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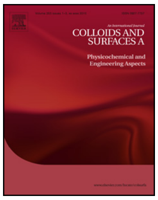

Comparative studies of sorption of phenolic compounds onto carbon-encapsulated iron nanoparticles, carbon nanotubes and activated carbon

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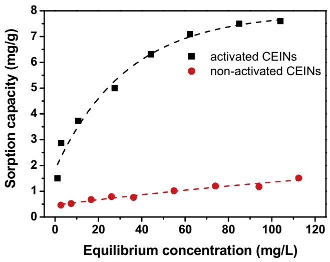
HIGHLIGHTS

- Sorption capacity changes in the following order: AC > CNTs > CEINs.
- 4-Chlorophenol has the highest adsorption affinity.
- Sorption performance of CEINs increases 7 times after surface activation.
- Sorption kinetics rate of CEINs and CNTs is 100 times higher in comparison to AC.
- CEINs have the highest regeneration yield.

GRAPHICAL ABSTRACT



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ABSTRACT

The systematic comparative adsorption studies of three phenolic compounds (phenol, 2-chlorophenol and 4-chlorophenol) from aqueous solutions onto three types of carbon sorbents are presented. The equilibrium sorption studies along with sorption kinetics were investigated onto carbon-encapsulated iron nanoparticles, multi-wall carbon nanotubes and granulated activated carbon. These carbon sorbents have significantly different morphological and textural properties. Their surface area varied between 36 and 1187 $m^2 g^{-1}$. The highest adsorption capacity (280–550 mg/g) was found for activated carbon. The uptakes of adsorbates onto carbon nanotubes and carbon-encapsulated iron nanoparticles were substantially lower, i.e. 24–87 mg/g and 5–11 mg/g, respectively. The performed sorption kinetics studies revealed that the sorption kinetic rates for carbon nanotubes and carbon-encapsulated iron nanoparticles are 2–3 orders of magnitude larger ($2–10 \times 10^{-2}$ $g\,mg^{-1}\,min^{-1}$) in comparison to activated carbon ($1.9–4.5 \times 10^{-4}$ $g\,mg^{-1}\,min^{-1}$). The sorption performance and sorption kinetics were systematically discussed in the frames of morphology and textural properties of sorbents and the properties of adsorbates. Additionally, it was demonstrated that the sorption capacity of carbon nanotubes and carbon-encapsulated iron nanoparticles can be largely improved by the post-synthesis activation process. In this case the adsorption capacities increased even 2–7 times. The spent sorbents were regenerated in acetone. It was also found that carbon nanotubes and carbon-encapsulated iron nanoparticles retain up to 65% of their pristine adsorption performance, whilst the sorption capacity of activated carbon is reduced of 80%.

1. Introduction

Phenol and its derivatives are considered as severe toxic pollutants in the environment [1]. Many of phenolic compounds are

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recognized as toxic or even act as carcinogens [2]. They have relatively high solubility in water and their presence causes unpleasant taste and fetid odor. The largest amount of phenolic compounds are emitted by coal gasification plants, pharmaceutical and steel industries, petrochemical units and chemical spills. Adsorption technology is widely applied for the decontamination of waters from phenolic compounds. Activated carbon (AC) is frequently used as a solid adsorbent of phenols because of its unique textural and chemical properties. Hundreds of papers on the use of activated carbons in the removal of phenols were published so far. The most fundamental and technical data on this topic can be found in the following review publications [3–5].

Carbon nanotubes (CNTs) are adsorbents with highly hydrophobic surface and exhibit high affinity to various organic compounds. Their surface area (in the case of multi-wall carbon nanotubes) usually does not exceed 300 $m^2 g^{-1}$ [6]. Carbon nanotubes have usually smooth surface and form bundles of randomly tangled individual tubes. This feature differentiates the carbon nanotubes from activated carbons. Carbon nanotubes, due to the significantly lower surface area, obviously have lower sorption performance in the removal of organic compounds (including phenol derivatives). Nevertheless the non-compacted structure of CNT bundles facilitates the sorption kinetics, which is also important for the realistic applications in sorption. The review of literature shows that carbon nanotubes are efficient sorbents for a variety of organic compounds, including phenols [7,8], aliphatic alcohols [9], substituted benzenes [10,11], pesticides [12] and natural organic matter [13].

The removal of phenol and its derivatives onto iron, iron oxides and their composites with activated carbon was also studied. The inclusion of a magnetic phase (e.g. iron or iron oxides) into the porous structure of activated carbon creates a new class of mobile sorbents, which can be easily separated from the solution. The iron/iron oxide doped activated carbons have usually worse textural performance in comparison to the pristine AC, however, they are still capable to adsorb relatively large quantities of the solute [14–17]. As for example Oliveira et al. studied the adsorption performance of carbon-iron oxide magnetic composites and found that the micropore volume is reduced by a factor of 1.5 when the composite contains 25 wt.% of the magnetic phase [14]. The adsorption capacity of phenol on this magnetic activated carbon was found to be 117 mg/g. Mihoc et al. demonstrated that nanostructured pure iron oxides can be used for the removal of phenol and 4-chlorophenol [18]. The reported uptakes were very low, i.e. 1–5 and 5–30 for phenol and 4-chlorophenol, respectively. The halogen derivatives of phenol can be also removed effectively by zero-valent iron nanoparticles [19,20]. In this case the uptake of the solute is marginal because of the non-porous texture of iron nanoparticles. The removal is driven by a red-ox reaction between the halogen derivative and the zero-valent iron, which leads to formation of ferrous and chlorine ions, and hydrogenated form of pristine halogenated phenol. Recently, Wu et al. described a dual material based on iron nanoparticles supported onto activated carbon for the removal of pentachlorophenol [21]. This original approach benefits from high adsorption capacity of activated carbon and the presence of iron particles which are able to decompose the adsorbed solute.

This aim of this work is to compare the sorption efficiency of three phenolic compounds, namely phenol (Ph), 2-chlorophenol (2-CP) and 4-chlorophenol (4-CP), onto three types of carbon materials: i.e. activated carbon (AC), multi-wall carbon nanotubes (CNTs) and carbon-encapsulated iron nanoparticles (CEINs). These three types of carbon materials have totally different morphological, structural and textural properties. A special attention is paid to carbon-encapsulated iron nanoparticles. This core-shell type nanomaterial combines the properties of the magnetic core and thin and tight carbon coating. Due to the small diameter (10–100 nm) CEINs have moderate surface area. The presence of the magnetic core makes CEINs mobile, and this feature may be utilized for their rapid separation from the solution. It was shown that CEINs have a great potential for adsorption of heavy metal ions from aqueous solutions [22–24]. Nevertheless, their sorption performance in reference to a narrow range of organic solutes was studied only by Niu et al. [25] and Wang et al. [26].

2. Experimental

2.1. Carbon sorbents and their characterization

Activated carbon (grain size between 0.3 and 0.5 mm) was purchased from Sigma–Aldrich. Multi-wall carbon nanotubes were obtained from TCNT (Taiwan). Carbon-encapsulated iron nanoparticles were fabricated in our lab using carbon arc discharge route. The detailed procedure is described elsewhere [27]. The synthesis route of CEINs is based on a simultaneous vaporization of an anode containing Fe and C species. The arc discharge between the solid graphite cathode and hollow graphite anodes filled with Fe powder (ca. 50 wt.%) leads to the formation of Fe–C vapor which subsequently undergoes rapid quenching. The discharge (80 A, 30 V) was maintained under $Ar–H_2$ atmosphere (50:50 vol.%) at the total pressure of 30 kPa. The as-obtained products which contained carbon-encapsulated iron nanoparticles and non-encapsulated iron particles were subjected to purification in order to remove the non-encapsulated particles. The purification procedure included 24 h refluxing in boiled 3 M HCl with further washing in excess of water and ethanol, and drying in air at 70 °C.

Carbon nanotubes and carbon-encapsulated iron nanoparticles were also subjected to the activation procedure. The dried samples were mixed with KOH and grinded in an agate mortar with addition of small amount of water. The mass ratio between the carbon material and KOH was 1:4. Next, the as-obtained paste was put on a quartz boat and inserted into the tube oven (outer tube diameter 30 mm, length of the oven 500 mm). The activation process was carried out under Ar flow (6 ml/s, at 298 K and 101 kPa) with the mean heating rate of 10 °C/min. The activation temperature and operation time was 850 °C and 60 min, respectively. The as-activated samples were first rinsed with ethanol and water, and then purified in boiled 1 M HCl for 60 min. Next, the samples were thoroughly washed with water until the pH of the resultant solution was neutral. The activated carbon nanotubes and carbon-encapsulated iron nanoparticles were labeled as act-CNTs and act-CEINs, respectively.

The porous structure of sorbents was evaluated by nitrogen adsorption at 77 K using a Micrometrics ASAP 2010 analyzer. The specific surface area was calculated using the BET equation. The pore volumes were obtained from the density functional theory calculations. The morphological features were studied by scanning (Zeiss Merlin) and transmission (Zeiss Libra 120 Plus) electron microscopy.

2.2. Equilibrium sorption studies

All experiments were carried out at temperature 22 ± 1 °C and at pH 6. The stock solutions of phenol, 2-chlorophenol and 4-chlorophenol were performed by dissolving 4000.0 mg ± 0.1 mg in a 2 L volume flask (deioinized water was used). The working solution of phenolic compounds were obtained by adequate diluting of the stock solution. The initial concentration of the working solutions was between 10 and 1750 mg/L. A mass of 25 mg of the respective sorbent (AC, CNTs, act-CNTs, act-CEINs) was added to a plastic vial containing 50 ml of the working solution. In the case of CEINs, due to the significantly poorer porosity, the mass of 200 mg was used. The vials were shaken for 8 h to assure that the sorption process was completed. Then, the suspensions was filtered