



Multicomponent adsorption of benzene and selected borderline heavy metals by poly (butadiene-co-acrylic acid) hydrogel



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ARTICLE INFO

Article history:

Received 6 May 2016

Received in revised form 12 July 2016

Accepted 14 July 2016

Available online 16 July 2016

Keywords:

Adsorption

Heavy metals

Multi-functional hydrogel

Non-point source pollution

BTEX

ABSTRACT

This study introduces a method to alleviate against non-point source water pollution which typically comprises both organic and inorganic pollutants. We synthesized a hydrogel adsorbent customized for simultaneous adsorption (and removal) of benzene and heavy metals ion pollutants. Two functional groups were successfully incorporated into the hydrogel system using solution polymerization and chemical cross-linking methods. The adsorbent was golden brown and insoluble in water, and its structural decomposition in the dry state started at around 175 °C. Other thermal properties, hydrogel characterization and adsorption mechanism are described herein. Exploiting the alkylating chemistry of mono-aromatic compounds, this hydrogel successfully adsorbed benzene onto its heterogeneous surface. The strong nature of adsorption with a relatively faster equilibrium time progressed according to second order kinetic model. However, competitive heavy metal ions adsorption was a diffusion-limited process and the adsorption capacity increased not only with the solution pH but also with ionic size and the amount of metal ions' electric charge. With both type of pollutants adsorbed onto PBA hydrogel, this work therefore opens up a possibility of synthesizing adsorbent systems customized for simultaneous removal of organic and inorganic pollutants in a multi-type polluted waters.

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1. Introduction

In Non-Point Source (NPS) water pollution, multi-variant contaminants originating from different sources such as industrial effluents, agricultural and urban run-off, domestic effluents, particulate tailings from wind and rainfall wash-off, congregate in a single polluted site [1]. This raises the complexity of remediating such polluted waters which contains both organic and inorganic pollutants. Decontamination efforts therefore require a system tolerable to the extreme conditions and with multiple selectivity for the various pollutants found therein including heavy metals and benzene, toluene, ethyl benzene and xylene (BTEX).

Borderline heavy metal elements are generally defined as having a specific density of at least 5 times greater than water (5 g/cm³) [2]. These metals are introduced into surface water by among others, industrial effluents (which is a major source of hydrosphere pollution), municipal wastes and mining activities [41]. Their toxicities have been fatal over the years, leading to acute cases like

the Mina-mata [3] and Itai-itai [4] diseases that caused widespread death of both man and aquatic life. As a result of these deleterious effects, common man-made metals like Cd, Hg, Ni, Zn, Cr, As, Cu and Pb have been ranked among the “Top 20 Hazardous Substances” in the priority list of hazardous substances published by the Agency for Toxic Substances and Disease Registry (ATSDR) every two years [5]. Previously employed techniques for purifying metal-contaminated surface waters include reverse osmosis and electrochemical treatments [6–8]. But adsorption has rapidly grown as a more suitable technique enabling cost effective, versatile and variable materials [9]. Adsorbents such as biomass, whose porous surface has been shown as able to be catalytically modified [10] have been used for metal adsorption. More recent approaches have however, concentrated on synthetic adsorbents, especially hydrogels for metal adsorption. Typical hydrogels for this purpose have been synthesized using various polymerization and cross-linking methods as shown by Saraydin (1995), Li Jin (2002), Yetimoglu (2007) and Hiroki et al. (2009) in their metal adsorption studies [11–14]. Adsorption mainly occurs through processes such as cation exchange and metal-chelating mechanism. Predictably, therefore, polyelectrolyte systems with functional groups such as carboxylate or the sulfonate [15], have been frequently used for metal adsorption. The monomer containing these groups have easily polymerizable vinyl carbons,

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which also enables blending with many other functional monomers for copolymerization reactions. Further, additional “smart” features such as pH, temperature and other stimuli responsiveness characteristic of such adsorbents, greatly improves the adsorption/desorption cycles [16–19]. Combining these characteristics therefore, a carboxylate-based monomer will be studied for possibility of a copolymer hydrogel formation for use in the metal-BTEX extraction experiments.

BTEX compounds are mono-aromatic and originally from petroleum derivatives such as gasoline. They have the same chemical properties and are hence usually identified as a group [20]. Despite being common industrial and laboratory solvents or starting materials in the synthesis of polymers, these are volatile organic compounds (VOCs) with carcinogenic and mutagenic effects [21–23] that need controlled usage and/or removal from polluted sites.

Attempts on BTEX adsorption from polluted aqueous sites used various natural adsorbents such as activated carbons but to limited commercial ineffectiveness. With increasing efforts towards cheaper and more practical adsorbents, porosity has stood out as a key characteristic that has led to discovery and synthesis of various adsorbents. Primary adsorbents of this nature included surfactant modified zeolites [24,25], or montmorillonite clay [26], diatomite rock [27] and other materials modified by non-ionic surfactants. Notably, all these materials comprised SiO₂ base groups in their structures, which unfortunately does not interact with the largely inert BTEX compounds. Meanwhile, organic-based adsorbents such as macroreticular resins [28] and carbon nanotubes (CNTs) have also been exploited for BTEX adsorption. Surprisingly hydrogels have found little to none applications on BTEX removal, despite their wide use as adsorbents. Attempts by Standeker et al. [29] instead used silica (SiO₂) based aerogels but even then the hydrophilic groups therein were replaced by hydrophobic fractions which limits their water interactions. The resultant aerogels, similar to zeolites, clay and CNTs mainly relied on extent of surface area and their porous nature for immobilizing adsorbates. Their surface groups on the other hand, exhibited little to no interactions with benzene, and this has stood out as a gaping weakness.

As earlier mentioned in the case of NPS pollution, various pollutants (including heavy metals and BTEX) are likely to be found within a single polluted site. Therefore, porous adsorbents will experience competition for the pore sites, leading to only one type of pollutant (BTEX or metal ions) favorably adsorbed than the others. Similarly, since the size and nature of porosity also influences adsorption, this necessitates surfactant modification of these adsorbents, which also causes exclusivity of only one type of pollutant; resulting in overall inefficiencies. Consequently, a material that is not only porous but also functionally active for adsorption of both BTEX and/or heavy metals is ultimately desired.

For this work therefore, we synthesized a multi-functional hydrogel for potential application in NPS water pollution remediation. The synthesis also relied on the Schuchowitzky theory [40], which posited the ability of having multiple active centers on a hydrogel. Various grafting techniques and/or direct syntheses have since collaborated this theory [30,31]. In continuing these efforts, butadiene and acrylic acid monomers were allowed to react and cross-linked to form a new hydrogel via solution polymerization in the presence of chemical cross-linkers. The hydrogel properties were then characterized including its thermal stability using DSC/TGA thermograms. Based on the number and types of functional groups derived therefrom; the gel's adsorbent properties was tested against aqueous benzene and heavy metal ion solutions while considering various factors such as pH and starting concentration.

2. Experimental

2.1. Materials and reagents

Acrylic acid and benzene were obtained from Wako pure chemicals (Japan) and acetone from Kanto chemicals (Japan). Butadiene monomer was supplied by Merck (Japan) whereas tetramethylethylenediamine (TEMED) together with acetic acid were supplied by Kishida chemicals (Japan). The multi-element metal ion stock solution, *N,N'*-Methylenebisacrylamide (NMBA) and ammonium persulfate (APS) were all supplied by Sigma Aldrich (USA). All references to water shall refer to the ultrapure water purified by Puric (Organo, Japan). All reagents were of analytical grade and used without any further purification.

2.2. Instrument and apparatus

The change in benzene solution concentration was determined by UV–vis spectrometer (USB4000 Ocean Optics, USA) with a Deuterium Tungsten Halogen UV–vis-NIR Light Source. An inductively coupled plasma mass spectrometer (ICP/MS, Agilent 7700 series, Japan) was used to measure the metal ion concentrations in aqueous solutions. Hydrogel functional groups and structural analysis was by FT/IR (Jasco 4100, Japan) and NMR (JEOL JNM-ECS 400 NMR, Japan) spectroscopic methods. Thermal analysis was performed via STA 449 F3 simultaneous TG–DSC thermal analyzer (NETZSCH, Japan). Additionally, microwave digestion system (ETHOS ONE, Italy) was employed in desorption analyses.

2.3. Hydrogel synthesis

The copolymerization of acrylic acid and butadiene was carried out in 25 ml standard sealed glass beakers. Using aqueous acetone solvent, the conventional solution polymerization proceeded as follows:

- (1) 10 ml of 60% v/v aqueous acetone were added into polymerization bottles.
- (2) Thereafter the main monomers, butadiene and acrylic acid in a 2:1 v/v ratio were charged into these solutions and the resulting mixture stirred until complete homogeneity.
- (3) This was followed by addition of cross-linking agent NMBA, polymerization initiator APS, and the reaction accelerator in the following quantities: 0.63%, 0.21% and 0.24% w/w, respectively.
- (4) The final mixture was further stirred and allowed to rest for 5 min. Sealed bottles were then incubated in a water bath at an isothermal temperature of 40 °C for 24 h.

Eight volumes of such solution mixtures were prepared and incubated until complete gelation.

2.4. Hydrogel washing and characterization

The synthesized hydrogels were washed in water for an extended period of time (24 h) until all soluble products could be eluted. Thereafter the hydrogels were dried and analyzed using ¹³C NMR, FTIR, TGA, and DSC spectroscopic techniques. Separately, hydrogel swelling/kinetics was also determined gravimetrically at regular intervals until equilibrium before the tests on adsorption properties.

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