



Research article

Magnetic semiconductor photocatalysts for the degradation of recalcitrant chemicals from flow back water



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ABSTRACT

In the present study treatability of persistent organic compounds from the flow back water after hydraulic fracturing was investigated. The combination of TiO₂ photocatalyst and magnetic oxide nanoparticles enhance the separation and recoverable property of nanosized TiO₂ photocatalyst. Fe₃O₄/TiO₂ and Fe₃O₄@SiO₂/TiO₂ nanocomposites were prepared by heteroagglomeration. The photocatalysts' characteristics by X-ray diffractometry (XRD), scanning electron microscopy (SEM), diffuse reflectance spectroscopy (DRS) showed that sample with the mass ratio of Fe₃O₄ to TiO₂ equal 1:4 and molar ratio of TEOS:Fe₃O₄ = 8:1 and NH₄OH:TEOS = 16:1 obtained by deposition TiO₂ P25 (Evonik) on magnetite core had about 124 m² g⁻¹ specific surface area and superparamagnetic properties. The prepared composites contained TiO₂ and Fe₃O₄ crystal phases. The photocatalytic activity was estimated by measuring the decomposition rate of three model pollutants identified in the flow back water from one of the Baltic Shale Basin. Regarding flow back water treatment after shale gas exploration, the progress of photocatalytic degradation of organic compounds was measured by chemical oxygen demand (COD) concentration. The Fe₃O₄@SiO₂/TiO₂ P25 composite nanoparticles were recovered and re-used without significant reduction of efficiency.

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1. Introduction

Water is a strategic resource for shale gas extraction, as it is used for hydraulic fracturing, the main method for fracturing rock during natural gas production (Chen and Carter, 2016). Fracturing technologies for shale gas production were developed mainly in the USA (Ray, 1976) and are currently being adapted to geological conditions and environmental requirements in China (Li et al., 2016), Germany, Poland (Baranzelli et al., 2015), Australia, New Zealand and other countries (Blythe et al., 2016). Hydraulic fracturing stimulate the flow of natural gas or oil, increasing the volumes that can be recovered. It is based on pumping fracturing fluid at very high pressure into the well, in order to prevent the fracture closing after reducing the pressure (Li et al., 2015). As shown in Fig. 1 the fracturing fluid, consists mainly of water and proppant (99.5%) and chemical additives (0.5%) (Gregory et al., 2011).

Proppant is a material which prevents fractures from closing. Usually it is sand, sometimes ceramic material or resin coated sand (Mader, 1989). Chemicals are used to stimulate a reservoir and have various tasks in the fracturing fluids (see Table S1 in supporting materials), they are: friction reducers, acids, corrosion inhibitors, biocides, iron control agent, gelling agent, cross-linker, breaker, KCl, NaCl (Brannon and Tjon-Joe-Pin, 1996).

Hydraulic fracturing consumes 8000–20,000 m³ of water per 1000 m horizontal well segment. After the hydraulic fracturing process is completed and pressure is released, between 20 and 30% of the original volume of the fracturing fluid will return to the surface as a flow back water (Stringfellow et al., 2014). The treatment and recycling of flowback water for reuse in hydraulic fracturing can enhance economic viability of gas production. It also minimizes potential environmental impacts, reduces demands on local water supplies, and meets regulatory requirements (Chen and Carter, 2016).

However, the flow back water management is one of the major challenges for shale gas exploration and development. It is especially difficult since the flowback contain high concentration of

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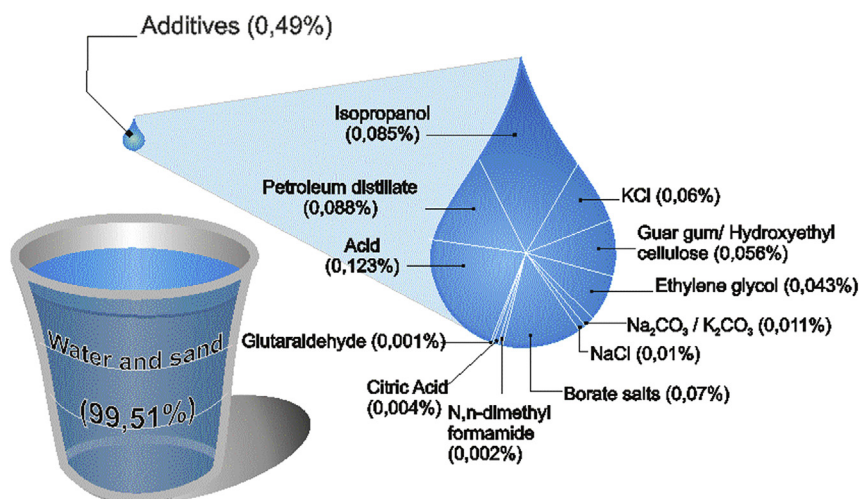


Fig. 1. Composition of fracturing fluid.

total dissolved solids (TDS). Depending on the well location, the TDS concentration in wastewater ranges from a few thousand mg/l to over 200,000 mg/l (Gregory et al., 2011). The concentration of salt in flow back water increases with time of residence down-hole. The main compound contributing to TDS value is NaCl; however, other soluble salts also affect this parameter (Gregory et al., 2011). Moreover, flow back fluid contains various combinations of heterocyclic organic compounds such as ethers, azines, ketones (acetone, MIBK, MEK), trihalomethanes, benzhydryl compounds (n-butylbenzene), aromatic hydrocarbons (trimethylbenzene, BTEX), tertiary alcohols (t-butyl alcohol), polycyclic aromatic hydrocarbons (naphthalene), alkylbenzenes (p-Cymene), organochlorides (Kargbo et al., 2010). Highly saline wastewater stream and some hydraulic fracturing chemical additives are difficult to treat with conventional processes. Therefore, there is a great demand for a more efficient and environmentally benign technology which can be applied for treating low concentration persistent organic pollutants from flow back water.

Chemical, biological, and physical methods have been implemented for treatment of flow back water. Pre-treatment techniques remove the suspended solids in the process of filtration. The nanofiltration and reverse osmosis processes are commonly used to desalinate water. However, the conventional processes are effective for TDS removal from flow back as the serial MF/UF membrane treatment and does not allow for the mineralization of organic impurities. The biggest problem is encountered in the removal of recalcitrant organic compounds.

Heterogeneous photocatalytic oxidation of organic pollutants occurred to be a promising process for water purification since many recalcitrant organic compounds at low concentration can be oxidized at a room temperature in the presence of a semiconductor photocatalyst (e.g. TiO₂) (Zielińska-Jurek et al., 2015). Photocatalysis has been used for the degradation of organic compounds such as alcohols, carboxylic acids, phenolic derivatives, or chlorinated aromatics, into harmless products e.g. carbon dioxide, water, and simple mineral acids (Lee et al., 2003; Sirtori et al., 2006; Chan et al., 2003). Water contaminated by oil can be treated efficiently by photocatalytic reaction (Jing et al., 2015). Herbicides and pesticides that may contaminate water such as 2,4,5 trichlorophenoxyacetic acid, 2,4,5 trichlorophenol, s-triazine herbicides and DDT can be also mineralized (Barbeni et al., 1987; Jang et al., 2005). Photocatalytic decomposition of ethylene glycol and propylene glycol by using UV-illuminated TiO₂ and platinum or palladium loaded TiO₂

photocatalyst led to carbon dioxide and water (Kim and Hoffmann, 2008).

However, the application of photocatalysts for wastewater treatment still needs to tackle a variety of technical problems (Zhang et al., 2014). The recovery and cyclic utilization of the nano-semiconductor photocatalysts is still a major problem hindering practical application in industrial processes (Fan et al., 2012). The combination of TiO₂ photocatalyst and magnetic oxide nanoparticles may enhance the separation and recoverable property of nanosized TiO₂ photocatalyst (Liu et al., 2011).

In this regard the aim of present study was preparation and characterization of Fe₃O₄/TiO₂ and Fe₃O₄/SiO₂/TiO₂ photocatalysts easier separable after water treatment process. The effect of TiO₂ matrix and molar ratio of TiO₂ to Fe₃O₄ on photocatalytic activity and magnetic properties in degradation of organic compounds present in flow back water were investigated.

2. Experimental

Detailed descriptions of materials, methods and instruments are available in the Supporting materials (S 2.1).

2.1. Preparation of Fe₃O₄/TiO₂ and Fe₃O₄@SiO₂/TiO₂ photocatalysts

The Fe₃O₄/TiO₂ nanocomposites of four different magnetite to titanium (IV) oxide molar ratios were prepared by an ultrasonic-assisted sol-gel method. Firstly, commercial Fe₃O₄ magnetic nanoparticles were dispersed in ethanol and ultrasonicated for 15 min. Then, TiO₂ was coated directly onto Fe₃O₄ nanoparticles by hydrolysis and condensation of titanium butoxide (TBT) in ethanol solution. The suspension was stirred for 2 h and ultrasonicated for another 1 h at temperature below 35 °C. The resulting Fe₃O₄/TiO₂ nanoparticles were separated, dried at 60 °C to dry mass and then calcinated at 400 °C for 2 h.

An inertial layer of silica between TiO₂ shell and magnetic core was proposed in order to avoid leaching of iron. In this regard, the magnetite particles (~50 nm) were dispersed in ethanol and homogenized by ultrasonication for 15 min. Then alcoholic solution of ammonia was added dropwise into magnetite dispersion and sonicated for another 15 min. Tetraethyl orthosilicate (TEOS), preliminarily diluted in ethanol was added to the magnetite particle suspension and the suspension was ultrasonicated for the next 15 min. The molar ratio of TEOS to Fe₃O₄ and NH₄OH to TEOS was

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