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Response surface methodology optimization of adsorptive desulfurization on nickel/activated carbon

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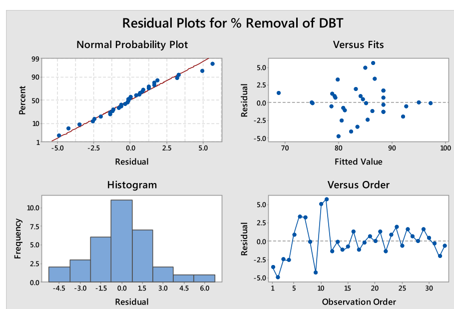
HIGHLIGHTS

- AC-Ni was prepared and evaluated for the removal of DBT using.
- Response surface method was applied to evaluate factors affecting the adsorption.
- AC-Ni was potent even after three regeneration cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

This work focuses on the optimization of the experimental factors affecting adsorptive desulfurization process in a continuous flow system using response surface methodology (RSM). To achieve that, AC-Ni was prepared by loading nickel nanoparticles on activated carbon (AC). Then, AC-Ni was evaluated for adsorptive desulfurization of DBT from model fuel using a flow system. A response surface method was applied to determine the significant factors affecting the adsorption of dibenzothiophene. A face centred central composite design (CCD) was used to statistically visualize the complex interactions of concentration, column length, dosage, and flow rate on the adsorption of dibenzothiophene. The factors having the poorest combinations in our CCD achieved a 70% removal of DBT based on the experimental analysis. However, to attain a 96% removal of DBT from a model fuel having an initial concentration of 59 ppm, a high dosage of the adsorbent (0.5 g), and a column length of 11 cm were required. In contrast, a flow rate of 50 r.p.m., and a contact time of five minutes were sufficient to achieve an exceptional removal. The optimized factors are highlighted with a composite desirability value of 0.92861. The synthesized adsorbent is relatively cheap and of double benefits to the environment solving waste management and desulfurization issues simultaneously.

1. Introduction

Response surface methodology (RSM) is a collection of mathematical and statistical techniques useful for developing, optimizing, and improving products and industrial processes. It is highly useful when many factors affect production, yield, or percent removal of a particular process. RSM initiated from the design of

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experiment (DOE) is used to determine the significant factors affecting an experiment. It aims at reducing the number of experimental runs while maximizing output through the data generated. The data can be used to develop empirical models that correlate the response to the experimental factors. The model facilitates the search for a better process response that is validated through experiments. The model iterates till an optimal process is identified or the limit of experimental resources is reached [1]. Types of symmetrical experimental design include three level factorial design, central composite design (CCD), Doehlert and Box-Behnken.

Removal of sulfur from petroleum products is an important step in the refining process. Sulfur compounds are found concentrated in the heavy part of crude oil as mercaptans, sulfides, disulfides and thiophenes. Consequently, dibenzothiophene and other refractory sulfur compounds inactivate catalysts used during the refining process, corrode refining equipment, and lead to the deterioration of air quality upon combustion, affecting public health and the ecosystem [2,3]. These effects are the major reasons why countries around the world have set regulations to lower the legal limits of sulfur in all kinds of petroleum products. In the US, the Environmental Protection Agency (EPA) has mandated 15 ppm (wt) as the allowable sulfur concentration in highway diesel since 2006 and the limit will be less than 10 ppm by 2017 [4]. However, attaining such a regulation is technically challenging because the conventional hydrodesulfurization (HDS) technique cannot achieve the target regulation, and poorly isolates the aromatic refractory sulfur compounds from fuel. Additionally, HDS is uneconomical due to its demand for high temperature and pressure and a high dosage of catalyst [5,6]. Several techniques have been developed to address the limitations of HDS, the most notable of which are: oxidative desulfurization, biodesulfurization, ionic liquid desulfurization, membrane separation, and adsorptive desulfurization [7,8]. The adsorptive desulfurization has several advantages over other techniques due to its facile and mild operating conditions. Moreover, its ability to isolate the refractory sulfur compounds efficiently using relatively cheap adsorbents has made the technique widely appreciated. The focus of researchers in the past decades was the search for more porous adsorbents that will be reasonably cheap, highly selective, consistently reliable, productively efficient, and easily regenerable [9,10].

The known adsorbents used in desulfurization include zeolites, modified bentonite and montmorillonite clay, alumina, zirconia, silica and different carbon materials such as activated carbon, graphene, graphite oxide and single wall carbon nanotube [11–14]. Of all the adsorbents, activated carbon proves to be amenable and susceptible to modifications. Besides, AC has a high surface area, a high adsorptive capacity, easily regenerated, and can be synthesized from a variety of sources such as sewage sludge, biochar, waste rubber tires, wood, lignocellulosic biomass, and animal bones [15,16]. Modifying AC with metals, metal oxides, and oxidizing agents has been investigated for adsorptive capacity to sulfur compounds. AC has been modified by various species for the removal of DBT including zinc, nickel, silver, copper, cobalt, and zirconium [17–19]. Nickel is considered the most effective in enhancing the adsorption efficiency of the activated carbon, partly due to its ability to easily react with sulfur to form NiS [20]. The formation of NiS initiates a cascade of reactions with the functional groups on the activated carbon surface facilitating the efficiency of the adsorbent.

Rubber tires are non-biodegradable materials indispensable to our transportation system. One billion waste rubber tires (WRTs) are generated yearly and four billion WRTs currently sit in the landfills according to a report by world business council for sustainable development [21,22]. The use and disposal of rubber tires present a serious challenge worldwide because they exert a significant pressure to the landfill linings at the termination of their use posing serious pollution problems through leachates, associated fire outbreaks, serious land management impacts, and a possible public health disruption. Despite their recalcitrant nature, the quest for management alternatives has been the focus of so many companies worldwide.

This study addressed the disposal issue of WRTs by converting the waste materials to AC. The synthesized AC was loaded with nickel nanoparticles and then evaluated for adsorptive desulfurization of DBT from model fuel. After a successful characterization of the synthesized adsorbents, we achieved nearly a hundred percent removal of DBT from model fuel. Therefore, we optimized the factors used during the adsorption process using CCD. Five factors namely concentration, adsorbent dosage, flow rate, contact time, and column length were varied, each having a high, a centre, and a low value. Our study addressed three pressing issues viz waste management, production of AC for various purposes, and desulfurization.

2. Experimental

The work includes the preparation of AC and AC-Ni and their characterization. The efficiency of AC and AC-Ni was evaluated in a batch system just for comparing their performance. Then, the efficiency of AC-Ni was studied in flow type with the design of experiment using RSM to investigate the related factors.

2.1. Adsorbent development

The proximate analysis of scrap tires has been reported in several studies and can be found in the review [23]. Optimized protocol for the conversion of WRTs to porous carbon has been elucidated in our previous publications [22,10]. In brief, WRTs were initially cut into small pieces, cleaned, washed thoroughly with deionized water, and dried in an oven at 110 °C for two hours. The synthesized granules were heated to 300 °C to isolate the black tire crude oil from the char. Carbonization was carried out in a muffle furnace heated under nitrogen flow at 200 ml/min at 20 °C/min to 500 °C and a holding time of 5 h. Carbon yield was 61%. Adhering organic impurities were oxidized by treating the char with hydrogen peroxide. The char was washed thoroughly with deionized water and dried at 110 °C in a muffle furnace.

The surface area and porosity of the carbon black were enhanced by activation under nitrogen flow at 200 ml/min at 20 °C/min to 900 °C and a holding time of 5 h. The final yield of AC was 58% calculated from the WRTs. The resultant AC was washed with deionized water and dried in a vacuum oven overnight. It is known that treating AC with acid helps develop the functional groups responsible for adsorption, so, 4 M HNO_3 was used to treat the AC at 90 °C for 3 h. Finally, the AC was washed with deionized water and dried in an oven at 110 °C for 24 h.

2.2. Loading nickel on AC

An impregnation including ion-exchange method was used for loading nickel nanoparticles onto the porous carbon. In a typical run, 7.0 g of HNO_3 treated AC was dispersed in 150 mL of deionized water and 100 mL ethanol by the use of a sonicator and stirred for five hours. Then, a 9.36 mL solution containing 2.96 g of nickel acetate (Ni $(C_2H_3O_2)_2{\cdot}4H_2O$ (1 M) was added drop-wise into the dispersed AC. It should be mentioned that the ratio of Ni to AC was initially studied and this ration of 10% Ni to AC provided the best performance. A 20 mL ethylene glycol was added serving as a linker between the porous carbon and the nickel particles. The mixture was stirred for two hours while maintaining the pH at 8.