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Cadmium removal and recovery from aqueous solutions by novel adsorbents prepared from orange peel and Fe_2O_3 nanoparticles

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ABSTRACT

An agricultural waste-orange peel powder (OPP) was successfully modified into a novel magnetic nano-adsorbent (MNP–OPP) by co-precipitating it with Fe_3O_4 nanoparticles (MNP) for cadmium ion removal from aqueous solutions. Characterization of MNP–OPP by FTIR, SEM, XRD, TEM and VSM revealed the covalent binding of hydroxyl groups of MNP with the carboxyl groups of OPP, and further confirmed its physico-chemical properties favorable for metal binding. The cadmium adsorption onto MNP–OPP, MNP and OPP was tested under different pH, ionic strength, natural organic matter, adsorbate concentration, contact time and temperature conditions. Results revealed a faster kinetics and efficiency of MNP–OPP in comparison to those of MNP and OPP and further confirmed a complexation and ion exchange mechanism to be operative in metal binding. The adsorption equilibrium data obeyed the Langmuir model and the kinetic data were well described by the pseudo-second-order model. Thermodynamic studies revealed the feasibility and endothermic nature of the system. Breakthrough capacity from column experiments, adequate desorption as well as reusability without significant loss of efficiency established the practicality of the developed system. Cadmium removal was achieved at 82% from a simulated electroplating industry wastewater. The experimental results reveal the technical feasibility of MNP–OPP, its easy synthesis, recovery, economic, eco-friendly and a promising advanced adsorbent in environmental pollution cleanup.

1. Introduction

Heavy metals, because of their non-degradable, persistent and accumulative nature are toxic when present in trace amounts and are a source of environmental concern [1]. Toxicity at trace levels leading to adverse health effect is usually associated with exposure to lead, cadmium, mercury and arsenic. A wide range of industries (mining, metal processing, electroplating, electronics, etc.) release such metals into the environment in amounts that can pose a risk to human health [2]. Therefore, metal remediation of wastewater prior to discharge, is of great importance. Strict limitations imposed on metal discharge as well as the complexity of effluents make the wastewater treatment process more difficult. Moreover, dissolved and sorbed organic matter like humic acid exists ubiquitously in natural aquatic environment. Such substances, having a variety of components including quinone, phenol, catechol and sugar moieties play a vital role in controlling physicochemical behavior of metal ions [3] and thereby necessitate metal remediation in the presence of such organic materials.

Adsorption is considered an effective, efficient, and economic method for water purification [4,5]. Since the performance of an adsorptive separation is directly dependent on the quality and cost effectiveness of the adsorbent, the last decade has seen a continuous improvement in the development of effective noble adsorbents in the form of activated carbon [6], zeolites [7], clay minerals [8], chitosan [9], lignocelluloses [10], natural inorganic minerals [11], functionalized polymers [12], etc. However, most of these adsorbents are either not effective (due to diffusion limitation or the lack of enough active surface sites) or have shown problems like high cost, difficulties of separation from wastewater, or generation of secondary wastes. Considering such drawbacks, recently nano-adsorbents viz. nano-alumina [13], functionalized carbon nanotubes [14] and hydroxyapatite nanoparticles [15] have demonstrated high adsorption efficiency for metal ion removal. One such advanced class of adsorbent – magnetic nano-adsorbent with the help of an external magnetic field has been further successful in circumventing the solid–liquid separation problem usually encountered with nanoparticles. Such novel adsorbent combining nanotechnology and magnetic separation technique has not only demonstrated high adsorption efficiency due to its large surface to volume ratio, but have also shown additional benefits like ease of synthesis, easy recovery and manipulation via subsequent coating and functionalization, absence

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of secondary pollutants, cost-effectiveness and environmental-friendliness.

Till date, several magnetic nanomaterials, including maghaemite nanoparticles [16], Fe_3O_4 magnetic nanoparticles [17], Fe_3O_4 nanoparticles functionalized and stabilized with compounds like humic acid [18], amino-functionalized polyacrylic acid (PAA) [19], and various biopolymers like gum arabic [20], chitosan [21] and polysaccharides [22] have been explored for the removal of metal ions.

In this work, a novel magnetic nano-adsorbent (MNP–OPP) was developed by the surface modification of Fe_3O_4 nanoparticles (MNP) with orange peel powder (OPP) with the aim of exploring its feasibility as adsorbent for the removal of cadmium taken as a model toxic metal ion. Orange peel – a low cost, non toxic biosorbent containing active functional groups of hydroxyl and carboxyl present in cellulose, hemi-cellulose and pectin components [23,24] is selected for its better application and management for wastewater remediation.

The objectives of this study are: (1) synthesis of MNP and MNP–OPP by co-precipitation method and their characterization with respect to FE-SEM, TEM, XRD, VSM, pH_{pzc} and FTIR, (2) comparative batch adsorption study of the three adsorbents (MNP, OPP and MNP–OPP) for Cd^{2+} with respect to various environmental parameters, (3) comparative isotherm, kinetic and thermodynamic studies, (4) column, desorption and reusability studies to investigate the practical utility of the developed adsorbent and lastly (5) to presume the underlying mechanism of metal binding.

2. Experimental

2.1. Reagents

Analytical-grade salt of cadmium $[Cd(NO_3)_2{\cdot}4H_2O]$ and humic acid was obtained from M/s Merck, India. A 200 mg/L stock solution of the salt was prepared in deionized water. All working solutions were prepared by diluting the stock solution with deionized water. Deionized water was prepared using a Millipore Milli-Q (Bedford, MA) water purification system.

All reagents (ferric chloride 6-hydrate, ferrous chloride tetrahydrate, ammonium hydroxide (29.6%), NaOH, H_2SO_4, $NaNO_3$, HNO_3), nickel chloride, zinc nitrate used in the study were of analytical grade and purchased from Wiswani Chemicals. Oranges were purchased from local market. All glassware were purchased from Borosil. Before each experiment, all glassware were cleaned with dilute nitric acid and repeatedly washed with deionized water.

2.2. Preparation of the adsorbents

The orange peel was washed with water and dried in a convection oven at 40 °C for 72 h. These were then crushed into smaller particles of approximate size between 0.1 and 0.2 mm (hereafter, abbreviated as OPP). MNP and MNP–OPP were synthesized by co-precipitation method modified from Refs. [25,26]. Briefly, 6.1 g of $FeCl_3{\cdot}6H_2O$and 4.2 g of $FeSO_4{\cdot}7H_2O$ were dissolved in 100 mL water and heated to 90 °C. Solution of 10 mL of ammonium hydroxide (26%) and the solution of 1 g of OPP dissolved in 200 mL of water were added rapidly and sequentially. The pH of the reaction medium was adjusted to 10. The mixture was stirred at 80 °C for 30 min and then cooled to room temperature. The black precipitate Fe_3O_4–OPP (MNP–OPP) was collected by filtering, washed to neutral with water, dried at 50 °C for 24 h and finally stored for further use.

The bare MNP was prepared in a similar way except that no OPP was added. Characterizations of the adsorbents are described in Supporting information.

2.3. Characterization of the adsorbent

LEO 435 VP (Leo Elektronenmikroskopie GmbH, Germany) scanning electron microscopy was used for scanning the adsorbent surface. The infrared spectra of adsorbents were recorded in KBr discs on an infrared spectrophotometer (Model Perkin Elmer-1600 Series). The BET surface area of the adsorbent was measured on micromeritics ASAP 2010 (UK). X-ray measurements were performed by using a Philips X-ray diffractometer employing Ni-filtered Cu KR radiation and Ni filters. TEM images of the composite were recorded by Transmission Electron Microscope (FEI TECNAI G2 microscope operating at 200 kV). The magnetic properties were evaluated using a Vibrating Sample Magnetometer (Model 155, Princeton Applied Research).

For pH_{pzc} determination, 0.01 M NaCl was prepared and its pH was adjusted in the range of 2–12 by adding NaOH or HCl. 50 mL of 0.01 M NaCl each was put in three different conical flasks and then 0.25 g of the three adsorbents was added to these solutions. These flasks were kept for 48 h and the final pH of the solution was measured by using pH meter (Model Cyberscan 510, Singapore). Graphs were then plotted for pH_{final} vs. $pH_{initial}$.

2.4. Batch adsorption and kinetic studies

Batch adsorption of cadmium ions onto the three adsorbents (MNP–OPP, MNP and OPP) was investigated in aqueous solutions under various operating conditions viz. pH 2–11, temperatures 298, 308, 318 K for initial Cd^{2+} ion concentration of 16 mg/L.

The adsorbent suspension (10 mg) and $NaNO_3$ (0.001 M, 0.01 M, and 0.1 M) were pre-equilibrated for 1 day. Cadmium nitrate solution (16 mg/L) and HA solution (10 mg/L) were then added in the 100 mL beaker and finally placed on an orbital shaker at 200 rpm. The pH of the solution was kept constant by adding 0.1 M NaOH or 0.1 M HNO_3. After equilibrium, the samples were centrifuged. OPP was removed by filtration while MNP–OPP and MNP were removed magnetically from the solution. The residual concentration of cadmium ions was determined by an atomic absorption spectrophotometer model Z-7000 (Hitachi, Japan) at a wavelength of 228.8 nm. The concentration of HA was determined spectrophotometrically on a Specord 200 UV–visible spectrophotometer (Model UV–vis 200) at wavelength of 254 nm.

For kinetic studies, experiments were conducted with 50 mL cadmium nitrate solutions of concentrations (4 mg/L, 16 mg/L), maintained at pH 7, temperature of 318 K at different contact time of 5–240 min. The adsorption capacity for cadmium uptake, q_e (mg/g), was determined as follows:

$$q_e = (C_0 - C)\frac{V}{W} \tag{1}$$

where C_0 and C are the initial and final concentrations (mg/L), respectively, V is the volume of solution (L) and W is the weight of adsorbent (g).

All the experiments were repeated three times and average values were reported. The standard deviation was found to be ±2.12%; values of correlation coefficient were in the range 0.98–0.99.

2.5. Desorption and reusability studies

Desorption studies were carried out in 5 mL of 0.1 M HNO_3 maintained at a constant temperature of 318 K. The Cd^{2+} adsorbed MNP–OPP were placed in the desorbing medium on a rotary shaker at 200 rpm for 30 min. The residual Cd^{2+} in the solution were