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Adsorptive removal of monocrotophos from aqueous solution using biopolymer modified montmorillonite–CuO composites: Equilibrium, kinetic and thermodynamic studies

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ABSTRACT

The present study is focused on the adsorptive removal of monocrotophos (MCP), an organophosphate insecticide onto biopolymer modified montmorillonite (MMT)–CuO composites viz. MMT–CuO–Chitosan (Ch), MMT–CuO–Gum ghatti (Gg), and MMT–CuO poly lactic acid (PLA). Optimization experiments were conducted by varying five parameters viz., pH (3–12), contact time (2–30 h), temperature (10–50 °C), initial MCP concentration (20–140 mg L^{-1}) and composite dosage (5–25 g L^{-1}). The removal of MCP followed the order: MMT–CuO–PLA (83.99%) > MMT–CuO–Ch (71.6%) > MMT–CuO–Gg (62.1%) > MMT–CuO (40.8%). Equilibrium and kinetic studies revealed a heterogenous and physical mode of adsorption with the highest adsorption capacity 212.23 mg g^{-1}. This was further confirmed by SEM analysis. Intraparticle diffusion and Boyd plot suggested that film diffusion was not the sole rate limiting process. Thermodynamic studies confirmed the spontaneous and endothermic nature of the process. FTIR analysis confirmed the major involvement of amines and carboxyl groups during MCP adsorption. EDX analysis confirmed the major participation of carbon atom followed by CuO nanoparticles and Si in the process. AFM analysis confirmed the homogenous distribution of CuO nanoparticles on the surface of MMT–CuO–PLA which validated the potentiality of PLA modified MMT–CuO composite for the remediation of MCP from aqueous environment.

1. Introduction

Monocrotophos [dimethyl(E)-1-methyl-2(methylcarbamoyl)vinyl phosphate, MCP], commonly known as Azodrin, is an organophosphorus, non specific systemic insecticide and acaricide, applied on plants to control the various sucking and chewing insects in cotton, peanut, sugar cane, tobacco and other vegetable crops (Bhalerao and Puranik, 2009). MCP is extremely toxic to birds and reported to show cytotoxicity and genotoxicity (IPCS, 1993; Saleha et al., 2001; Bing et al., 2002). It is poisonous to mammals causing high irritation to the eyes and slurred speech, loss of reflexes, weakness, involuntary muscle contractions, and paralysis of the body (Smith, 1993; Anonymous, 1997) and reported as potent endocrine disrupting chemical (Tian et al., 2009). Monocrotophos affects the central nervous system by inhibiting cholinesterase, an enzyme essential for normal nerve impulse transmission (Chakravarthi et al., 2009). The residues of MCP in shallow groundwater, vegetables and food have been reported (Tian et al., 2012). Though MCP was withdrawn from many countries but it is still widely used in India. MCP at the concentration ranging from 0 to 125 mg L^{-1} was detected in the waste effluent collected from an MCP manufacturing factory located in Pune, India (Bhadbhade et al., 2002). High levels of pesticide residues have led to excessive MCP levels in the environment causing several incidents of contamination.

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There are few reports on the removal of monocrotophos using adsorbents (Shankar et al., 2004; Anandan et al., 2006). Clay minerals are good adsorbents for cationic and very polar pesticides (Cox et al., 1997; Hermosin and Perez Rodriguex, 1981). Montmorillonite (MMT), a clay mineral has attracted much attention in recent years. The high adsorption, ion exchange and expansion properties as well as high surface area, layered structure, abundance and low cost make MMT clay to be an attractive material widely used for removal of pollutants (Tong et al., 2010; Wu et al., 2011; Nesic et al., 2012; Dukic et al., 2015).

Recently, the application of composites has become a novel approach for environmental applications such as adsorption of heavy metals, dyes and herbicides (Pereira et al., 2013). Clay based nanocomposites and bionanocomposites have become the materials of increasing interest due to their nanosized structural and functional properties (Celis et al., 2012). Biopolymer based composites have gathered a lot of attraction and have many advantages over other adsorbents such as low cost, environment friendly nature and easy availability (Fosso-kankeu et al., 2014). Physico-chemical characteristics of biopolymers are also deterministic in their quality as sorbents and presence of a number of reactive groups on their chains and high reactivity adds to their adsorption capacity (Abdel-Halim and Al-Deyab, 2011).

Chitosan is a natural poly-aminosaccharide which has been proved to be an effective and promising adsorbent because of its low cost, biocompatibility, biodegradability and nontoxicity. The presence of functional groups like NH_2 and OH on chitosan ensures a high binding capacity (Ziaei et al., 2014). Gum ghatti (Gg), an anionic natural polysaccharide has been used in many industrial applications for the treatment of wastewater (Rani et al., 2012; Mittal et al., 2013). Poly-lactic acid (PLA) is considered to be as one of the most important bio based polymer due to its biocompatibility, biodegradability, compost ability and good mechanical strength (Garlotta, 2001; Auras et al., 2004).

In addition to clay (MMT) and biopolymers, oxide nanoparticles (NPs) also exhibit unique chemical and physical properties and are massively enrolled in removal of pollutants because of their limited size and a high density on their edge surface sites. NPs are biologically, thermally and chemically stable and can be used safely (Dehaghi et al., 2014).

The present study is focused on the application of biopolymer modified MMT–CuO composites for the removal of organophosphate pesticide, monocrotophos (MCP) from aqueous environment. The common biopolymers viz. chitosan (Ch), gum ghatti (Gg) and poly (lactic acid) (PLA) have been used for the preparation of biopolymer modified MMT–CuO composites. There is a report on the use of MMT–Chitosan composite as an adsorbent for the removal of herbicide clopyralid from aqueous solution (Celis et al., 2012). To the best of our knowledge, no report is available on the application of biopolymer modified composites for the effective removal of monocrotophos from the aqueous environment. The process was optimized and monitored in terms of adsorption kinetics and equilibrium employing different isotherm models for the removal of MCP. Fourier transform infrared (FT-IR) analysis was done to study the potential binding sites on MMT–CuO composites and possible functional groups involved during MCP removal. Mechanism of MCP adsorption onto the various forms of MMT–CuO composites was elucidated using SEM, AFM and EDX analysis.

2. Materials and methods

2.1. Chemicals

The chemicals viz. monocrotophos (MCP), montmorillonite (MMT), chitosan (Ch), gum ghatti (Gg) and poly lactic acid (PLA) were purchased from Sigma Aldrich Chemicals Co. (USA). $CuCl_2$, as precursor of copper was purchased from Hi media, Mumbai, India. Acetic acid, acetonitrile, ammonia and chloroform were purchased from Sisco Research Laboratories, India. Stock solutions of MCP were prepared by dissolving the required amount of insecticide in double distilled water.

2.2. Preparation and characterization of MMT–CuO composites

MMT–CuO composite was prepared according to the procedure reported in the literature (Bagchi et al., 2013) with minor modifications. Initially, fine suspension of MMT (10.0 g) was prepared in 100 ml of distilled water. To the above suspension, 1.0 M copper chloride was added under magnetic stirring. Ammonia solution was added until the formation of dark blue colour under vigorous stirring for 60 min. The precipitate containing MMT–CuO composite was centrifuged and dried for 6 h at 60 °C.

For preparation of chitosan modified MMT–CuO composite, 10.0 g MMT–CuO composite was added to 2% (v/v) acetic acid. The mixture was stirred on magnetic stirrer for 30 min after which 2.0 g chitosan (Ch) was added to the suspension, stirred for 30 min to obtain a homogenous suspension. The suspension was left overnight allowing the adsorption of chitosan on MMT–CuO composite. The suspension dried for 12 h at 60 °C.

Gum ghatti (Gg) modified MMT–CuO composite was prepared by dissolving 10.0 g MMT–CuO composite in 100 ml of distilled water followed by the addition of 1.0 g of gum ghatti and stirred on magnetic stirrer for 30 min. The pH of the solution was adjusted to 4.0 by adding 0.1 N HCl. The resulting solution was kept overnight for adsorption. After adsorption, the suspension was centrifuged, washed and dried for 12 h at 60 °C.

Poly lactic acid (PLA) modified MMT–CuO composite was prepared following the same procedure described above for the preparation of MMT–CuO–Ch. In this case, acetic acid and chitosan were replaced by chloroform and poly lactic acid respectively.

The BET surface areas of various forms of MMT–CuO composites were calculated following the standard procedure (Elwakeel et al., 2013). Thermogravimetric analysis of the MMT–CuO composites was carried out under high purity helium supplied at a purge gas flow rate of 0–1000 ml min^{-1} (Diamond TG/DTA, Perkin Elmer, USA). All samples were subjected to a 10 °C min^{-1} heating rate and were characterized between 25 °C and 800 °C. The point zero charge (pH_{PZC}) of composites was evaluated following the standard method (Charumathi and Das, 2012).

2.3. Batch adsorption studies

The experiments were conducted in 250 ml Erlenmeyer flasks at 28 ± 1 °C on a rotary shaker at 120 rpm varying the parameters viz. pH (3.0–12.0), MMT–CuO composite dosage (5.0–25.0 g L^{-1}), initial MCP concentration (20–140 mg L^{-1}), contact time (2–30 h) and temperature (10–50 °C). The samples were collected at regular time intervals, filtered and analyzed for the residual pesticide monocrotophos (MCP) concentrations using a UV–vis spectrophotometer adjusted to 232 nm.

To know the residual concentration of MCP, initially, a standard curve was drawn using the data which was obtained by varying the concentrations of monocrotophos. The sample concentrations were calculated using the linear equation of the standard curve. Verification of the analytical process was done using the high performance liquid chromatography (HPLC) analysis. The mobile phase used was acetonitrile: double distilled water in a ratio of 60:40 (v/v). The peak areas of