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Proceeding Paper

Batch Adsorption Studies Incorporating Response Surface Methodology for the Elimination of Acephate [†]

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Abstract: Banned pesticides are continuously preferred by the planters of the Idukki District irrespective of their toxicity. Among the banned ones acephate is preferred to its high solubility in water and persistent character. Unfortunately, it detriments the biota leading to neurogenic, carcinogenic and physiological disorders in fish. The plantation near to Periyar River basin is contaminated with residues of pesticides and eventually drains to the river. There is an urgent need for the removal of acephate. So, we have focused on the removal of acephate into the lab scale. Batch adsorption studies were carried onto the removal of acephate. We selected a material Fe-MMT (Fe_3O_4-montmorillonite) which is benign and possess a high adsorption capacity towards acephate. Adsorbent properties were examined by various analytical tools XRD, SEM, FTIR, and Surface area analyser. Adsorption followed Langmuir with first-order kinetic. Kinetic plots exhibited multistage adsorption indicating film diffusion and pore diffusion during the adsorption or the mechanism of adsorption is chemisorption, physisorption, and Lewis's acid-base interaction. Response surface methodology involving CCD (central composite design) was extracted to maximize the adsorption of acephate onto Fe-MMT. Dosage and concentration seem to be the major parameters that influenced the adsorption. Adsorption achieved peak (83.18%) at optimum conditions corresponding to pH 6, initial acephate concentration 2 mg/L, and adsorbent dosage corresponding to 0.5 g/L.

Keywords: acephate; magnetically modified montmorillonite; multistage adsorption; response surface methodology

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1. Introduction

Acephate, (O, S dimethyl acetyl phosphoroamidothioate) an organophosphorous pesticide and its metabolite have immense potential to harm the biota. Acephate residues is present in the cardamom plantations of Periyar River basin and eventually found in river in ppb ranges [1]. Additionally, residues is present in blood, breast milk thereby transferring to the new born [2]. Immediate removal is mandatory as it effects the biodata leading to death. Among several techniques adsorption is preferred due to easy and cost-effective nature. Then selection of adsorbent paves another important role in the adsorption process. Fe-MMT was selected as the adsorbent for the removal of acephate as it is environmentally benign in nature [3]. The paper focussed on the properties of the adsorbent characterised by SEM, FTIR and surface area analyser and the adsorbent performance for the removal of acephate was evaluated.

2. Materials and Methods

FTIR spectra of the samples obtained using spectrometer (500–4000 cm^{-1}). XRD experiments were carried out using diffractometer (Make: PAN Analytical Philips, Netherland, and Model: XPERT-PRO). Morphology was studied by SEM (Make: TESCAN, Model: VEGA 3 LMU), chemical composition was evaluated (EDX). Surface area by surface area analyser (Make: Micrometrics, Model: Tristar II 3020 Version 3.02, USA). The concentration of acephate was measured with the help of a UV-Vis spectrophotometer (Make: Shimadzu, Japan, Model: UV-1800). Montmorillonite was purchased from Sigma-Aldrich Company Response model and Central Composite Design were employed to investigate the effect of adsorption efficiency of acephate onto Fe-MMT.

3. Results and Discussions

Montmorillonite exhibits typical diffraction peaks at 2θ= 19.5, 26.7, and 40.04 and additional peaks at 2θ = 26.5 and 47 corresponding to silica and aluminum. Diffraction peaks at 2θ of 36 and 42 indicates the presence of magnetite suggesting that the modified phase is magnetite (Figure 1a) which led to a dramatic increase in the adsorption efficiency to 87% rather than the bare MMT possessing 60% adsorption capacity. FTIR interpretation revealed that Fe-MMT exhibited strong characteristic peaks at 536 cm^{-1}, 1438 cm^{-1} in addition to 3377 cm^{-1}. Bands at 520–570 cm^{-1} represents Fe-O stretching vibration (symmetrical), band at 3377 cm^{-1} are due to Fe-OH (Figure 1b). SEM image indicates flower like morphology with EDX spectrum indicating rise in the content of Fe (Figure 1c) which improved the material adsorption capacity. Figure (1d) pictures the adsorption-desorption isotherms of Fe-MMT. The BET surface area of MMT (256 m^2/g) is higher than that of modified material (28 m^2/g) highlighting chemical adsorption onto Fe-MMT rather than physisorption.

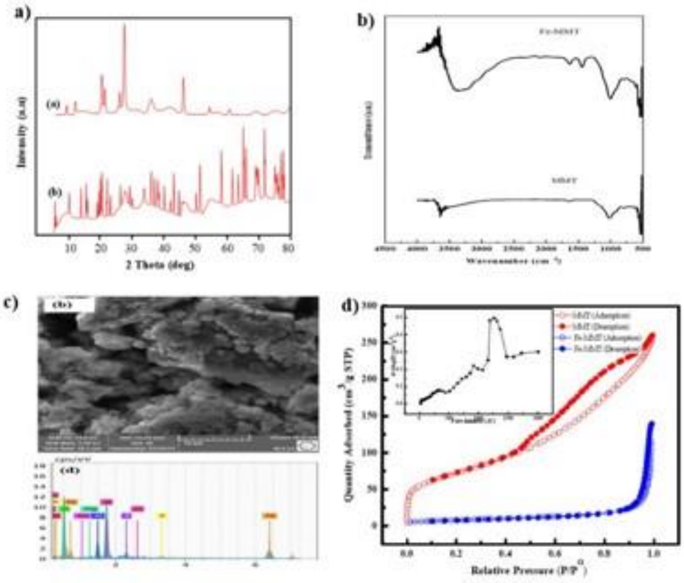

Figure 1. Images of (**a**) XRD (**b**) FTIR (**c**) SEM-EDAX (**d**) N_2 adsorption-desorption isotherms of Fe-MMT.

4. Batch Adsorption Studies

Optimization of Parameters for Acephate Adsorption

RSM (Response surface methodology) based on the central composite design (CCD) was employed to examine the performance of adsorption. CCD was opted to achieve accurate predictions around extremes of the factors. Concentration, pH, and dosage were the factors, which were identified as key parameters contributing to adsorption. Response surface plots were generated using design expert, for the determination of the effect of the input factors on the responses. pH parameter was optimised for the batch adsorption of acephate onto Fe-MMT by testing with pH (1–10) [4]. Figure 2a observed acidic medium favoured the adsorption and the peak of adsorption was achieved at 5. As the pH increase from 5 to 8 the adsorption of acephate decreases. The reduced adsorption of acephate onto clay may be due to the electrostatic repulsion between the adsorbent and the adsorbate. Adsorption increased with an increase in initial acephate. Quantity of adsorption increased with an increase in initial acephate concentration and was found to be 0.9, 2.175, 4.2, 5.925, and 7.4 mg/g for initial acephate concentration of 2, 5, 10, 15, and 20 mg/L respectively. Dosage is another vital factor that influenced the adsorption of acephate onto Fe-MMT. As dosage increases (0.1–0.5) adsorption increases and the peak of adsorption is reached at 0.5g/L with an efficiency of 90%. Temperature [5], another parameter effects the adsorption. As temperature increases, adsorption efficiency also enhanced (endothermic nature) [5].

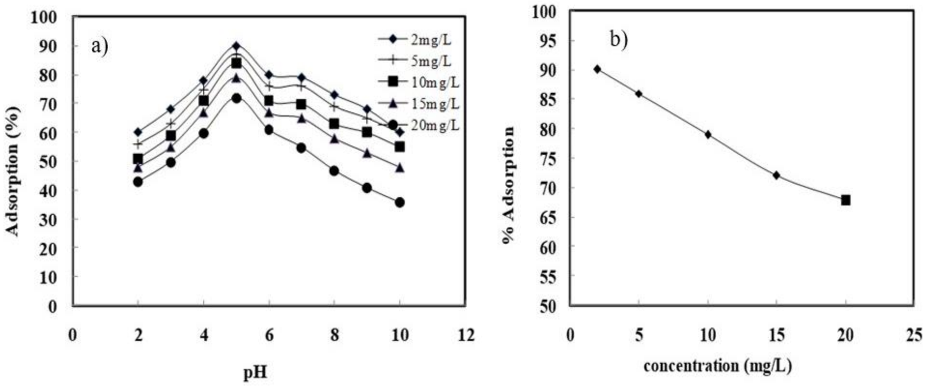

Figure 2. Effect of (**a**) pH and (**b**) initial acephate concentration on the adsorption of acephate onto Fe-MMT.

5. 3D Response Surface Plots

pH, dosage, and concentration significantly influenced onto the adsorption of acephate by Fe-MMT and are summarised in Figure 3. Figure 3 reveals the synergistic effect of two parameters on the adsorption capacity of acephate onto Fe-MMT, the other parameter was retained at the zero level. According to Figure 3, the concentration and adsorbent dose are the most influential factors on the adsorption capacity. Meanwhile, pH contributes partly to the adsorption results. It was found that higher dosage and lower concentration gave the highest adsorption capacity.

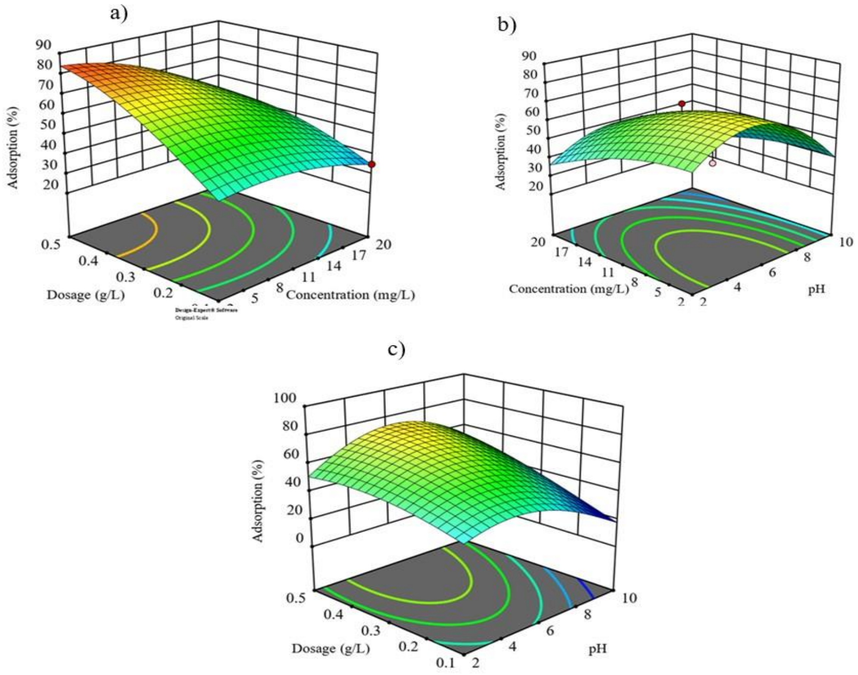

Figure 3. Effect of (**a**) pH and (**b**) initial acephate concentration and (**c**) dosage on the adsorption of acephate onto Fe-MMT.

6. Adsorption Kinetics, Isotherm, and Thermodynamic Parameters

Lagergren pseudo-first-order, and pseudo-second-order, Elovich, and Weber and Morris's Intraparticle diffusion models were scrutinised to study the kinetics of adsorption. Kinetics of adsorption and the model of isotherm obeyed pseudo-first –order ($R^2 > 0.99$) and Langmuir model (adsorbed homogeneously on a monolayer surface of Fe-MMT). The maximum Langmuir capacity at pH 5 and 303 K is 13.66 mg/g. Thermodynamic parameters revealed that the adsorption is endothermic (ΔH^0 = 22.855kJ/mol, ΔS^0 = 105.920 J/K) and spontaneous in nature (ΔG^0 = −7.99, −8.087, 9.245, and −10.357 kJ/mol)

7. Mechanism of Adsorption

Mechanism of adsorption corresponds to chemisorption (positive group of phosphorous in acephate and deprotonated silanol group), physisorption (hydrogen bearing amino group of acephate and the oxygen atoms of MMT), and Lewis's acid-base interaction nitrogen atom of the amino group of acephate and Al^{3+} montmorillonite.

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