The pH of the solution was lowered from 13.1 to 7.5 using a solution of sulfuric acid (10% H_2SO_4). Because the amount of ferric sulfate added varied, the final pH was adjusted between 7.0 and 7.3 using sodium hydroxide ([NaOH] = 0.5 M) to avoid the re-solubilization of metals and PCP due to acidification (pH between 6.0 and 7.5) by the addition of $Fe_2(SO_4)_3$. Between 0.1 and 0.9 mL of ferric sulfate solution (140 g Fe L^{-1}) was added under agitation. These experiments were performed in triplicate on 100 mL of leaching solution placed in 200-mL beakers. Leachates were analyzed for the determination of metals, PCP and DF contents before and after leachate treatment. The speciation of Cr (trivalent or hexavalent) was determined by co-precipitation according to the USEPA method 7195, even if, it is expected that