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Research article

# Fabrication of novel sandwich nanocomposite as an efficient and regenerable adsorbent for methylene blue and Pb (II) ion removal

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An adsorbent, which is easy to be separated and reused after adsorption, is very important for the removal of pollutants in aqueous solution. Hence, a novel nanofibrous sandwich structured adsorbent of silica nanofiber/magnetite nanoparticles/porous silica (SNF/MNP/PS) was designed and synthesized for the first time. The magnetite nanoparticles with diameter less than 10 nm were evenly distributed on the surface of silica nanofiber, which was subsequently fully covered by a layer of porous silica. The novel adsorbent was proved possessing good adsorption capacity for both methylene blue (MB) and Pb (II) ion ($Pb^{2+}$), and the adsorption equilibrium could be well described by the Langmuir-isotherm model with the maximum adsorption capacity of 103.1 mg/g for MB and 243.9 mg/g for $Pb^{2+}$ at 288 K. Moreover, in MB-$Pb^{2+}$ mixed system the measured adsorption capacity reached 74.5 mg/g for MB and 202.4 mg/g for $Pb^{2+}$, respectively. The saturated adsorbent could be readily magnetically separated from the solution and then efficiently regenerated by heterogeneous Fenton-like reaction (for MB) or acidic desorption process (for $Pb^{2+}$), respectively. After 5 cycles of adsorption-regeneration, the adsorption capacity of the reused adsorbent still reached 81.0% (for MB) and 70.9% (for $Pb^{2+}$) of the initial value. The SNF/MNP/PS behaves good adsorption properties for different types of pollutants, high magnetic recoverability and regeneration efficiency, which make it applicable to different contaminants removal.



## 1. Introduction

Organic dyes and heavy metals are indispensable chemicals in many manufacturing industries (Rajput et al., 2016; Sansuk et al., 2016). It is well known that the organic dyes are mostly toxic and not able to degrade spontaneously in natural environment, meanwhile, the heavy metal ions in aquatic environments also pose serious risks to human health and the sustainability of ecosystem (Hao et al., 2014; Lei et al., 2017). Therefore, the removal of dyes and heavy metal ions from the water is an urgent requirement to the environmental management. Various methods have been reported for the treatment of organic dyes and heavy metal ions including biological (Rai et al., 2005), physical and chemical processes (Gao et al., 2013; Hong et al., 2016). In the adsorption method, the adsorbents are generally dispersed in polluted water to fully contact with contaminants, which leads to an efficient adsorption process. After adsorption, however, two problems have to be faced. The one is the saturated adsorbents are difficult to be separated from the water, the other is the used adsorbents are hard to be regenerated and reused. As a result, it is essential to develop novel adsorbents that can be effectively separated and regenerated after removal of contaminants from the water.

One of the useful routes to solve the separation problem is introducing magnetic $Fe_3O_4$ nanoparticles into adsorbents to prepare composite. Under an external magnetic field, the magnetic adsorbents are easily enriched to achieve solid-liquid separation. In the past decades, various magnetically modified adsorbents have been synthesized, such as activated carbon (Kyzas et al., 2014), mesoporous iron oxide (Wang and Lo, 2009), zeolite (Wang et al., 2015a), graphene oxide (Geng et al., 2012) and so on. As a promising adsorbent material in practical applications, the magnetic modification of porous silica has also received much interest in recent years (Barakat and Kumar, 2015; Wang et al., 2015b).

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Meanwhile, the regeneration and reuse of adsorbents have always been the focus of attention. The heavy metal ions can be easily desorbed by a sample acidic or alkaline elution process for different types of adsorbents as described in previous report (Rajput et al., 2016). However, the situation is much more complicated for the regeneration of dye-loaded adsorbents. Some methods, such as thermal treatment (Ledesma et al., 2014), photocatalytic decomposition (Huang et al., 2017; Xing et al., 2010) and Fenton degradation (Huling et al., 2005) have been explored to reclaim the spent adsorbent after dye adsorption. Among them, the Fenton reaction has been considered as a promising route due to the high reaction rate and mineralization ability (Brillas et al., 2009; Liu et al., 2008). However, the extensive application of Fenton degradation was limited by its significant disadvantage including excessive Fe ion emission in treated water and the formation of large amount of iron-containing sludge (Ramirez et al., 2007a). Therefore, improved heterogeneous Fenton-like system using solid $Fe_3O_4$ as catalyst was proposed. Several reports have researched the heterogeneous Fenton-like reaction with $Fe_3O_4$ nanoparticles as iron source (Do et al., 2011; Hu et al., 2011), and many studies have shown that the nano-$Fe_3O_4$ heterogeneous Fenton-like catalysts exhibited good degradation effect (Ramirez et al., 2007b).

Inspired by the above-mentioned routes to separate and regenerate the adsorbents, a novel sandwich composite adsorbent combining with the advantages of high adsorption capacity, magnetic separation and high regeneration efficiency is proposed in this paper, as shown in Scheme 1. The core of the composite is silica nanofiber (SNF) extracted from natural mineral chrysotile with a diameter about 30–60 nm and length about several microns (Liu et al., 2007). The SNF possesses large specific surface area (nearly 400 $m^2/g$) and good adsorption capacity (e.g. more than 50 mg/g for Rhodamine B) (Tang et al., 2018a), and can be used as adsorbent and substrate to support nanoparticles (Tang et al., 2016). A myriad of monodispersed magnetite nanoparticles (MNP) are distributed on the surface of SNF to form intermediate product of SNF/MNP, which endows the composite with the magnetism to achieve magnetic separation, and provides the adsorbent with the heterogeneous Fenton-like reaction to degrade adsorbed dyes and regenerate the adsorbents. Finally a layer of porous silica (PS) is coated on the surface of SNF/MNP as the outermost shell to adsorb dyes and heavy metal ions due to its good adsorption capacity (Liu et al., 2008; Yang et al., 2008), in addition, to improve the structural stability of MNP.

In this work, the novel sandwich composite adsorbent was synthesized and characterized for the first time, which was absolutely consistent with above designed structure. To evaluate the adsorption capability and regeneration efficiency of the adsorbent, methylene blue (MB) and Pb (II) ion ($Pb^{2+}$) were selected as target adsorbates due to their toxicity and widespread presence in water and soil (Saber-Samandari et al., 2014). Furthermore, the structural and chemical stabilities of this nanocomposite were also evaluated.

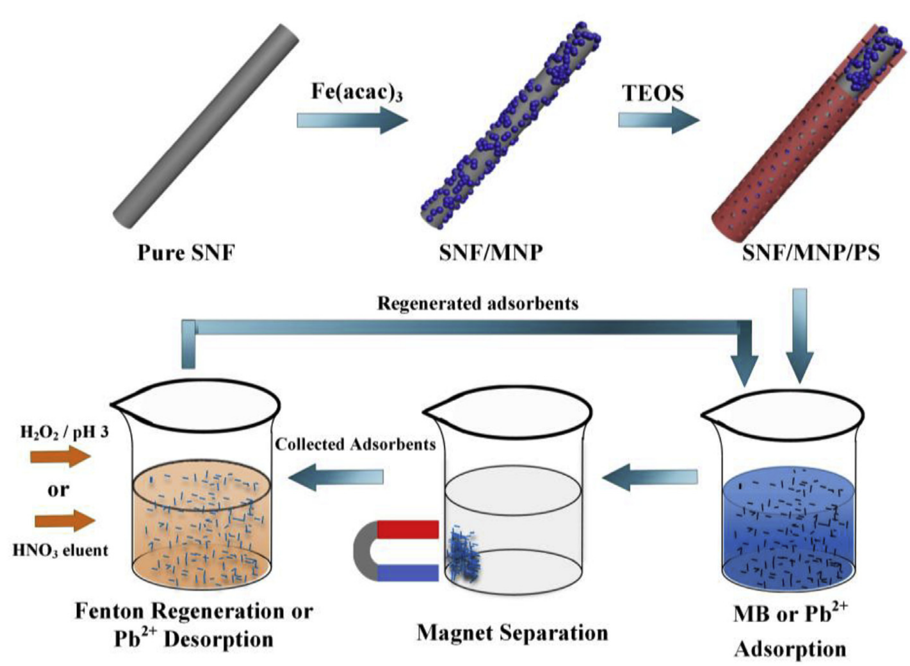
## 2. Materials and methods

### 2.1. Materials

Methylene blue trihydrate (MB, $C_{16}H_{18}ClN_3S\cdot 3H_2O$), hydrochloric acid (HCl, 36.0%), nitric acid ($HNO_3$, 65%), hydrogen peroxide ($H_2O_2$, 30%), triethylene glycol (TREG, $C_6H_{14}O_4$) and bis(2-ethylhexyl) sulfosuccinate sodium ($C_{20}H_{37}NaO_7S$) were obtained from Sinopharm Chemical Reagent Company (Shanghai, China). Iron (III) acetylacetonate ($Fe(acac)_3$, $C_{15}H_{21}FeO_6$), cetyltrimethyl ammonium bromide (CTAB, $C_{19}H_{42}BrN$), tetraethyl silicate (TEOS, $C_8H_{20}O_4Si$, 28%), ammonia solution ($NH_3\cdot xH_2O$, 28–30%), lead nitrate ($Pb(NO_3)_2$) and ammonium nitrate ($NH_4NO_3$) were purchased from the Aladdin Industrial Corporation (Shanghai, China). All chemicals were analytical grade (AR) and used as received without any further purification. Deionized water was used throughout this study.

### 2.2. Fabrication of SNF/MNP/PS sandwich structured adsorbent

Silica nanofiber (SNF) was prepared from purified chrysotile by a physicochemical dispersing and acid leaching method. Briefly, the




**Scheme. 1.** Synthesis of SNF/MNP/PS and its application for MB and $Pb^{2+}$ adsorption and heterogeneous Fenton-like regeneration or $Pb^{2+}$ desorption process.