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Simultaneous removal of organic and inorganic pollutants from synthetic road runoff using a combination of activated carbon and activated lignite

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ABSTRACT

Road runoff presents a unique case when it comes to selecting adsorbents for the simultaneous removal of organic and inorganic pollutants. In this study, a series of rapid small-scale column tests (RSSCTs) were conducted to investigate the performances of granular activated carbon (F300) and granular activated lignite (HOK) in removal of the ubiquitous pollutants methyl tert-butyl ether (MTBE), naphthalene, and zinc (Zn^{2+}). F300, HOK, and a combination of both materials were studied in RSSCTs. The experimental data were fitted with the Thomas and Yan models. In the experiments, naphthalene was efficiently removed by both F300 and HOK. Expectedly, both F300 and HOK showed high naphthalene removals. Further, F300 showed a higher selectivity towards MTBE than Zn^{2+}, while HOK had a significantly higher selectivity towards Zn^{2+}, while the lowest selectivity towards MTBE. Although the adsorption capacity of MTBE was reduced from 19.9 mg/g to 11.6 mg/g, a combination of HOK and F300 drastically increased the adsorption capacity of Zn^{2+} by three times from 1.13 mg/g to 3.36 mg/g. Hence, the combination of F300 and HOK offers a promising solution for removal of organic and inorganic pollutants from road runoff.

1. Introduction

Road runoff occurs when precipitation flushes the surfaces of roads. It contains a complex matrix of pollutants originating from both the atmosphere and road surface. Organic pollutants, such as volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), and inorganic pollutants, such as heavy metals constitute the main contaminants in road runoff [1,2]. No matter road runoff runs directly into environment or mixes with other polluted water entering waste water treatment plant, where the specific treatment step for road runoff is devoid, most of the pollutants in road runoff would persist, and thus, pose a significant threat to the quality of urban receiving waters (ground water, lakes, rivers, etc.) [3].

Methyl tert-butyl ether (MTBE), a representative VOC, is well known and has been in widespread use since the 1990s as a gasoline additive to improve the utilization of fuel and reduce the amount of tail gas. Its unpleasant taste and odor can be detected at very low concentrations (2–2.5 μg/L) [4]. Moreover, MTBE is regarded as a suspected carcinogen for human beings. Its high water solubility means that MTBE rapidly spreads in aqueous environments and is difficult to remove. In storm water, MTBE has been detected as high as 13.5 μg/L (with a median value of 1.5 μg/L) [5]. Similar to MTBE, PAHs also have mutagenic and carcinogenic characteristics. Some PAHs are regarded as priority hazard substances by the European Environmental Agency [6]. Compared to other PAHs, Naphthalene has the lowest values of log K_{OW} (partitioning coefficient between octanol and water, 3.37) and log K_{OC} (organic carbon partition coefficient, 3.11) and therefore, is the most difficult compound from all PAHs to remove from water [7]. Heavy metals such as Cu^{2+}, Zn^{2+}, and Pb^{2+} have been studied in depth due to their toxicity and accumulation in road runoff [8]. Specifically, Zn^{2+} is a typical heavy metal with a high dissolved fraction of 27–71% in road runoff [9,10]. Results a highly trafficked urban road showed a median value for dissolved Zn^{2+} of 160 μg/L [10]. The presence of dissolved metals in road runoff may eventually lead to increased toxicity due to wider dispersion in aqueous environments.

Activated carbon and activated lignite are traditional adsorbents due to their low price, wide availability, and high adsorption capacity [11,12]. Moreover, as a base material, without complex activation processes, lignite is considered to contain more functional groups than activated carbon, which are beneficial for adsorption. Therefore, the two materials were selected for this study. Both materials are frequently cited in literature for pollutant removal; however, the combination of them for simultaneous adsorption of pollutants in road runoff has not yet been reported.

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The rapid small-scale column test (RSSCT) is an accelerated testing tool used to evaluate the performance of adsorbents in a small-scale, model treatment system [13]. In contrast to the static nature of batch experiments and tendency to reach equilibrium, RSSCTs can help to predict the behavior of large-scale (or pilot scale) adsorbers with continuous influent, specific empty bed contact time (EBCT), and specific influent flow rates [14]. Snoeyink and Summers (1999) used breakthrough curves to present the performance of the adsorbent in RSSCTs [15].

The goal of this study was to test the performances of two adsorbents (granular activated carbon (F300) and granular activated lignite (HOK)) for the simultaneous removal of MTBE, naphthalene, and Zn^{2+} from a representative synthetic road runoff. Therefore, F300, HOK, and a combination of both materials were studied in a series of RSSCTs. Finally, the role of adsorbent placement in the column (mixed versus stacked) on the pollutant removal efficiency was investigated. With this information, steps can be taken to set up a prototype adsorbent filter, as a component of an on-site treatment plant for urban road runoff treatment [10].

2. Materials and methods

2.1. Adsorbents and adsorbates preparation

Granular activated carbon (F300, Chemviron Carbon GmbH, Germany) and granular activated lignite (HOK, Rheinbraun Brennstoff GmbH, Germany) were used as adsorbents in RSSCTs.

Before experiments, both F300 and HOK were washed several times with ultra-pure water (Milli-Q, 18.2 MΩ cm). After overnight drying at 105 ± 2 °C, F300 and HOK were sieved to the size fraction of 1–2.5 mm. The sieved materials were then dried again at 105 ± 2 °C to achieve constant weight, and finally stored in desiccators until future use.

MTBE (⩾99.9%, Sigma–Aldrich Chemie GmbH, Germany), naphthalene (⩾99.7%, Sigma–Aldrich Chemie GmbH, Germany) and Zn^{2+} (standard solution of $ZnNO_3$ at 1000 mg/L, Merk KGaA, Germany) were the adsorbates tested in RSSCTs, representing the pollutants in the synthetic road runoff.

2.2. Experimental setups

Table 1 lists the parameters and conditions used in each RSSCT. RSSCTs were conducted at ambient temperature (23 ± 2 °C). Milli-Q water was used for influent preparation. The experimental apparatus was constructed of glass and Teflon® to minimize adsorption of organics onto the surfaces. The glass column had a diameter of 1.8 cm and a length of 23 cm, providing an adsorbent bed height of 23 cm. A glass screen was placed at the bottom of the column to support the filter materials. The influent went through the glass columns in up-flow mode (from bottom to top), since it has been shown to be more efficient than down-flow mode (from top to bottom) [16]. The flow rate of the influent was regulated at 3 mL/min by a peristaltic pump (Ismatec IPC-04, IsmatecSA, Zurich, Switzerland). As a result, EBCT was maintained at 20 min.

Prior to each RSSCT, Milli-Q water was fed into the adsorber columns for approximately 1 h in order to soak the adsorbent material and remove the air bubbles inside so as to maintain identical experimental conditions. Next, the RSSCTs were started by switching the influent to the experimental solution containing the specific pollutant. Effluent samples were taken at designated times and filtrated with a glass micro-fiber filter (Whatman GF/C 1.2 μm filter) and then stored at 4 ± 1 °C. Glass vials (24 mL for MTBE and 2 mL for Naphthalene) with Teflon-lined screw caps were used for sampling.

Apart from the tests with Zn^{2+}, phosphate buffer (3.48 g/L phosphate monobasic, KH_2PO_4, Sigma–Aldrich Chemie GmbH, Germany, and 7.26 g/L di-sodium hydrogen phosphate dehydrate, $Na_2HPO_4{\cdot}2H_2O$, Merck KGaA, Germany) was used to obtain a constant pH value of 7 in the influent. For the case of Zn^{2+}, pH 7 was regulated by HNO_3 and NaOH instead of phosphate buffer to avoid the possible precipitation of $Zn_3(PO_4)_2$.

All experiments were done in duplicate.

2.3. Analytical method

MTBE was analyzed by gas chromatography coupled with mass spectrometry (GC/MS) (Varian, 2200) using the headspace-GC/MS method (EPA Method 8260/5021) [17,18] with the detection limit of 0.1 μg/L and accuracy of ±10%.

The naphthalene concentration was measured by GC/MS (Varian, CP 3800 Saturn 2200) according to EPA Method 610 [19], with the detection limit of 0.1 μg/L and accuracy of ±10%.

The concentration of Zn^{2+} was measured by atomic absorption spectrometry (AAS) (Varian Spectr AA-240Z with GTA 120) according to the Standard Methods 3111 and 3113 [20] with a detection limit of 0.5 μg/L. Total organic carbon (TOC) was analyzed using Elementar High TOC II analyzer (Elementar Analysensysteme GmbH, Germany) according to the Standard Method 5310 [20] with the detection limit of 1 mg/L.

3. Results and discussion

In this study, breakthrough curves were created by plotting effluent concentrations versus bed volume. They were subsequently used to analyze the adsorption behavior of each RSSCT. The adsorbent usage rate (AUR), which indicates the amount of adsorbent needed per volume of contaminated water (g/L), and adsorption capacity, which denotes the amount of adsorbed

Table 1
Parameters of each RSSCT.

Experiment number	Pollutant	Influent concentration (mg/L)	Adsorbent(s)	Adsorbent weight (g)	At 50% breakthrough point	
					Adsorbent capacity (mg/g)	Adsorbent usage rate (AUR) (g/L)
1	MTBE	16	F300	30	19.5	0.59
2	Naphthalene	5	F300	30	–	–
3	Zn^{2+}	15	F300	30	5.22	2.29
4	MTBE	16	HOK	35	2.32	4.70
5	Naphthalene	5	HOK	35	–	–
6	Zn^{2+}	15	HOK	35	13.7	0.85
7	MTBE + Zn^{2+}	16/11	F300	30	19.9/1.13	0.57/5.89
8	MTBE + Zn^{2+}	16/11	F300/HOK (50:50 Mixture)	15/17.5	11.5/3.36	0.94/2.54
9	MTBE + Zn^{2+}	16/11	F300/HOK (50:50 Layers)	15/17.5	11.6/3.28	0.93/2.68