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Extensive Employment of Chemically Treated *Elephas maximus* Dung in Sequestration of Oxyfluorfen: Batch, Isothermal and Kinetic Modeling

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ABSTRACT

Presently, one of the most employed herbicides is Oxyfluorfen, used to control the growth of annual broadleaf and grassy weeds. On the other hand, effective disposal of redundant *Elephas maximus* dung (EMD) is important for environmental protection and utilization of resource. Aim of the article is focused on sequestration of Oxyfluorfen from aqueous media employing *Elephas maximus* dung (EMD), a natant biowaste, seldom reported elsewhere. Experimental setup is planned via batch mode under varying operational factors viz., particle size, initial Oxyfluorfen concentration, MEMD dosage, contact time, pH and temperature. The obtained results validated through isothermal and kinetic models imply notable fit in of Langmuir isotherm and Pseudo II Order kinetic models with a maximum of 88.9% oxyfluorfen removal. Based on the derived observations, supported by theoretical calculations, it is concluded that *Elephas maximus* dung (EMD) powder, possess maximum potential towards chelation of Oxyfluorfen, thereby succoring an alternate eco-friendly process.

Keywords: Redundant, Adsorption, Oxyfluorfen, Isotherms, Herbicide, Biowaste, Operational factors.

INTRODUCTION

Pesticides have an outstanding importance in agriculture as to improve productivity of crops[1]. In their absence, crop yield would drop linearly resulting in the price hike of commodities, a relevant ratio. Typically, herbicides are xenobiotic, toxic and complex to be biodegraded. They are strongly adsorbed by different types of soil, but later, after a certain period they are prone to leaching into surface or groundwater[2]. Oxyfluorfen, a non-ionic halogenated organic herbicide issued in controlling annual broadleaf and grassy weeds in a variety of tree fruit, blackberries, sunflowers and field crops[3,4]. Oxyfluorfen is classified as low acute toxicity compound by the World Health Organization (WHO) and by the Environmental Protection Agency (EPA). Limit of oxyfluorfen is 0.01–0.27 μg/L in Normal water according to US EPA standards. Oxyfluorfen is a type of contact herbicide[5] which requires sufficient light for its activity through the formation of free radical via inhibition of protoporphyrinogen oxidase, in turn curbing necrosis in plants[6,7]. However, it is considered as lethal to aquatic organisms, further, impose adverse impact on terrestrial plants and ecological systems at all levels[8]. Thence, few inevitable treatment methods are of prime necessity before discharging the wastewaters into landfills and aquifers[9]. Several methods reported for removal of pesticides from wastewaters include anaerobic decolourisation, chemical oxidation, reverse osmosis, ion exchange, adsorption, electro-coagulation, sono electrolysis, UV assisted Electrolysis and biological treatment methods, among which adsorption using biomaterials is referred to as an effective method[10]. This is due to its initial cost, simplicity of design, easy operation, insensitivity to toxic substances, sludge free clean process and high adsorption capacity[11].

Utilization of biomaterials viz., plant/animal/industrial/marine wastes as pesticides scavengers is accountable in terms of their chemical and thermal stabilities. The current investigation is focused on the employment of a seldom reported material, elephant dung for the removal of Oxyfluorfen from aqueous media. Elephant dung disposal leads to dumped solid waste generation and air pollution once burnt. In view of this, expediate use of elephant dung as a bio-sorbent not only minimizes their litter problem, but also favors solution for trapping excess pesticides leachates. Further, the zero or negligible cost of elephant dung makes this project feasible and cost effective for the removal of Oxyfluorfen, a herbicide from aqueous solution.

The study objective comprises of

- Determination of EMD sorption capacity in chelating Oxyfluorfen
- Best optimization of operating factors viz., particle size, adsorbent dose, initial pesticide concentration, pH, temperature, co-pesticides and contact time on the sorption process
- Ascertainment of adsorption/desorption and regeneration parameters
- Applicability of isothermal and kinetic data pertaining to Oxyfluorfen–EMD system.

MATERIALS AND METHODS

Adsorbent–Preparation and Characterization

Elephas maximus dung (EMD) generally available in large quantities throughout the year in the western districts of Tamil Nadu and Kerala[12,13] was collected for the present work from the forests of Sathyamangalam, Erode, TamilNadu, India. Later, the dried dung was hammered into smaller pieces, washed off the impurities with doubly distilled water, completely sun dried and arid for 3 h in hot air oven to ensure moisture elimination. The obtained lumps were crushed, pounded in electrical mixer and assorted into varying mesh sizes (22, 36, 52, 76 & 85 BSS) using molecular sieves which are scientifically tested[14]. Following, these sized materials were immersed in boiling 0.1N HCl/NaOH, for 3 h each, rinsed in DDW to neutralize pH, oven dried and labeled as MEMD (Modified Elephas maximus dung) in air locked containers. Images of pulverized EMD and MEMD (85BSS) are depicted in Fig. 1 a and b[15].

Fig. 1a. Pulverized EMD

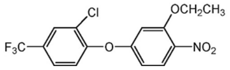
Fig. 1b. Modified EMD (MEMD)

MEMD (raw and granular–85 BSS) was characterized using Binocular Microscope to categorize the particle size (Ocular micrometer [OLYMPUS make, Model CX21I]), Surface Analyzer to derive Brunauer, Emmett, Teller (BET)/Barrett, Joyner, Halenda (BJH) plots (Micrometics, BEL, Japan, Inc) for determination of surface area/porosity/pore volume of MEMD. Raw and OX-loaded MEMD was subjected to to analyze the presence of surface functional groups by Fourier Transform Infra-red Spectroscope (Shimadzu Infrared Spectrometer), determination of surface topography/elemental composition through Scanning Electron Microscopy/Energy Dispersive X-Ray Analyzer (Automated JOEL JEM–6390 Scanning Electron Microscope under a vacuum of 1.33* 10^{-6}m Bar) and to assess the thermal stability of sized material employing Thermogravimetry/Differential Thermal Analyzer (Perkin Elmer, USAA of range 0–1000°C). Specific analysis were studied for pre and post experimental run MEMD samples. Physico chemical properties of MEMD were determined by adopting various standard operating procedures, to mention a few are Drift method and Surface acidic group was determined by Boehm titration studies.

Oxyfluorfen–Preparation of Standards

Oxyfluorfen of high technical quality was purchased from Kongu Agro Chemical Pvt Ltd, Sathyamangalam in the marketing name of Marshal. Configuration of Oxyfluorfen is listed in Table 1. A stock solution (1000 mg/L) was prepared by dissolving 1 mL Oxyfluorfen in 1000 mL ethanol. Working standard solutions ranging from 50–300 mg/L were diluted appropriately. All solutions were made using DDW only to confirm to non–interference of other ions present in water. Complexing agents for UV-Visible spectrophotometric analysis with respect to chosen pesticide viz.,0.5% -1,2-naphthoquinone-4-sulfonate (NQS) and KCl–NaOH buffer (pH 13) were prepared[16].

Table 1: Oxyfluorfen-Structure and Physicochemical Properties

Common Name	Oxyfluorfen
Chemical Structure	
IUPAC Name	2-Chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene
Pesticide group	Diphenyl Ether
CAS Number	42874-03-3
Activity	Systemic Herbicide
Molecular formula	$C_{15}H_{11}ClF_3NO_4$
Molecular Weight	361.70
Formulation	23.5% EC

Batch Adsorption Studies

Oxyfluorfen removal using MEMD was experimentally verified by Batch mode. Varying controlling parameters viz., particle size (0.18mm–0.71mm)/dose (50–250 mg: 50 mg) of MEMD, initial Oxyfluorfen (OX) concentration (50–300 mg/L: 50 mg/L), pH (1–11), temperature (283–333K: 10K) and agitation time frames (10–60 mins: 10 mins) were screened to fix the MEMD sorption efficiency. Appropriate volumes of NQS and pH 13 buffer were added to the supernatant solutions, post filtration, allowed to stand for 20 min, followed by the absorbance measurement of complexed samples in UV-Visible spectrophotometer at a λ_{max} value of 460nm. Generated MEMD solid residue of batch experiments were dried and agitated with 0.1N HCl as desorbing agent to favor the leaching of loaded OX from the MEMD surface matrices, further stirred with DDW to neutralize the pH condition. Regenerated MEMD was dried and subjected to successive adsorption-desorption cycles, in order to register its regenerating efficacy. Adsorbed Oxyfluorfen concentration was calculated[17] as per mass balance equation 1.

$$q_e=C_0–C_e/W*V \qquad (1)$$

Where, C_0, C_e, V, W and q_e refer to initial and equilibrium OX concentrations (mg/L), volume of solution (L), mass of the adsorbent (g) and amount of OX adsorbed (mg/g). Desorption percentage was calculated from equation 2.

$$\%Desorption=q_{de}/q_{ad}*100 \qquad (2)$$

Where, q_{ad} and q_{de} imply the amounts of adsorbed and desorbed OX concentrations. Notable theoretical models (isotherm/kinetic) were applied to validate the experimental data so as to support and predict the studied system parametrics, through coefficient of determination (R^2).

Effectual nature of MEMD in trapping OX was encountered in presence of other competing pesticides viz., malathion, carbosulfan and phorate at varying concentration ranges between 50-300 mg/L. Experimental set up was planned in such a way that a mixture of the three pesticides and OX at specific concentrations were agitated at pre-set time frames and MEMD dosage, followed by systematic registration of residual OX concentration under the influencing pesticides at UV–Visible spectrophotometer.

RESULTS AND DISCUSSION

Characterization studies

Microscopic analysis: The particle size calculated was 0.18mm against the mesh size 85 BSS for native and modified granular EMD are depicted as microscopic images in Fig. 2 a & b. The distinct and enlarged open porous nature of MEMD is in favor of extended sorption capacity of the modified material.

Physico-Chemical Analysis

Physio-Chemical parametric values of modified Elephas maximus dung (MEMD–0.18 mm) are listed in Table 2.

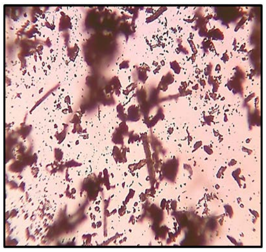


Fig. 2a. Raw EMD

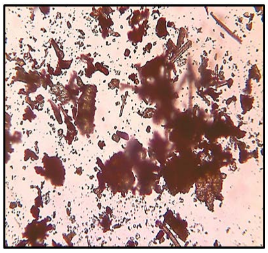


Fig. 2b. Modified EMD

Table 2: Physio-Chemical Characteristics

Properties	MEMD (0.18 mm)
pH of 1 % solution	6.52
Moisture (%)	1.64
Bulk density (g/L)	0.66
Specific gravity	1.39
Porosity	54.59
Ash content (%)	3.29
Acid Soluble Matter (%)	2.16
Water Soluble Matter (%)	1.02
Ion Exchange Capacity (meq /g)	0.67
pHzpc	4.13
Surface area (m^2/g)	35.31
Mean Pore volume (nm)	2.4
Surface Acidic groups (m mol g^{-1})	
Phenolic	0.63
Carboxylic	1.58
Lactonic	0.14

Neutral pH and lower moisture content values exhibited by MEMD are indicate by its stable nature. Calculated bulk density being less than 1 g/L implies the presence of porous particles. This statement is supported by the standard porosity value and appreciable surface area/mean pore diameter values evidenced from BET/BJH plots (Figs. 3a & b)[18]. Internal pore structure mostly decides the extent of adsorption for any material. BET analysis provided a precise surface area value 35.31 m^2/g, done by nitrogen multilayer adsorption method, wherein, the measurement had been carried out as a function of relative pressure using an automated analyzer. Pore size distribution and specific pore volume which is independent of external area due to sample's particle size were determined by BJH analysis[19]. The centered BJH peak display the sample pore diameter as 2.4nm, favoring mesoporous nature of the sample.

FT-IR

FT-IR spectra of raw, modified and OX-loaded EMD is shown in Fig. 4. Peaks at 3,289 and 2,959 cm^{-1} could be assigned to –OH and –NH_2 groups and –CH stretching vibrations, respectively. Other bands on the ED surface refer to: 1,687 cm^{-1} (–C=O stretching, –C–N (amide), 1,519 cm^{-1} (amine groups), 1,424 cm^{-1} (–N–H bending), 1,352 cm^{-1} (–S=O stretching vibrations), 1,161 cm^{-1} (–C–O–C stretching), 1,031 cm^{-1} (–C–N, –C–O–C, and –C–C stretching vibrations), and 912 cm^{-1} (–S=O stretching. Overall peak shifts, confirm the participation of functional groups present in the biomass surface during pesticide binding process. A peak at 1038 cm^{-1} in OX loaded spectrum, referring N-O stretching, register the sequestration of nitrogen ions by the modified material.

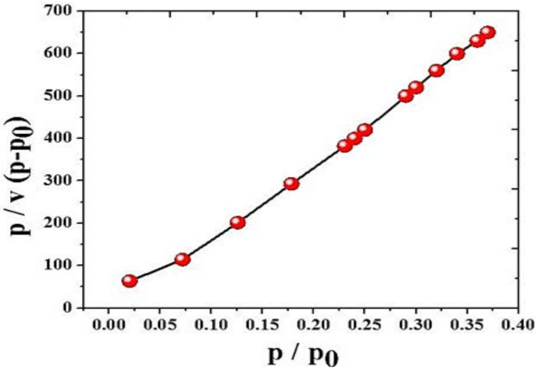


Fig. 3a. BET Plot

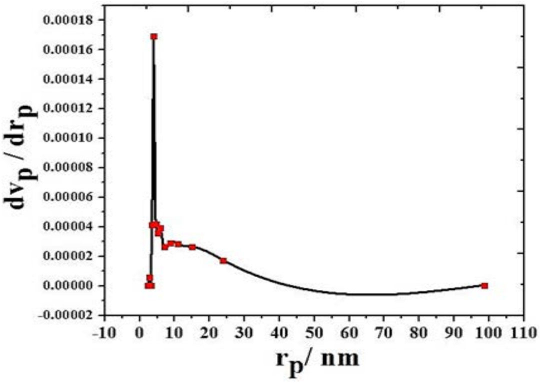


Fig. 3b. BJH Plot

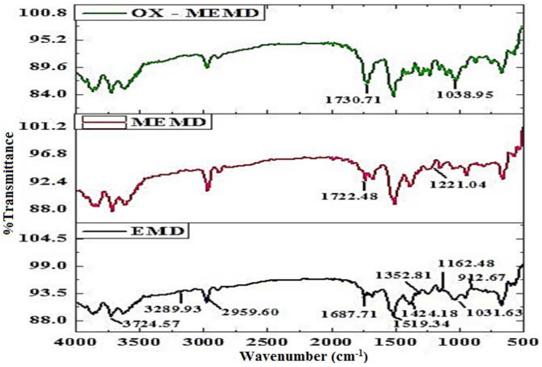


Fig. 4. FT-IR Spectra

SEM/EDAX Analyses

The appearance of heterogeneous surface with aggregate particles was found to undergo surface morphological changes with opened pores due to chemical modification (Fig. 5a). Smoothening of unoccupied pores after the experimental run with oxyfluorfen moieties reflect homogenous structures instead of porous nature (Fig. 5b) facilitating the adsorption of oxyfluorfen.

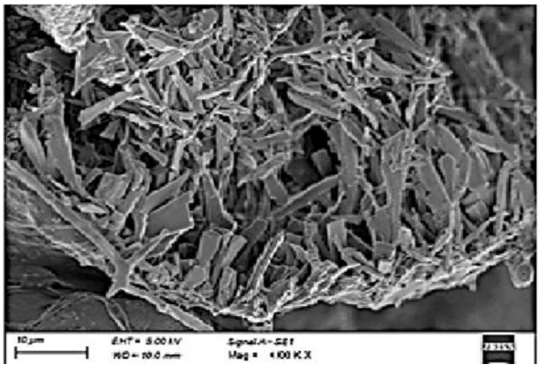


Fig. 5a. SEM-MEMD

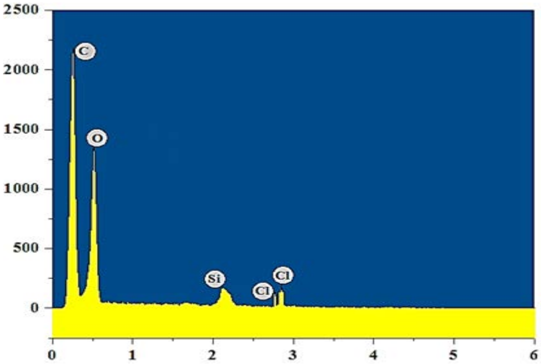


Fig. 5b. EDAX-MEMD

Presence of Chlorine, Nitrogen and Fluorine peaks at 2.6, 0.39, 0.67 keV respectively substantiate the adsorption of oxyfluorfen onto MEMD surface (Fig. 6a) against their absence in the unloaded spectra (Fig. 6b).

TG–DTA Analysis

Thermo Gravimetric analysis of MEMD is shown in Fig. 7. MEMD is thermally stable up to 230°C. At higher temperatures, the material underwent decomposition leaving behind ash residue. The initial weight loss at 100°C is attributed to 5.6 % moisture loss[20]. However, decomposition of MEMD had occurred between 230°C-570°C. 14% of MEMD residue constituted ash content. Thermo gravimetric data obtained are complementary with proximate analysis results.

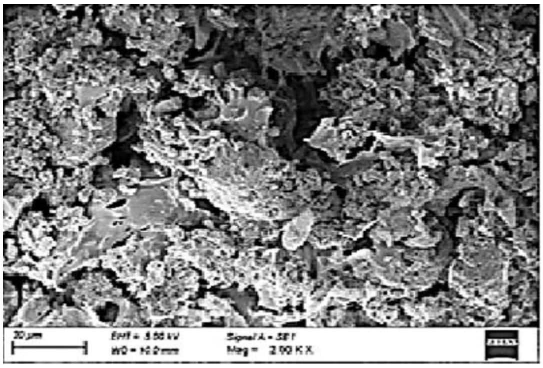
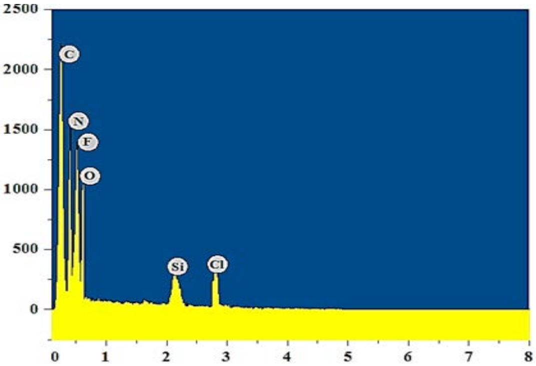


Fig. 6a. SEM-OX-MEMD



6b. EDAX-OX-MEMD

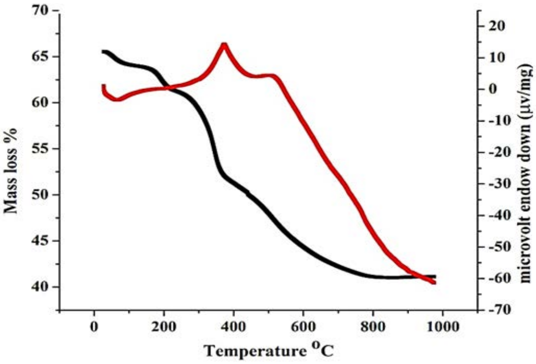


Fig. 7. Thermogram of EMD

Adsorption Studies[17]

i) Impact of Particle Size

Sequestration of chosen pesticide using different particle sizes viz., 0.18mm, 0.24mm, 0.30mm, 0.42mm and 0.71mm of MEMD are shown in Fig. 8. Smooth gradient decline of the curves indicate that a maximum of 89% pesticide chelation had occurred at a smaller particle size (0.18mm), which may be due to extended surface area, promoting greater toxicant trapping. Further, lower gradation in the sorption rate at increasing particle size shall be contributed by the higher diffusional resistance to mass transport property, thereby ensuring least utilization of utmost internal surface for sorption. From the above observations, 0.18mm particle size of MEMD had been fixed for the verification of other factors.

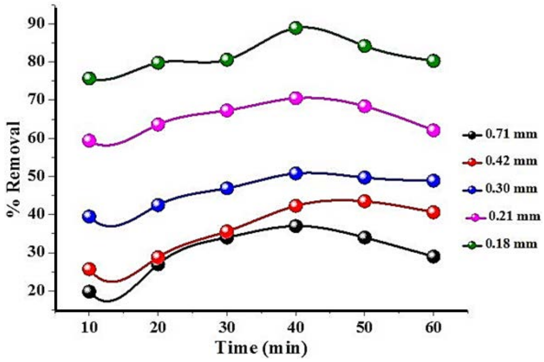


Fig. 8. Impact of Particle Size

ii) Impact of MEMD Dosage

A smooth rise in the dosage patterns is evident from Fig. 9 at a time frame of 40 mins, beyond which a decline was observed for further agitation periods except for 250 mg, where an equilibrium was attained. This suffice the statement that higher sorption (89%) had occurred at 250 mg dose.

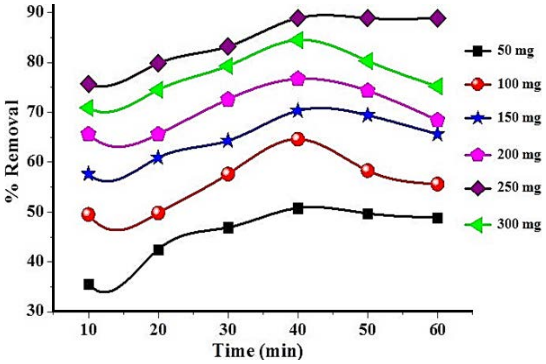


Fig. 9. Impact of MEMD Dosage

iii) Impact of Oxyfluorfen Concentration and Agitation Time[21]

Initial concentration of any sorbate species plays a key role in an agitation experiment in the process of determining sorbents' sorption capacity. A trend of wave patterns (Fig. 10) similar to that envisaged in Fig. 9 was obtained while studying the influence of sorbate concentration and agitating time intervals. Maximum oxyfluorfen removal at 40 mins was observed for 200 mg/L concentration. This may be due to the attainment of dynamic equilibrium on the biomass surface leading to increased number of unadsorbed pesticide moieties from the aqueous solution.

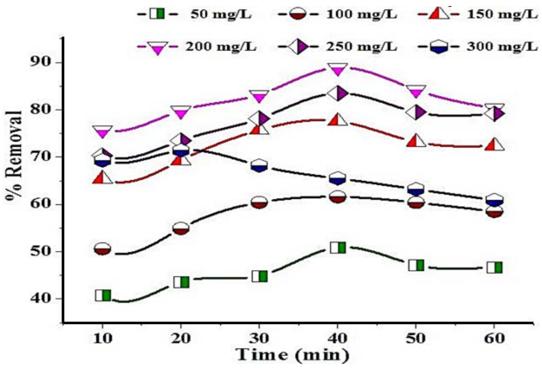


Fig. 10. Impact of Oxyfluorfen Concentration and Agitation Time

iv) Impact of pH

pH variations play a pivotal role in the adsorption process through dissociation of functional groups on the surface-active sites. This leads to a change in reaction kinetics and equilibrium characteristics. A maximum percentage removal of oxyfluorfen was registered at pH 5 (Fig. 11), later a minimal dip was encountered in the curve at higher pH ranges, indicating the attainment of saturation. The reason for the decreased sorption at acidic pH values shall be favored by protonation of surface groups, thus restricting removal of the selected pesticide.

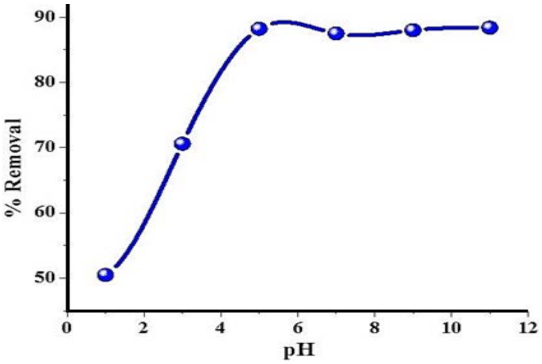


Fig. 11. Impact of pH

v) Impact of Temperature

Figure 12 shows the adsorption profiles

at different temperature environs (283–333 K) for OX–MEMD system. The first half of the curve registered an inclined paradigm upto 303K, however, further temperature rise, triggered an uneven uptake by MEMD, recommending the follow up of an exothermic process.

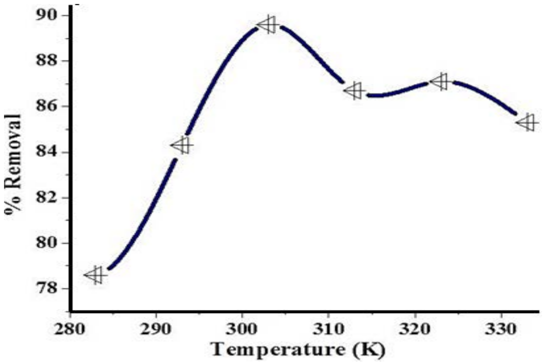


Fig. 12. Impact of Temperature

vi) Impact of Co-pesticides[22]

Influence of Co–pesticides on OX-MEMD system at varied initial pesticide concentrations (50–300 mg/L) showed 23% decrease in pesticide removal due to the inhibition by malathion at a concentration of 150 mg/L, in preference to carbosulfan and Phorate under similar conditions (Table 3). This is due to the binding capability of phosphate and sulphate ions present in malathion with the surface acidic groups of MEMD. Influence of Co-pesticides on OX removal shall also be attributed to the varying molecular weights, complexity and functional groups of the former.

Table 3: Impact of Co-pesticides

S.No	Pesticides	%Removal Concentrations (mg/L)					
		50	100	150	200	250	300
1	Oxyfluorfen (in absence)	50.9	61.6	77.6	88.9	83.5	65.5
2	Malathion	41.7	60.3	74.3	65.8	60.6	50.5
3	Carbosulfan	47.2	55.2	70.8	82.1	80.3	60.4
4	Phorate	42.4	50.9	60.9	84.2	70.1	53.5

vii) Desorption/Regeneration Studies

Desorbing ability of MEMD loaded with oxyfluorfen and its regenerating capacity studied consecutively for four cycles, are represented in the bar chart (Fig. 13). It is evident from the diagram, that a maximum of 79.35, 77.86, 75.76 and 70.65 mg/g adsorption capacities for the first, second, third and fourth cycles with corresponding desorbed amounts as 33.12, 35.76, 32.96 and 30.65 mg/g had been registered. This observation suggests the marked regenerating capability and reusable nature of MEMD.

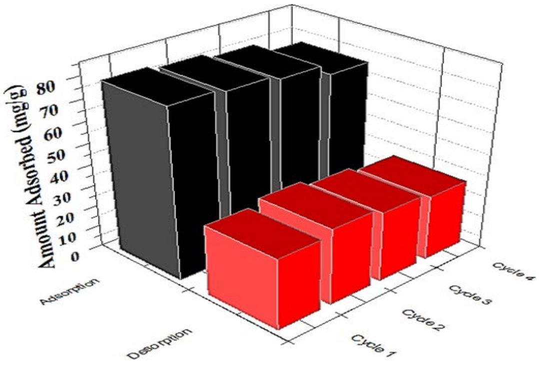


Fig. 13. Regeneration Studies

Theoretical validations of the selected sorption system based on the experimental results were studied. The obtained data were validated using isothermal and kinetic equations.

Biosorption isothermal studies[23]

Fit of the recorded values pertaining to Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm corresponding to their plots and their derived constant are shown in Figs. (14–17) and Table 4. A better linearity exhibited by Langmuir isotherm is supported the correlation co-efficient value close to unity (R^2–0.9877) and amount of OX adsorbed (qmvalue-70.12 mg/g). Constants of Temkin-BT (Heat of Adsorption <10 J/mol) and AT (Equilibrium Binding Constant), Freundlich-1/n (>1) and DKR-E (mean free energy <20 J/mol) values registered dissimilar results than the obtained batch data, representing a weaker interaction between the sorbate species and sorbent moieties. A comparison of the varied isothermal studies reveal the order to be as Langmuir > Freundlich >Tempkin > DKR, with respect to R^2 values. This shows that the studied system follows monolayer adsorption, favoring the fit in of Langmuir model.

Table 4: Isothermal Constants

Models	Constants		
Langmuir	q_m(mg/g)	B(L/g)	R^2
	70.12	0.13	0.9877
FreundlichK (mg/g)	1/n	0.8632	
	60.92	1.23	
Temkin	AT(L/g)	BT (J/mol)	
	58.76	143.87	0.4293
DKR	q_s(mg/g)	E(KJ/mol)	
	56.75	2.10	0.7783

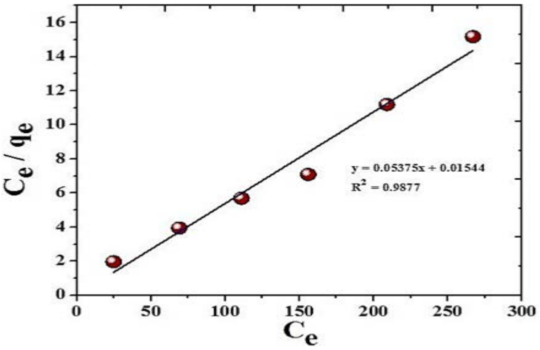


Fig. 14. Langmuir Plot

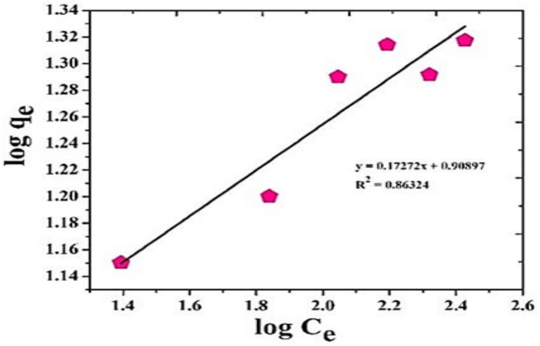


Fig. 15. Freundlich Plot

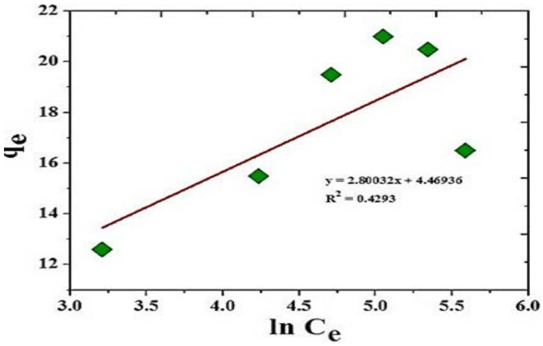


Fig. 16. Temkin Plot

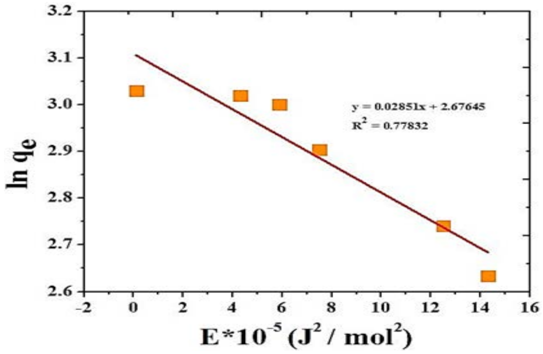


Fig. 17. DKR Plot

Biosorption kinetic studies

Pseudo first order and Pseudo second order model equations were solved using the experimental data, wherein the calculated values are plotted as log (q_e–q_t) and t/qt vs time (t) (Figs. 18 & 19). Deviations of the marked values is obvious in Fig. 19, whereas, almost all the plotted points lie in the straight line as far as Fig. 19 is concerned. This clearly is indicative of best fit of Pseudo first order for the studied system.

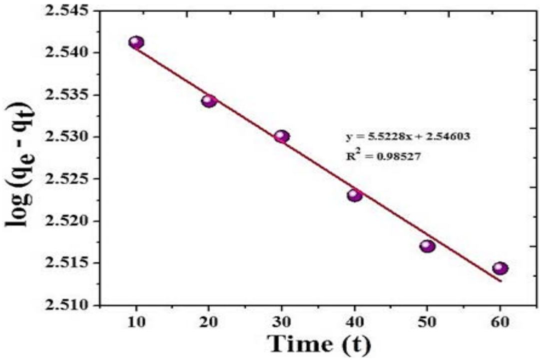


Fig. 18. Pseudo First Order

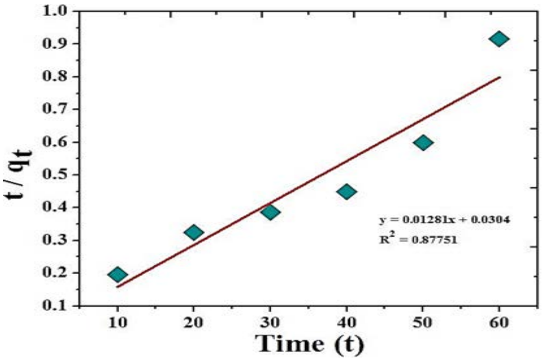


Fig. 19. Pseudo Second Order

CONCLUSION

Modified Elephas maximus dung (MEMD), an animal litter, being seldom reported elsewhere was employed for the confiscation of diphenyl ether pesticide (Oxyfluorfen) from aqueous environs under variable conditions. Optimized states of the batch studies for ≈ 89% Oxyfluorfen removal was established as 0.18mm particle size, 250 mg MEMD dosage, 200 mg/L initial Oxyfluorfen concentration, 40 mins agitation time, pH 5 and temperature 303K. Pesticide laden MEMD and its precursor were characterized viz., Microscopic, BET/BJH, FT-IR, SEM/EDAX and TG-DTA to assess the MEMD particle size, presence of functional groups, surface morphology/elemental composition and thermal stability. Four Isothermal and two Kinetic models were validated where, Langmuir and Pseudo first order plots well described the experimental data, indicating monolayer adsorption. From the results, it is arrived that Elephas maximus dung, serve as an excellent alternate to chelate the chosen toxicant, oxyfluorfen pesticide from aqueous matrices.

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Conflict of interest

The authors declare that we have no conflict of interest.

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