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Uptake of pantoprazole drug residue from water using novel synthesized composite iron nano adsorbent

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ABSTRACT

Pantoprazole drug residue is present in some water bodies leading to toxicity to human beings. The uptake of pantoprazole drug residue from water is reported on composite iron nano adsorbent. Adsorbent was prepared by green method and characterized by FTIR, XRD, SEM, TEM and EDX techniques. The pantoprazole concentrations in adsorption experiments were determined by HPLC on new generation Sunshell C_{18} column (150 × 4.61 mm; 2.6 μm). The optimized parameters were 30.0 min., 50 μg L^{-1}, 7.0, 1.0 g L^{-1}, and 25.0 °C as contact time, concentration, pH, adsorbent amounts and temperature. The data obeyed Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms. ΔG° values were −9.53, −9.57 and −9.62 kJ/mol at 20, 25 and 30 °C temperatures. ΔH° and ΔS° values were −3.39 and 20.19 × 10^{-3}. These magnitudes showed favorable and exothermic adsorption. Pseudo-first-order and liquid film diffusion mechanisms of the adsorption were reported. The reported adsorption method was fast, environmental friendly and low-priced due to its nature to be applicable under natural conditions of water resources. The developed method may be applicable for the removal of pantoprazole drug residue in natural water resources at pH 7.0 with low amount of adsorbent and contact time. The adsorption method may be used for pantoprazole removal from any water body at large and economic scale.

1. Introduction

Nowadays, water contamination by drug residues is a serious concern. The drug residues present in water enter into our body and disturb several biological activities. The most important effecting biological activities are hormonal, enzymatic and genetic [1]. Pantoprazole is among top twenty selling drugs in the world under various trade names. This drug is used to treat stomach and esophagus problems such as acid reflux and damage to the esophagus. It is also used for the treatment of Zollinger–Ellison syndrome [2]. Besides, this drug is also prescribed frequently in combination therapy with antibiotics, profens and others; to avoid the digestive system problems [3]. In this way, the rate of consumption of pantoprazole is quite high worldwide. It is very important to mention here that pantoprazole has also several side effects. The severe side effects include uneven heart beats, muscle cramps, muscle weakness, limp feeling, feeling jittery, diarrhea, cough or choking feeling, memory problems, confusion, headache, loss of appetite, weight changes, nausea, vomiting, dizziness, drowsiness, joint pain and fracture and insomnia [4,5]. Besides, long term use of this drug results in hypomagnesia, osteoporosis, bone fracture and poor absorption of vitamin B-12, ampicillin esters, ketoconazole, atazanavir, iron salts, mycophenolate moftetil and certain minerals. Moreover, long term use of pantoprazole has sown carcinogenic and gastrointestinal tumors in rodents [6–12].

It is worthy to mention here that pantoprazole is contaminating our water resources. This drug residue has been reported at Granada city metropolitan areas, South of Spain [13]. Besides, this drug residue has been found in other water bodies at different places of the world [14–16]. Therefore, the removal of pantoprazole drug residue from water is demanding in the present scenario. It is important to emphasize that there is no method available for the removal of pantoprazole from water. Among many removal methods, adsorption is considered as the best one due to its many characteristic features [17–20]. Presently,

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nano adsorbents are supposed as the best one owing to their unique features of adsorption. Moreover, these adsorbents have good capacities to adsorb different contaminants [21]. Therefore, the attempts were made to prepare and characterize composite iron nano adsorbent for the uptake of pantoprazole drug residue from water. The results are described in this article.

2. Experimental

2.1. Chemicals and reagents

All the chemicals and reagents used were of HPLC and A.R. grades. Acetonitrile, methanol, 2-propranolol, ethanol, triethylamine, acetic acid and *n*-hexane were supplied by Merck, Mumbai, India. Black tea was collected from local market. Ferrous sulfate, carboxymethyl and cellulose epichlorohydrin were supplied by Qualigens Mumbai, India. Millipore water was collected from Millipore-Q, Bedford, MA, USA system. Pantoprazole standard was obtained from Sigma Aldrich Co., USA. Polypropylene membrane (pore size 0.1 μm) was supplied by GVS Filtration Technology, Italy.

2.2. Instruments

All the experiments were carried out on thermostatic water bath shaker and magnetic stirrer. The concentrations of pantoprazole were determined by HPLC system of Shimadzu (Japan) having solvent delivery pump (LC-10 AT VP), manual injector, UV–VIS detector (SPD-10 A) with system controller (SCL-10AVP ver 5.33) and Class VP software. New generation Sunshell C_{18} (150 × 4.61 mm; 2.6 μm) column was of Chromanik, Japan. As well, other equipments were sonicator, digital pH meter, centrifuge machine, weighing balance, UV–Visible spectrophotometer.

2.3. Synthesis of composite iron nanocomposite adsorbent

2.3.1. Biosynthesis of iron nanoparticles by green method

Black tea (30.0 g) was heated with 500 mL water at 80 °C for 1 h. After cooling, it was filtered using Whatman no. 1 filter paper. Tea extract was mixed with 100 mM ferrous sulfate solution (2:1, *v*/*v*) with continuous shaking for 1 h. The color from faint yellow to blackish brown was seen; indicative of iron nanoparticles formation. Ion nanoparticles were separated by centrifugation followed by washing with water. These were dried in air and rehabilitated into powder form.

2.3.2. Preparation of composite iron nano adsorbent

Iron nanoparticles (1.0 g) were mixed with epichlorohydrin (1.5 mL) and 20% acetic acid (20 mL). The mixture was shaken for 24 h with addition of carboxymethylcellulose (CMC) (1.0 g) with continuous stirring for 5 min. Reaction was carried out for 24 h. The product was dried at 60 °C.

2.3.3. Characterization of composite iron nano adsorbent

The prepared composite iron nano adsorbent was characterized by FTIR, XRD, TEM, SEM and EDX methods.

2.3.4. Preparation of pantoprazole solution

Pantoprazole solutions were prepared of 10–70 μg L^{-1} concentrations. The solutions for HPLC analysis were prepared of 1–10 μg L^{-1} concentrations.

2.3.5. Adsorption studies

The batch mode was carried out in thermostatic water bath shaker. The composite iron nano particles were separated by centrifugation. HPLC was used to determine the equilibrium concentrations of pantoprazole. Adsorption isotherms were carried out at 10–70 μg L^{-1} concentrations, 5–60 min. Contact time, 0.1–2.0 g L^{-1} dose, 3–9 pHs and 20.0–30.0 °C temperatures. Thermodynamics and kinetics parameters were determined by the different models. Equilibrium concentrations of pantoprazole were calculated using the following formula.

$$C_e = (C_i - C_t)/m \quad (1)$$

where, C_i, C_t, C_e and m are the initial, at time (t) and equilibrium amounts (μg L^{-1}) of pantoprazole and weight of adsorbent (g L^{-1}). The percentage removals of pantoprazole were determined by the following equation.

$$\%\text{Removal} = [(C_i - C_t)/C_0]100 \quad (2)$$

where, C_i and C_t show the usual meanings.

2.3.6. Kinetics studies

The kinetics study of pantoprazole was completed by uptake at various time periods. The various concentrations of pantoprazole were shaken with exact amount of composite iron nano adsorbent till equilibrium achieved. Remaining pantoprazole was monitored by HPLC. Erlenmeyer flasks (100.0 mL) with exact and known concentrations of pantoprazole were shaken on thermostatic water bath shaker. The solutions were centrifuged and the supernatants were determined for pantoprazole. The blank experiments were done for the determination of the experimental errors.

2.3.7. HPLC analysis

The various amounts of pantoprazole were analyzed by HPLC as described above. The separation was ascertained using new generation Sunshell C_{18} (150 × 4.61 mm; 2.6 μm) column. The solvent system was acetonitrile:phosphate buffer (10 mM, pH 7.0) (30:70, *v*/*v*) at 1.0 mL min^{-1} flow rate (detection at 220 nm). The solvent system was filtered and degassed every day before application. Chromatographic parameters *viz.* capacity (k), separation (α) and resolution (Rs) factors were calculated using general HPLC equations.

3. Results and discussions

3.1. Biosynthesis of iron nanoparticles using tea extract

Iron nanoparticles were prepared by green methods [22,23]. The polyphenol and caffeine molecules present in tea extract have antioxidant properties. These acted as capping and reducing molecules. Iron nanoparticles [Fe(II) to Fe(0)] were prepared with 90% yield.

3.2. Preparation of composite iron nano adsorbent

The composite iron nano adsorbent was synthesized from iron nanoparticles and carboxymethyl cellulose using epichlorohydrin as cross linker. The composite iron nano adsorbent was having 90% yield. First of all, epichlorohydrin had reacted with iron nanoparticles given that chloro functional group for additional reaction with carboxymethyl cellulose. Oxygen group of carboxymethyl cellulose had reacted with chloro group of epichlorohydrin; following composite iron nano adsorbent.

3.3. Characterization

The synthesized composite iron nano sorbent was characterized by FTIR, XRD, TEM, and SEM–EDX methods. The results are described herein.

FT-IR was used to ascertain the functional group of composite iron nano adsorbent. The peaks were in the range of 4000 to 400 cm^{-1}. The wave numbers 3460 cm^{-1} and 1637 cm^{-1} corresponded to hydroxyl and ketonic groups. Wave numbers 1058 cm^{-1} corresponded the turnout of an alcoholic C–O stretching. These results established the