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Role of synthesis process variables on magnetic functionality, thermal stability, and tetracycline adsorption by magnetic starch nanocomposite

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ABSTRACT

Poor understanding and possible control of influence of synthesis variables on intrinsic properties/characteristics, has negatively impacted full utilization of magnetic polymer nanocomposite in potential applications. This study was therefore designed to investigate the synthesis variables that control the magnetic functionality, thermal stability, yield and tetracycline adsorption by magnetic starch nanocomposite. Subsequent upon this, the study is set to further develop a goal oriented multiple response optimization (GOMRO) approach for simultaneous control of these intrinsic properties and their potential applications. Magnetic starch nanocomposite was synthesized by in-situ co-precipitation of Fe^{2+} and Fe^{3+} in the presence of soluble starch, and characterized with FTIR, TEM, XRF, and TGA/DTA. The characterization tests confirmed that magnetic starch nanocomposite was successfully synthesized. Model evaluation parameters showed that quadratic model adequately ($r^2 > 0.98$) described the experimental data for all the studied properties and tetracycline adsorption. Variance analysis of influence of quantity of starch gave F-values of 695.95, 22.43, and 134.89 for magnetic functionality, thermal stability, and tetracycline adsorption, respectively, while Prob > F gave value of < 0.0001, in each case. These data indicated that quantity of starch and ammonia volume were the dominant factors controlling the studied properties and tetracycline adsorption. For the first time, response surface methodology (RSM) was successfully applied in elucidating the adsorption interaction mechanism, as both experimental and RSM trend confirmed that π-cation interaction was the dominant interaction mechanism for tetracycline adsorption by magnetic starch nanocomposite. Besides controlling the process cost from the yield, the GOMRO approach opened additional degree of freedom on cost control by creating opportunity for manipulating the quantities of reactants for achieving a set goal.

1. Introduction

Nanostructured magnetic polymer materials have gained increasing attention in recent years with regards to emerging industrial (Konwarh et al., 2009), analytical (Chen and Li, 2012; Faraji, 2016) environmental (Kalia et al., 2014), biological and medical applications (Alexiou et al., 2006; Barreto et al., 2011; Berry and Curtis, 2003; Coffel and Nuxoll, 2015; Cole et al., 2011; Ito et al., 2005; Ruiz et al., 2013). Among the various applications, targeted drug delivery, controlled release of pharmaceuticals and treatment of chemical water pollution, are the potential applications of magnetic starch polymer nanocomposite where adsorption is the fundamental principle of operation/application.

In view of its efficiency, effectiveness, and operational cost reduction, magnetic polymers have attracted much attention for adsorption-based water treatment applications in recent times (Kalia et al., 2014). In development of effective magnetic adsorbents, effective adsorption performance, reasonable magnetic functionality, thermal stability, and acceptable level of hydrophobicity, are some of the specific criteria (Kalia et al., 2014; Kydralieva et al., 2016). These requirements are necessary due to the mechanistic processes involved in these applications. It has been established that the control of thermal behaviour, magnetic and structural functionalities of the magnetic nanocomposite, which is applied in adsorption/controlling the release of the loaded active pharmaceutical agents, is vital in the design of magnetic nanocomposite drug carriers (Brazel, 2009; Klouda, 2015). In a similar vein, other parameters like surface area, particle size, particle size distribution, thermal stability, and others, are very important in assessing the suitability of any magnetic nanocomposites for most potential applications.

In view of the wide potent and proven adsorption applications of magnetic starch nanocomposites, there is obvious need to develop a

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reliable method for simultaneous control of these vital intrinsic properties of magnetic starch using standard synthesis route, and establish their role in the adsorption of molecules from aqueous media. However, each of the intrinsic properties is being controlled by complex combination of series of synthesis process parameters. Thus, the influence of the synthesis process parameters needs to be understood for effective control of the relevant properties of the magnetic nanocomposite. The use of response surface methodology (RSM) in combination with experimental design (DoE) has proved to be a method of choice for investigating the effect of process variables on certain properties of a material, with one set of experiments (Ebrahimzadeh et al., 2012). The RSM, which is a more reliable advanced multivariable (MVA) optimization technique, enables determination of the optimum operating conditions in an effective manner and evaluates the effect of interaction of multivariable system using statistical methods compared to a one-factor/variable-at-a-time (OFAT) experimental design, which is time consuming and does not cater for the interactive effects of variables (Nwabueze, 2010). Despite the exploits of RSM for optimization of process conditions, most RSM optimizations reported in literature dealt with single response and sequential multiple response optimization, where the optimum condition for each of the properties of interest, is optimized as an independent response, without respect to the effect of the chosen optimum condition to other properties of interest (Myers et al., 2016). However, in real-time engineering applications, optimum conditions for one response are often different for different responses, and hence, simultaneous multiple optimization is more desirable.

It is against this backdrop that this study was set out to investigate the role of the intrinsic properties of magnetic starch on tetracycline adsorption and develop/apply a methodology for simultaneous multiple response optimization (tuning) of the magnetic functionality, thermal stability, % synthesis yield, and tetracycline adsorption of magnetic starch nanocomposite. The specific objectives were to: (i) synthesize and characterize series of magnetic starch nanocomposite specifications using different synthesis conditions (ii) investigate the influence of the synthesis conditions on yield, magnetic functionality, thermal stability and tetracycline adsorption of the nanocomposite, (iii) elucidate the mechanism of tetracycline adsorption based on the role of the components of magnetic starch, and (iv) develop a reliable optimization method for simultaneous control (tuning) of these important characteristics and adsorption application of the magnetic starch nanocomposite with regards to synthesis conditions and cost minimization. Considering the recent trend and challenges in combating pharmaceutical water pollution, tetracycline was selected for this study due its widespread applications in human health and livestock management, and possible evolution of antibiotic resistant bacteria which in turn may minimize the effectiveness and therapeutic value of antibiotics.

2. Experimental

2.1. Materials

Soluble starch was purchased from Merck KGaA, Darmstadt, Germany. Ferric Chloride hexahydrate, Ferrous Sulphate heptahydrate, and ammonia solution were purchased from Associated Chemical Enterprises (ACE), South Africa. Ethanol and other reagent grade chemicals were purchased from LabChem Gauteng, South Africa. Ultrapure water was processed with Siemens LaboStar model purification machine. Mylar XRF polyester film (6 μm thickness) was supplied by Oxford instruments, United Kingdom.

2.2. Methods

2.2.1. Synthesis of magnetic starch nanocomposite

The magnetic starch nanocomposite was synthesized in three-necked round bottom flask (reactor) mounted on a temperature-controlled heating mantle. Firstly, aliquot of 80 mL of distilled water was degassed by applying vacuum for about 20 min at a predetermined temperature variable of 40, 60, 80 °C, to remove all traces of oxygen in the reactor. Thereafter, nitrogen gas was continuously passed through the reactor system to create an inert atmosphere needed for the synthesis reaction. At this juncture, 3.1 g of Ferric Chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) and 2.1 g of Ferrous Sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$) were added into the reactor and stirred at about 150 rpm/min for about 10 mins to enable the complete dissolution of the salts, before introducing aliquots of 25% aqueous ammonia (1.0, 20.5, and 40 mL) into the reactor while the stirring continued. After 5 mins of introducing aqueous ammonia, aliquots of soluble starch (0.50, 3.25 and 6.00 g) were introduced into the reactor and stirring was allowed to continue for a predetermined time (30, 45, and 60 mins), after which the reactor was dismantled to harvest and process the synthesis product. The synthesized magnetic starch nanocomposite was copiously washed with water until a neutral pH was obtained, and thereafter washed with ethanol to remove any trace of organic contaminants. The nanocomposite was thereafter dried in a vacuum oven at the temperature of 50 °C and negative pressure of 0.8 bar for 18 h. The dried magnetic starch nanocomposite was stored in a desiccator until when needed.

2.2.2. Experimental design for synthesis of magnetic starch and statistical analysis

In this study, the RSM design known as central composite design (CCD) was used to study the influence and interaction of the synthesis variables for the synthesis of magnetic starch nanocomposite. Based on the synthesis procedure, the independent variables selected were the quantity of starch (x_1), ammonia volume (x_2) reaction time (x_3) and reaction temperature (x_4). The number of experimental runs (N) generated from a partial factorial design for the four variables consisted of sixteen factorial points, eight axial points and six replicates at the centre points, indicating that altogether 30 experiments were required (Table 1), as calculated from Eq. (1)

$$N = 2^n + 2n + n_c \tag{1}$$

where n is the number of variable factor (which is 4 for the present study) and n_c is a constant which has a value of 6

The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. The four responses (Y) were magnetic functionality (Y1), thermal stability (Y2), tetracycline adsorption (Y3) and% yield (Y4) of the synthesized nanocomposite. Each response was used to develop an empirical model which correlated the response to the four synthesis variables using a second-degree polynomial equation as given by Eq. (2)

$$Y = b_0 + \sum_{i=1}^{3} b_i x_i + \sum_{i=1}^{3} b_{ii} x_i^2 + \sum_{i=1}^{3} \sum_{j=i1}^{3} b_{ij} x_i x_j \tag{2}$$

where Y is the response variable (magnetic functionality, thermal stability, antibiotic adsorption, and% yield), b_o is the constant coefficient, b_i the linear coefficient, b_{ii} the quadratic coefficient, *bij* the interaction coefficient, while x_i and x_j are the coded variables which determine the response Y.

2.2.3. Magnetic functionality, thermal stability, % synthesis yield and tetracycline adsorption response assessment

The responses of magnetic functionality, thermal stability, % synthesis yield and tetracycline adsorption were independently assessed with relevant experimental procedures.

The magnetic functionality of the magnetic nanocomposite was assessed by determining the percentage of magnetite (Fe_3O_4) in the magnetic starch nanocomposite. The% Fe_3O_4 content was measured with a Rigaku NEX-QC model X-ray fluorescence (XRF) machine, using magnetite analysis application mode.