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Magnetic Fe_2CuO_4/rGO nanocomposite as an efficient recyclable catalyst to convert discard tire into diesel fuel and as an effective mercury adsorbent from wastewater

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ABSTRACT

Nowadays, abundance of wastes, like discard tires, and heavy metal ions contaminants, like Hg (II) ions, in water sources are big challenges for mankind. In this research, magnetic spinel Fe_2CuO_4/rGO nanocomposite was successfully prepared, instrumentally characterized and subsequently used as a catalyst to pyrolyze discard tires. This pyrolytic process was conducted, modeled and optimized using experimental design method when the process parameters, including temperature, time, particles size of tire rubber, the flow rate of inert gas (Ar), and amount of Fe_2CuO_4/rGO nanocomposite as the catalyst were controlled. In the optimized condition (401.2 °C, 20.0 mL min^{-1} Ar, 12.6 mm, 1.1 g Fe_2CuO_4/rGO, and 58.9 min), the pyrolytic products included liquid (43.3 wt%), gas (16.6 wt%) and char (40.1 wt%). These products were practically evaluated as pyrolytic fuel, combustion gas and activated carbon, respectively. As the result of this research, the pyrolytic fuel represented comparable physiochemical properties, including flash point of 47 °C, the cetane number of 49, the sulfur content of 0.09 wt%, and remaining ash of 0.01 wt%, to the commercial and Euro 5 diesel fuels. Moreover, the resulted char was activated as activated carbon by gasification process since its specific surface area (SSA) was increased from 62.0 to 1184.0 m^2g^{-1}. Moreover, the catalyst was further applied as an effective mercury adsorbent after its inefficiency with poisoning by sulfur compounds resulted from 17 repeated pyrolyses. Accordingly, the relevant conditions for pH of waste water, temperature, the catalyst amount, and exposure time were optimized as pH 7.0, 24 °C, 0.8 mg mL^{-1} and 60 min, respectively. Mercury (II) removal was modeled based on Langmuir and Freundlich isotherms models, which Langmuir isotherm was a more fitted model. Hence, mercury (II) ions could be acceptable adsorbed as a monolayer on the catalyst surface by the maximum adsorption capacity of 1250 mg g^{-1}, the affinity constant of 0.0186 L mg^{-1}, and adsorption constant of 50.074 $mg^{-0.5}$ $L^{-0.5}$ g^{-1}. In conclusion, the successful prepared magnetic nanocomposite indicated high efficient performance to pyrolyze waste tires into valuable products and subsequently to adsorb mercury ions from aqueous wastes.

1. Introduction

Large amounts of waste tires that have been produced massively per year are estimated to more than seven million tones in the European Union and USA (Zhang et al., 2015). In addition to the large production of waste tires, their chemical stability against degradation plus their adverse harmful effects toward environmental when their disposal is carried out is serious problems on mankind life. Accordingly, prompt development of green chemistry and/or (derived) green analytical chemistry modern approaches based on environmentally friendly processing, pretreating and/or determination of hazardous substances of a different kind has been taking place so far. So, some works have been recently reported in the literature. Galuszka et al. (2013) purposed a set of principles including known concepts such as reduction in the utilization of reagents and energy, and removal of waste, risk and hazard and a new idea of natural reagent usage. Alexovic et al., (2016a, 2016b)

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reviewed the technical approaches utilized for the automation of static and dynamic liquid phase microextraction (as green analytical system) in two reported works. Zandi-Atashabr et al. (2017) also reported the conversion of discard engine oil into fuel as an eco-friendly process. Also, Wieczerzak et al. (2016) reported a review of bioassays for green chemistry application to assess the environmental quality by pollutant analysis and environmental monitoring. Regarding waste tires processing, researchers have also been looking for eco-friendly methods, such as cement kilns, material recycling, and rubber industries converting them to energetic valuable products like fuels as reported by Ahoor and Zandi-Atashbar (2014). In addition, in another work by Luo and Feng (2017), the addition of degradation-inhibiting fillers in tire causes the difficulty of tire recycling, and 11 million tons of discarded tires were disposal, which may lead to serious environment pollution. Among them, pyrolytic conversion of waste tires into oil, char, and gaseous products has been studied since each product can be beneficially applied in different industries. The obtained oil, char and gas can be employed as a fuel for combustible diesel engines, activated carbon for adsorbent applications, and energy supply, respectively. These products can be found in catalytic processes reported by Ahoor and Zandi-Atashbar with $MgCl_2$ (2014), Ayanoğlu and Yumrutaş, 2016 with CaO, and reviewed report of Czajczyńska et al. (2017). The steel present in waste tires can be also used for manufacturing of steel wires. As an estimate of pyrolysis outcome, the products can be fuel oil (40–45%), carbon black (30–35%), steel wires (10–15%) and gas (10–12%). The pyrolysis conditions, especially considered catalyst can alter these values (Bičáková and Straka, 2016). Waste tires are a synthetic rubber, mainly composed of astyrene-butadiene polymer. Hence, pyrolytic oil obtained from it includes aromatic (59.3–75.6 wt%) and aliphatic compounds (19.8–37.0 wt%), can be changed by controlling process parameters of pyrolysis (Ding et al., 2015). An adverse character of the pyrolytic oil is the presence of sulfur compounds. Theses compounds are adverse products of vulcanization process in tire manufacturing, which make cross-linked bonds of rubber fibers to enhance the hardness of the tire. Thus, obtained fuel should be refined from these sulfur compounds by the desulfurization. It has been performed by various methods including shifting the boiling point by alkylation, extraction, precipitation, and physical and chemical adsorption (Al-Lal et al., 2015). The desulfurization of fuel, as a subsequent refinery process, can be avoided by applying suitable catalyst in the pyrolytic process (Ahoor and Zandi-Atashbar, 2014). This catalyst should be able to apply in the repeated cyclic process without exceeding the sulfur lever from permissive limits in most of the countries (Europe, S. Africa, China, Taiwan, Brazil, Australia, etc. - 10 ppm; Canada, USA, Chile, etc. - 15 ppm).

Graphene and graphene oxide (GO) have been widely employed for immobilizing active species on itself to catalyze reactions owing to high surface area, electrical and thermal conductivity, chemical and mechanical durability, facile surface modification and high adsorption capacity. So, Lv et al. (2016) reported direct synthesis of 2,5-diformyfuran from fructose using two-step reaction with the catalytic effect of GO without the presence of any metal. In addition, Metin et al. (2016) reported the facile formation of aniline from nitroarenes by catalytic transferring hydrogenation in the presence of FePd nanoalloy on reduced GO as the catalyst. Xue et al. (2017) also reported preparation of tunnel-like cyclopalladated arylimie catalyst as immobilized of GO to catalyze Suzuki–Miyaura coupling reaction of aryl halides (I, Br, Cl) with arylboronic acids with a very low amount of catalyst. Moreover, metal nanoparticles, as well as magnetic ones, have been paid attended, because of their high surface area-to-volume ratio, and also unique physical and chemical properties. This phenomenon can be observed by the works of Shi et al. (2016) for visual discrimination of phenylenediamine isomers using observable color changes. This is due to H_2O_2-mediated oxidation in the presence of Fe_3O_4/nitrogen-doped graphene. Sharma et al. (2016) introduced magnetic Fe_3O_4-supported nanocatalyst, as an isolable and recyclable catalyst, in organic coupling reactions. Wu et al. (2016) have reported dopamine-functionalized Fe_3O_4 as a recoverable Pd^0 support to catalyze C–C coupling reaction. Hence, Coupling these metal oxide nanoparticles with graphene nanosheets can lead to prepare nanocomposite owning additional effects, especially preventing the aggregation of nanoparticles and facile interaction of materials because of the presence of $\pi-\pi$ interactions (Saikia et al., 2016).

Mercury ions are toxic contaminants that can be present in environmental samples like water. They adversely cause some severe effects on the nervous system leading to neurological disease and disorder (De et al., 2013). They also reported that around 8 tonnes of mercury have been emitted from anthropogenic origins in a year in Canada. In addition, Yu et al. (2016) have reviewed removal of mercury by adsorption. They reported that mercury, widely emitted from electrical and industrial production including plastics, metallurgy, and electronics, has been known as one of the most toxic metals can adversely influence the health of human being because of its volatility, persistence, and bioaccumulation. Hence, mercury can be accumulated in organs and strongly interacts with biomolecules, especially with the sulfur atoms from amino acids and proteins (Toma, 2015). Hence, removal of mercury ions from water samples, especially those of daily consumption is important. Numerous materials have been reported to separate mercury (II) ions from water by magnetic nanoparticles (Dalpozzo, 2015), graphene oxide foam (Henriques et al., 2016), and coupling of them (Cui et al., 2015).

To broaden the impact of the paper, it can be explained that the researches on novel materials and their applications have been reported such as intelligent sensing (Alippi, 2016); Multi-Leap motion sensor based demonstration for robotic refine tabletop object manipulation task (Jin et al., 2016); study on key technologies of unmanned driving (Zhang et al., 2016); hybrid stochastic fractal search and pattern search technique based cascade PI-PD controller for automatic generation control of multi-source power systems in presence of plug-in electric vehicles (Padhy and Panda, 2017); and temperature sensing (Guan et al., 2016).

Herein, a new magnetic nanocomposite, Fe_2CuO_4/rGO, was prepared and applied as an efficient catalyst for pyrolytic conversion of discard tire into pyrolytic fuel as a substituent of diesel fuel. The synthesized nanocomposite was characterized using various analytical methods including Fourier transform infrared (FT-IR) spectroscopy, energy-dispersive X-ray (EDX) spectroscopy, X-Ray diffraction (XRD), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), Brunauer-Emmet-Teller (BET) analysis, microscopic monitoring of field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). All experiments were conducted based on experimental design method of response surface methodology (RSM) to optimize and model the yields of the products rather than operating process parameters. The pyrolytic fuel was also compared to commercial diesel fuel based on their physiochemical properties. The elemental composition of the feed and the products were analyzed using the elemental analyzer. The char obtained from pyrolysis was successfully activated to activated carbon. After using the catalyst in the repeated pyrolysis, it was used to adsorb mercury (II) ions from waste water in accordance with optimizing the experimental conditions.