Organo-Clay as Adsorbent for Removal of Fenoxaprop-*p*-ethyl from Water Samples; A Statistical Approach

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Summary: In this study, fuller's earth (FE) modified with sodium dodecylbenzene sulphonic acid was used for adsorptive removal of fenoxaprop-p-ethyl (FPE) herbicide from water samples and statistical validation of the experimental observations was accomplished. All the adsorption experiments were conducted in batch mode. The effect of pH, agitation time, adsorbent dose and initial herbicide concentration on adsorption process was studied. About 98.5% adsorption efficiency was achieved at initial analyte concentration of 1000 mg L^{-1} at pH 6 within 60 min at adsorbent dose of 0.1 g. The adsorption kinetics were studied and pseudo-second-order kinetic model was found to follow the adsorption kinetics with R^2=0.998. The isotherm studies show that the adsorption data fit well to the Freundlich isotherms. In statistical evaluation, the individual as well as the interaction effect of various factors on adsorption was investigated and it was found that concentration, pH and adsorbent dose are the significant factors with p values of 0.0001, 0.004 and 0.006 respectively, while contact time was found statistically insignificant having p value greater than 0.05. The coefficient of determination (R^2=0.930) shows that % adsorption is highly dependent on the studied factors and their interactions. Under the optimized set of conditions, high absorption capacity of 200.22 mg g^{-1} was achieved.

Key words: Organo-clay, Sodium dodecylbenzene sulphonic acid, Fenoxaprop-p-ethyl, Adsorption.

Introduction

Fenoxaprop-*p*-ethyl is a member of aryloxyphenoxypropionate (AOPP), post-emergence herbicides, mainly used against different weeds such as wild oats and foxtail in wheat fields [1]. The herbicide FPE has been used for more than fifteen years in Pakistan against canary grass and wild oat, both being the most upsetting weeds for wheat [2, 3]. The Cancer Assessment Review Committee (CARC) and the United States Environmental Protection Agency (USEPA) have classified FPE as chemical with suggestive evidence of carcinogenic potential [4]. It influences the sperm motility and thus fertility and possibly induces toxicity and injury to liver [5]. Thus, its removal from water is gaining attention among the researchers.

Various environmental remediation processes including photocatalytic degradation with enhanced reactivity and selectivity of semiconductor materials have been reported and can be significantly extended to degradation of pesticides, dyes and drugs [6-8]. Besides, for the removal of pesticides from different aqueous systems, a number of methods have been reported in the literature [9-12]. Two major types of these methods are mineralization via heterogeneous catalysis or photocatalysis and the adsorptive removal on the surface of porous solids. Pesticides removed using the former method include fluroxypyr [13],

bromacil and metribuzin [14], carbofuran [15] and pirimiphos-methyl [16] among others. The method of adsorptive removal has been reported for pesticides like fluroxypyr using activated carbon fibers and cloth, monosulfuron-ester with Chinese soils [17] and trichloroacetic acid using ion-exchangers [18].

Clay minerals have been reported to show high adsorption capacity due to their lamellar texture, small particle size and high specific surface area. Clay adsorbs ions and polar organic molecules in interlayer locations and on particle external site. The surface activity of the clay and chemistry of the organic molecule being adsorbed controls the adsorption and desorption mechanism [19]. Clays have been widely used for removal of pesticides such as paraquat using activated bleaching earth [20, 21], 2,4-D and acetochlor using bentonites [22], picloram using montmorillonite [23], simazine using acid-activated beidellite [24], atrazine using organo-clay [25] and 2,4-D using NCP-modified bentonite and zeolite [26].

FE is sandy clay. It is also known as bentonite clay and comprises of high percentage of minerals of the smectite group [27]. A variety of treatment techniques have been reported for surface modification of clay. These include acid treatment,

alkali treatment and organic treatment [28, 29]. The modifications with organic compounds include treatment with cationic surfactants such as hexadecyltrimethyl ammonium chloride and cetylmethylammonium bromide [30, 31]. Cationic surfactant modified clay has been reported for the removal and adsorption of acidic and basic dyes [32].

So for, clays have not been reported for removal of FPE and other members of its group as per the available literature. The objective of this study was to modify the FE with sodium dodecyl sulphonic acid (SDS), characterize it and investigate its adsorption capacity as potential sorbent of FPE from aqueous solutions. All the adsorption experiments were done in batch and percent adsorption as a function of pH, contact time, adsorbent dosage and initial concentration of FPE was investigated. Various kinetics, isotherms and mass transfer mechanisms were studied for the adsorption of FPE from water samples and individual and interacting effect of different controlling factors on the adsorption of the analyte was statistically evaluated.

Experimental

Materials

FPE (99.0 %) standard was purchased from Dr. Ehrenstorfer GmbH, Germany. FE (Fisher Scientific Co., Hampton, NH, USA) powder of 100 mesh size having an average particle diameter of 128 μm was purchased through local vendor and was used as delivered. SDS ($\geq$98.0%, Merck KGaA 64.271, Darmstadt, Germany) was purchased and used without further purification. All other reagents, including solvents, acids and salts for buffering, employed in this work were of analytical grade.

Instruments

Scanning Electron Microscope (30KV SEM, JEOL-JSM 5910 LV, JEOL Ltd., Tokyo, Japan), under high–vacuum microprobe was used for morphological investigation and the FTIR spectra of FE and surface modified FE (SMFE) were obtained with FTIR Spectrophotometer (IRPrestige-21, Shimadzu, Japan). Spectrophotometric determination of the concentration of FPE was carried out by measuring absorbance using a UV/VIS Spectrophotometer (SP-300 Plus, Optima Inc., Tokyo, Japan). For pH measurements, a digital pH meter (ISTEK Inc. China) was used. Stability of the SMFE and FE was measured with thermogravimetric analyzer, Diamond TGA/DTA (Perkin Elmer Instrument, CA, USA).

Solutions

In 100 mL methanol, FPE (0.01 g) was dissolved to prepare the stock solution (100 μg mL^{-1}). For preparation of Britton-Robinson (BR) buffer, acid mixture was prepared by mixing 11.42 mL of CH_3COOH, 13.6 mL of H_3PO_4 and 12.3 g of H_3BO_3, in distilled water in a 500 mL flask. Buffers of different pH in the range of 2-10 were prepared by adding NaOH (0.1 mol L^{-1}) solution to the acid mixture in different proportions and pH was adjusted using pH meter.

Preparation of and characterization of the adsorbent

In order to modify FE with SDS, a known mass (50 g) of FE was mixed with 4% solution of SDS; an anionic surfactant, in a 500 mL beaker. For equilibrium to be achieved, the mixture was stirred for 30 min and left overnight. After filtering, the mixture was dried in an oven at 100°C. After drying, the sample was ground, sieved through a mesh of 100 μm and stored in air tight bottle. The FE was labelled as SMFE.

A scanning range of 4000 to 400 cm^{-1} was used for measurement of FTIR spectra. SEM, under high-vacuum microprobe was used to determine the surface morphology of the modified fuller`s earth before and after adsorption of FPE.

Adsorption experiments

All the adsorption experiments were done in batch mode using SMFE as adsorbent, methanolic solution of FPE as the adsorbate and BR buffer (pH, 2-10) for maintaining the pH of the medium. The concentration of unadsorbed analyte was determined from an already constructed calibration curve (concentration of FPE (μg mL^{-1}) vs absorbance) at λ_{max} = 280 nm. The % adsorption of the analyte was calculated by using the formula given in equation (1).

$$\% \text{ Adsorbed} = \frac{C_i - C_e}{C_i} \times 100 \qquad (1)$$

where, C_i = Initial FPE concentration (μg mL^{-1} added) and C_e= Equilibrium concentration of FPE (μg mL^{-1} unadsorbed).

The influence of pH on the adsorption process was investigated by weighing the adsorbent SMFE (0.1 g) in a series of beakers. To each beaker, 1.0 mL of the stock solution of FPE (1000 µg mL^{-1}) was added. Then 2.0 mL of BR buffer in the range of 2-10 pH in a series was added. The mixtures were diluted with methanol: distilled water (3:7) up to 25 mL. All solutions were equilibrated for 60 min, then filtered and the absorbance of each filtrate was measured at 280 nm. The amount of FPE adsorbed (%) calculated using formula given in equation (1).

The influence of the dose of adsorbent on the adsorption efficiency was also investigated. The adsorption experiment was carried out at room temperature with mass of SMFE in the range of 0.05-0.3 g, 1.0 mL of FPE (1000 µg mL^{-1}), 2.0 mL of BR buffer of pH 6, equilibration time 60 min with shaking and dilution with 3:7 methanol and distilled water up to 25 mL.

The effect of contact time and shaking on the adsorption of FPE was studied by carrying out the adsorption experiment with and without shaking at pH 6 with all the conditions and concentrations the same. The contact time was varied in the range of 30-100 min. Without shaking the % adsorption was almost below 80%, therefore, further study of the contact time was done with shaking as the mandatory step.

In another step, keeping all the remaining variables and procedures constant, the effect of the initial concentration of FPE on the adsorption was studied by shaking various concentrations of FPE solution ranging from 100-600 µg mL^{-1} with SMFE (0.15 g) for 60 min. Under the optimized conditions, a comparative study of the adsorption efficiency of raw FE and the SMFE was conducted. It was observed that modification of FE increases the adsorption by about 53%.

For carrying out the kinetic experiments in batch, at room temperature (average 30 °C), in a series of 250 mL capped Pyrex glass bottles, 1.0 mL of 1000 µg mL^{-1} of FPE solution and 0.1 g of the adsorbent were taken. All the solutions were buffered to variable pH level. Shaking was done on an orbital shaker (100 rpm) for variable time ranging from 30-100 min. Different kinetic models were applied to the kinetic data obtained at pH 6 and variable contact time for equilibration.

FPE concentration in the range of 500-2000 µg mL^{-1} was used for applying the adsorption isotherms to the data of adsorption of FPE on the SMFE, keeping all other parameters (pH, mass of SMFE, and equilibration time) in the optimum range. Equation (2) was used to calculate the amount of analyte adsorbed per unit mass of adsorbent.

$$q_e = \frac{(C_i - C_e)V}{m} \qquad (2)$$

where, C_i and C_e are the initial and equilibrium FPE concentrations (µg mL^{-1}) respectively, q_e (mg g^{-1}) is the amount of FPE adsorbed per unit mass of adsorbent at equilibrium, m is the mass of adsorbent (g) and V is the volume of the solution (L).

Statistical analysis

For statistical analysis, the software package IBM SPSS Statistics V18.0.0 was used. Data was collected form the adsorption experiments performed having five different variables: (1) the dependent variable; % adsorption; (2) the independent variable; adsorbent dose having two categories "0.15 g" and "0.25 g" (3) the independent variable; pH which has two categories: "pH 4" and "pH 10" (4) the independent variable; the initial concentration of adsorbate which has two categories: "100 µg mL^{-1}" and "200 µg mL^{-1}" and (5) the independent variable; the contact time which has two categories: "30 min" and "60 min".

Results and Discussion

Characterization of the adsorbent

In order to confirm surface modification of fullers' earth with SDS, the FTIR spectra of both raw FE and SMFE were recorded. In Fig 1, in comparison to the spectrum of raw FE (a), the spectrum of SMFE (b) shows supplementary peaks at 2850 cm^{-1} and 2940 cm^{-1}. These peaks can be undoubtedly assigned to the symmetric and asymmetric stretching vibration mode of -CH$_3$ and -CH$_2$- groups. The absorption bands of the modified SMFE samples at 3450 cm^{-1} are flat and weak and can be assigned to the -OH stretching and bending vibration of H$_2$O in FE. This fact indicates that the surface properties of FE change from hydrophilic to hydrophobic as the H$_2$O content is replaced by the hydrated cation of surfactant ions in SMFE. The spectra also show that the crystal structure of FE remain intact upon modification with SDS. This fact is revealed by the existence of the peaks at around 600 cm^{-1} to 1200 cm^{-1} related to Si-O-Al/Mg and Si-O (Si-O-Si) in both of the spectra.
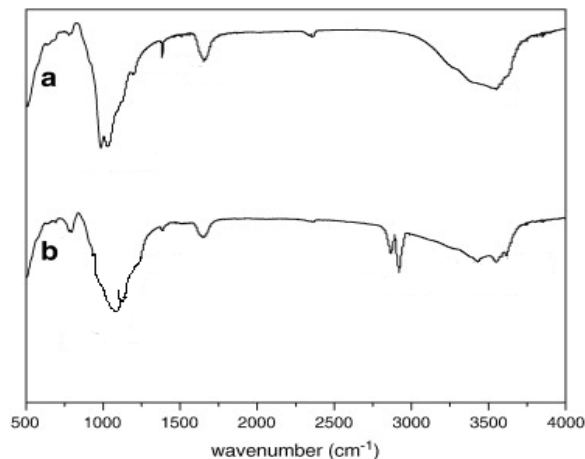
Fig. 1:   FTIR spectra of (a) Raw fuller's earth and (b) SMFE.

Fig 2 shows the morphologies of (a) raw FE (30,000 X), (b) SMFE before adsorption and (c) SMFE after adsorption of the analyte at the same magnification power (15,000 X). From the SEM micrographs, it is evident that FE shows rough surface with non-uniform particles. While the morphology of SMFE before adsorption shows that the layers form small tactoids having larger spacing in between the layers. It can also be seen that the surface is like a wrinkled network possessing irregular pores, which became somewhat flat and the pores become invisible after adsorption of the analyte. This suggests that the whole external surface of the beads is covered with a thin layer of the analyte. Similarly, after adsorption, the surface texture becomes coarse and uneven because of the penetration of FPE molecules into the porous packets of the SMFE.

Fig 3 shows the thermogravimetric (TG) curve of FE. In the thermogram, three stages of thermal decomposition are evident. The loss of adsorbed water in the temperature range of 65℃ - 200℃, elimination of coordinated water and partial loss of intercalated organic moieties over a temperature range of 300℃ - 500℃ and dehydroxylation of silanol groups over the temperature range of 500℃-900℃, results in mass loss. The drastic difference between the percentages of the first mass loss can be attributed to the reaction of FE with the surfactant that cause modification in the typical hydrophilic character of FE.
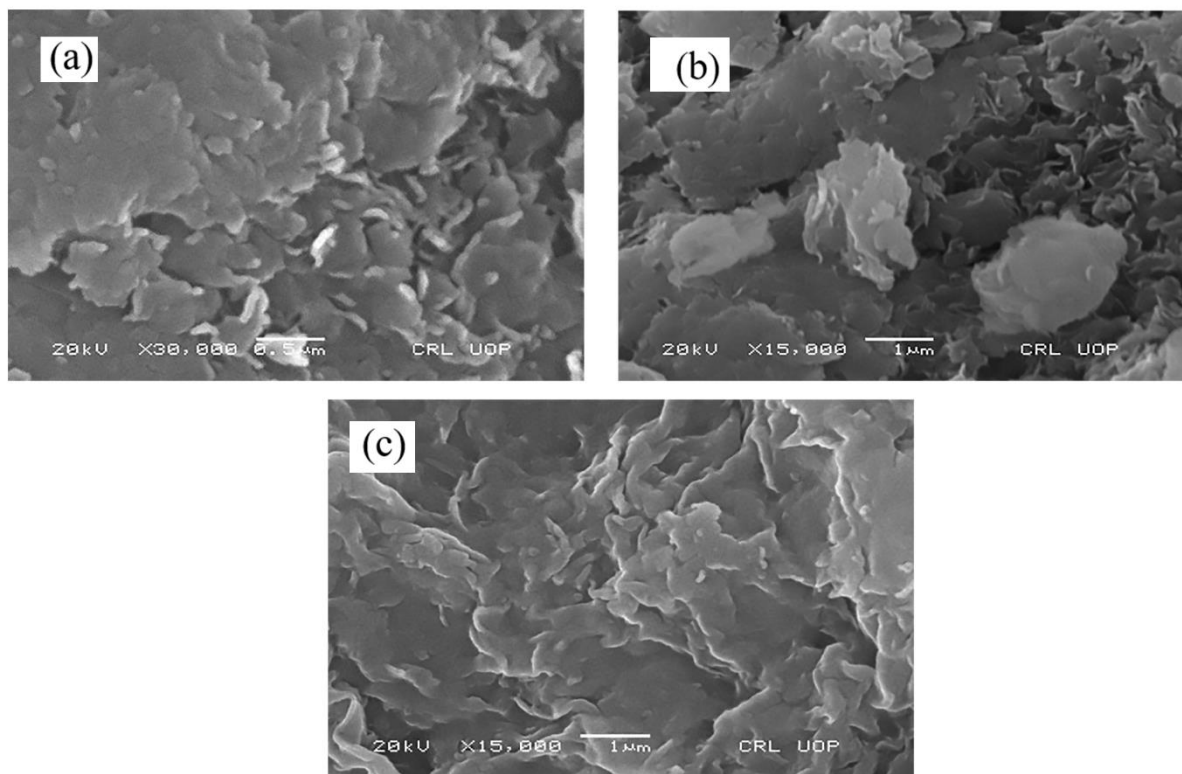

Fig. 2:   SEM micrographs of (a) raw FE, (b) SMFE (FPE unadsorbed) and (c) SMFE (FPE adsorbed).
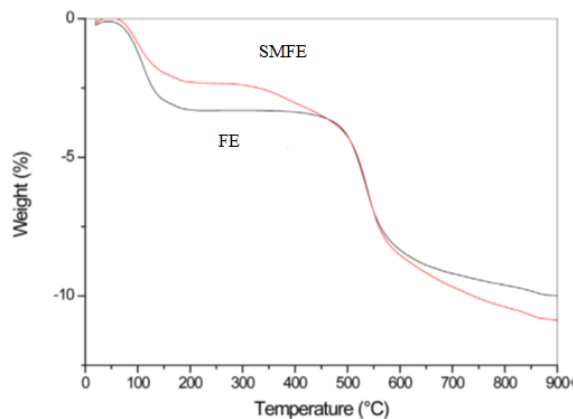
Fig. 3: Thermogravimetric analysis of SMFE and FE.

Effect of mass of adsorbent and concentration of adsorbate

The effect of the mass of adsorbent on adsorption of FPE (1000 µg) was also investigated. As shown in Fig 4, the adsorption capacity of SMFE increases with increasing its mass from 0.05 g to 0.15 g. This is because of the increase in the amount of surfactant intercalated into the surface galleries and interlamellar packets, resulting in an increase in the absorption of the analyte. Though, beyond this limit the adsorption capacity remains almost constant because the solution becomes short of adsorbate, though the number of active sites increases. Thus, under the present experimental conditions, 0.15 g of SMFE possesses maximum adsorption capacity for 1000 µg of FPE.

The effect of adsorbate concentration on removal efficiency was also studied at variable concentration ranging from 100–600 µg mL^{-1}. As shown in Fig 4, percent adsorption decreases as the concentration increases and is maximum at 100 µg mL^{-1}. This is due to the large number of molecules in solution which are always in competition for the available binding sites of the adsorbent at higher concentrations. Thus, maximum adsorption capacity of 0.15 g of SMFE is 100 µg mL^{-1}. It might be attributed to maximum surface area of modified FE which decreases with increase in the adsorbent dose [9, 33, 34].

Effect of pH and contact time

It is a well-known fact that the process of adsorption is influenced by the pH of the medium. It not only influences the degree of ionization and speciation of the adsorbate but also affects the

functional groups on the active sites of the adsorbent and the surface charge of the adsorbent. Fig. 5 shows the effect of pH of the solution on the adsorption of FPE under equilibrium conditions in the range of pH (2.0–10.0), where % adsorption of FPE was plotted against pH. It is evident that pH has a significant effect on the adsorption process. FPE is reported to undergo rapid degradation with decrease or increase in pH and is fairly stable in slightly acidic or neutral media. In strongly acidic conditions, the benzoxazolyl-oxy-phenyl ether linkage of FE cleaves to form ethyl 2-(4-hydroxyphenoxy) propanoate and 6-chloro-2, 3-dihydrobenzoxazol-2-one. Whereas in basic medium, the ester bond of the molecule breaks down [35]. Maximum adsorption was found to occur at pH 6. Under strongly acidic conditions, % adsorption is about 75% which may be attributed to analyte's degradation as well as the change in surface charge of the sorbent. Variable interactions between FE and FPE are possible which may be Vander Waal's forces, electron donor–acceptor interaction and hydrogen bonding. The adsorption of FPE on FE takes place through physical interaction in which Vander Waal's forces between adsorbent and herbicide are involved [36, 37].
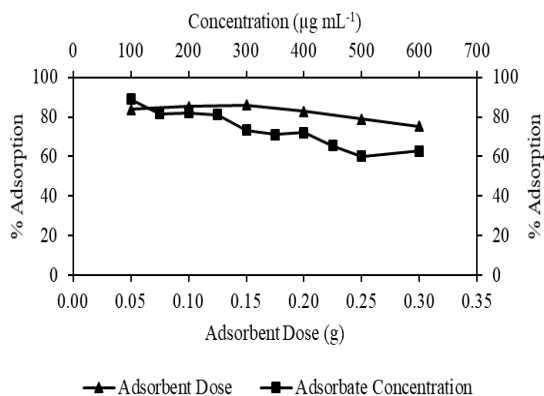

Fig. 4: Adsorption as a function of the adsorbent dose and concentration of FPE.

The rate of uptake of FPE by SMFE was investigated by following the change in % adsorption with and without shaking as a function of time. As evident from Fig 5, maximum analyte uptake occurs with shaking at contact time above 60 min, which is the point of equilibrium.

Beyond equilibrium point, the % adsorption curve becomes almost linear. The increase in adsorption occurs because a higher ratio of FPE molecules to reactive vacant adsorbent sites, cause a boost in the mass transport driving force.
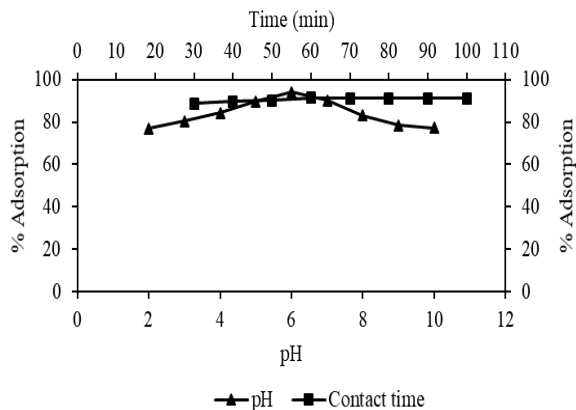
Fig. 5:   Adsorption as a function of pH and contact time.

Effect of concentration of salts

The availability of salts in water affects the efficiency of the adsorption process because it leads to high ionic strength. The effect of concentration of different salts [NaCl (0.01, 0.05 0.1 mol/L), KCl (0.01, 0.1) and $CaCl_2$ (0.01, 0.0 mol/L)] on the adsorption of FPE onto SMFE was studied. The present investigations show that the sorption of FPE, on FE and SMFE remains the same or nonsignificant change in adsorption occurs upon addition of salts (Fig 6). The diffused double layer on the adsorbent seems to get compressed at higher ionic strength in aqueous solution. This helps the adsorbate and adsorbent to approach each other, leading to increased adsorption. The second reason of increased adsorption may be due to decrease in the solubility of FPE in the presence of ionic species and a hydrophobic effect would favor the hydrophilic and hydrophobic interaction of the adsorbent and the adsorbate.

Adsorption kinetics

Several kinetic models have been reported to elucidate the adsorption mechanism. In the present study, kinetics of adsorption was described by pseudo first order model [38], pseudo second order model [39], intraparticle diffusion model [40] and Elovich model [41].

The linear form of the equations for pseudo-first-order model, the pseudo-second-order model and the intra-particle diffusion model [42] and the Elovich model [43, 44], are given in Table-1 along with the experimental values of the kinetic parameters. A good fit for either kinetic model would require correlation coefficient (R^2) values close to unity as well as calculated adsorption capacity (qe)

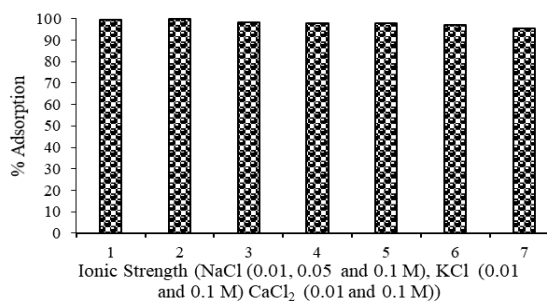values that come in a good agreement with the experimental values [9].

Fig. 6:   Effect of ionic strength on the adsorption of FPE onto SMFE.

As evident from the data in Table-1 and Fig 7 (a), the large difference of experimental and theoretical values of (qe) and very high deviation of R^2 value from unity, means that adsorption mechanism does not follow the pseudo-first order model. However, in case of pseudo-second order model (Table-1, Fig. 7 (b)), a very close agreement of qe (exp) with qe (calc) and R^2 value very close to unity suggest that the model is best fit for interpretation of adsorption data. Fig 7 (c) shows that intraparticle diffusion is not fitting because the plot of qt versus $t^{1/2}$ is not passing through the origin and is multilinear. Also, the R^2 value confirms the inapplicability of intraparticle diffusion model to the absorption data. The Elovich constants as given in Table-1 and the curve as shown in Fig 7 (d) suggest that the low R^2 values of this model make it inapplicable for interpretation of the experimental data. This suggests that in the adsorption process, chemisorption; such as chemical bonds between the FPE and SMFE with heterogeneous surface, is not a rate controlling factor.

Equilibrium studies/Adsorption isotherms

A number of isotherms model are reported in the literature to find the effect of equilibrium concentration (mg L^{-1}) 'Ce' on the amount of solute adsorbed per gram of adsorbent 'qe'. The experimental data was treated using four isotherm models i.e. Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) model. The linear forms of these equations are given in Table-2. The isotherms were compared based on the value of regression coefficients (R^2) as the fitting criteria.

Table-1: Kinetic parameters for the adsorption of FPE onto SMFE.

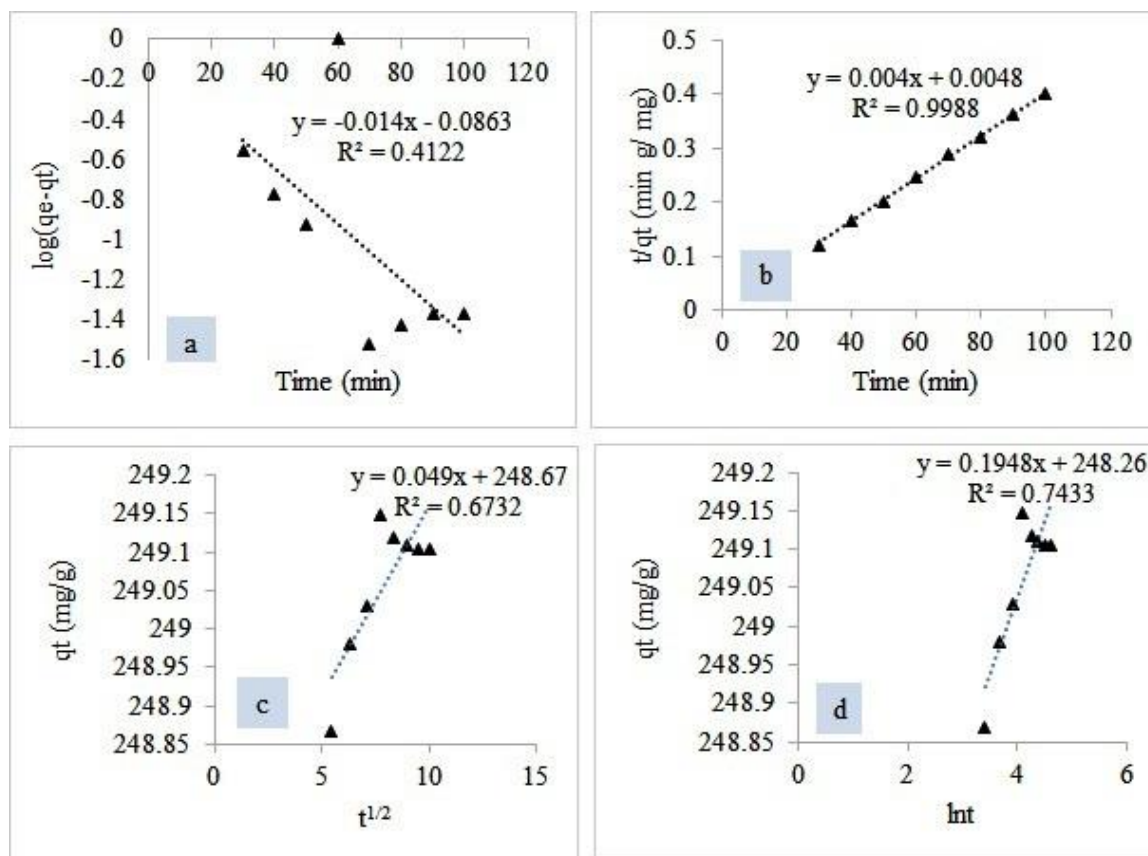| Model	Equation	Parameters	Values
Pseudo-first-order kinetic	$\log(q_e - q_t) = \log q_e - \dfrac{k_1}{2.303} t$	K_1 (min^{-1})	0.0322
		q_e (calc) (mg g^{-1})	0.819
		R^2	0.412
Pseudo-second order kinetic	$\dfrac{t}{q_t} = \dfrac{1}{k_2 q_e^{\,2}} + \dfrac{1}{q_e}$	k_2 (mg g^{-1} min^{-1})	1.6x10^{-7}
		q_e (calc) (mg g^{-1})	250
		R^2	0.998
Intraparticle diffusion	$q_t = k_{int} t^{1/2} + C$	K_{int} (mg g/min$^{1/2}$)	0.049
		C (mg g^{-1})	248.67
		R^2	0.673
Elovich	$q_t = \dfrac{\ln \alpha\beta}{\beta} + \dfrac{1}{\beta} \ln t$	α (mg g^{-1} min^{-1})	∞
		β (gm g^{-1})	5.13
		R^2	0.743
		q_e (exp) (mg g^{-1})	249.14

Fig 7: Pseudo-first order kinetics plot (a), Pseudo-second order kinetics plot (b), Intraparticle diffusion (c) and Elovich model plot (d) for the adsorption of FPE on SMFE (Ci=1000 mg L^{-1}, pH 6.0, T=298K).

The linear form of Langmuir adsorption isotherm (Fig 8 (a)) is given by the equation as depicted in Table-2 and is sufficient for evaluating the Langmuir parameters where a theory of smooth energy of sorption on adsorbent surface is the main feature [11]. The value of Langmuir parameter, Q° (maximum monolayer adsorption capacity, mg/g) obtained for the adsorption of FPE onto SMFE was 200.22 mg g^{-1} at 30°C. This confirms substantial practical limiting adsorption capacity under the conditions of full coverage of the surface with analyte molecules. Here also the R^2 value (0.9364) indicates that the data does not fit well to Langmuir adsorption isotherm. The inapplicability of Langmuir model to the data suggests that, in this case we cannot assume chemisorption or chemical adsorption which is a strong chemical bond between molecules of adsorbate and the surface of adsorbent. Also, it reflects that the adsorption sites on the surface of SMFE are not evenly dispersed. Langmuir isotherm

assumes monolayer coverage on a homogeneous surface with matching adsorption sites. But these assumptions are effective for gas adsorption on solid surface. Langmuir isotherm does not essentially reflect the validity of the above-mentioned assumptions in solution-solid systems, where due to hydration forces, mass transport effects etc. the system is much more dynamic and complex. In such systems, the isotherm suitability can be seriously influenced by the experimental conditions, predominantly, the range of concentration of the solute/adsorbate [9].

The non-uniform adsorption heat distribution on irregular surface is the key feature of Freundlich isotherm [11]. As given in Table-2, the value of K_F; the Freundlich constant (38.81) shows more homogeneity of the surface (Fig 8 (b)). The value of R^2 for the Freundlich model is considered reasonable enough to indicate that the model represents the equilibrium data. The applicability of Freundlich isotherm indicates that the adsorption is based on partitioning as well as interactions.

Temkin isotherm model explains the effects of some indirect adsorbate/adsorbate interactions on adsorption and reveals sorption heats usually, lowering with growing coverage [11]. The experimental equilibrium data of adsorption of FPE onto SMFE was assessed according to Temkin isotherm model equation (Table-2) and a plot of qe vs. ln Ce (Fig 8 (c). As given in Table-2, the low R^2 value of this model shows its unsuitability for explanation of the experimental data.

For interpretation of the nature of sorption, the Dubinin–Radushkevich isotherm model (D–R) is used. A theory of dissimilar physico-chemical sorption is the main feature of D-R isotherm. Gaussian energy distribution on uneven surface is clarified by this isotherm [11]. The Gaussian energy distribution onto a heterogeneous surface was

calculated to be 13.60 kJ mol^{-1} at 30 °C. These results in Table-2 show that the free adsorption energy is higher than 8.0 kJ mol^{-1} and the adsorption of FPE on SMFE follows a chemisorption phenomenon. The E (kJ mol^{-1}) value 8-16 kJ mol^{-1}, confirms the adsorption process to be chemisorption whereas, E<8 kJ mol^{-1} match with physiosorption [45].

This plot of ln qe versus $\mathcal{E}^2$ for the present experimental data is not linear as shown in Fig. 8 (d). As given in Table-2, the regression coefficient (R^2) obtained from the D-R isotherm model is far away from unity and the Dubinin-Radushkevich (D-R) isotherm model is not appropriate description of the data for adsorption of FPE on SMFE.

Statistical Analysis

To statistically determine the impact of different factors on the % adsorption, three-way between-subjects ANOVA technique (Univariate analysis) was employed and p value of 0.05 was considered statistically significant. The individual effect of different factors such as contact time, pH, adsorbent dose, and initial concentration was investigated followed by checking the interactive effect of all the factors. Table-3 shows that concentration, pH and adsorbent dose are the significant factors with p values of 0.0001, 0.004 and 0.006 respectively. On the other hand, contact time was found statistically insignificant because here the P value is greater than 0.05. Furthermore, to investigate the interactive effect, the interaction of concentration, pH and adsorbent dose was found highly significant (p<0.05) while the rest of the interactions were found to show low significance. The coefficient of determination (R^2=0.930) shows that % adsorption is highly dependent on the studied factors and their interactions.

Table-2: Summary of equilibrium isotherm parameters.

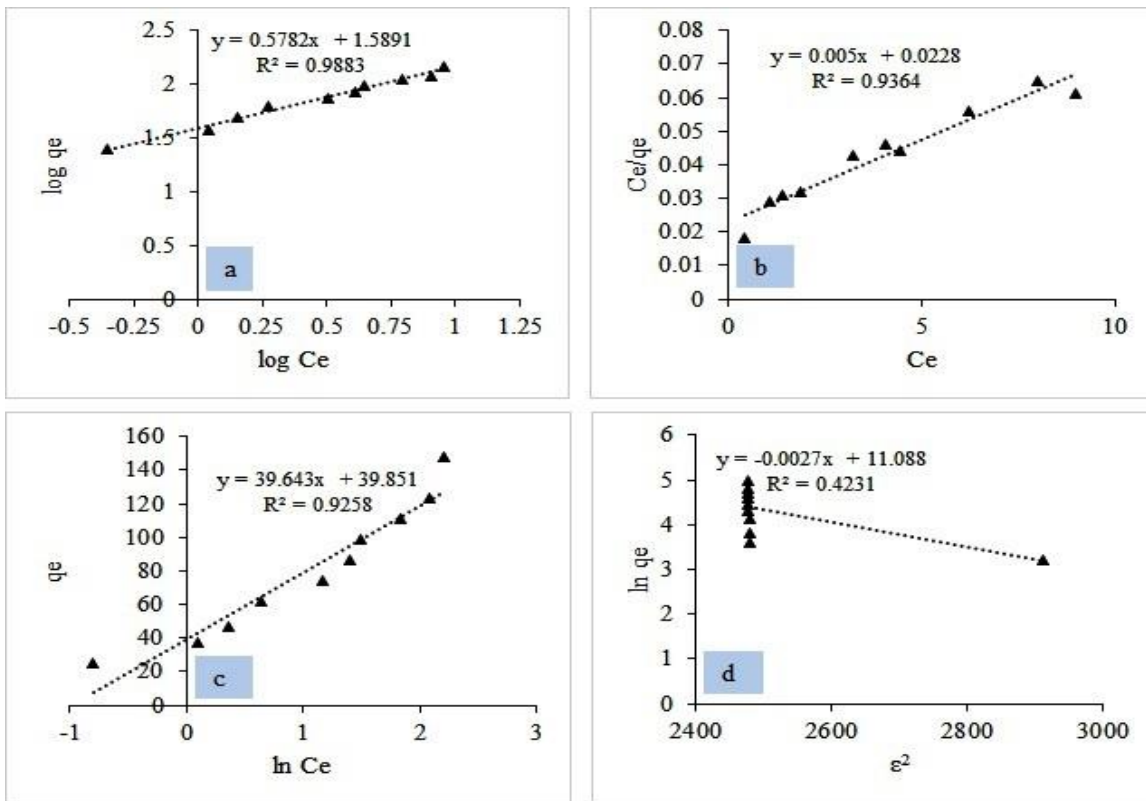| Model	Linear Equation	Parameter	Value
Langmuir	$$\frac{C_e}{q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}}$$	b (L mg^{-1})	43.85
		Q_{max} (L mol^{-1})	0.219
		Q°(mg g^{-1})	200.22
		R^2	0.936
Freundlich	$$\log q_e = \log K_F + (1/n)\log C_e$$	K_F	38.81
		1/n	0.578
		R^2	0.988
Temkin	$$q_e = B_T \ln A_T + B_T \ln C_e$$	A_T	2.73
		B_T	62.49
		R^2	0.925
Dubinin-Radushkevich (D-R)	$$\ln q_e = \ln Q_{max} - K_{DR}\varepsilon^2$$	Q_m(mg g^{-1})	64860.88
		E (KJ mol^{-1})	13.60
		R^2	0.423

Fig 8: Linear fitting plots of (a) Langmuir, (b) Freundlich, (c) Temkin and (d) Dubinin-Radushkevich isotherm models for the adsorption of FPE onto SMFE.

Table-3: Tests of Between-Subjects Effects.

Dependent Variable: % Adsorption

Source	Type III Sum of Squares	df	Mean Square	F	Sig.
Corrected Model	2244.495[a]	15	149.633	14.219	.000
Intercept	214199.852	1	214199.852	20355.041	.000
Concentration	775.885	1	775.885	73.731	.000
pH	116.625	1	116.625	11.083	.004
Contact Time	23.171	1	23.171	2.202	.157
Adsorbent dose	3.245	1	3.245	.308	.006
Concentration * pH	516.088	1	516.088	49.043	.000
Concentration * Contact time	277.125	1	277.125	26.335	.000
Concentration * Adsorbent dose	19.609	1	19.609	1.863	.001
pH * Contact time	28.671	1	28.671	2.725	.118
pH * Adsorbent dose	28.445	1	28.445	2.703	.003
Contact time * Adsorbent dose	33.764	1	33.764	3.209	.092
Concentration * pH * Contact time	45.577	1	45.577	4.331	.054
Concentration * pH * Adsorbent dose	152.033	1	152.033	14.447	.002
Concentration * Contact time * Adsorbent dose	176.485	1	176.485	16.771	.045
pH * Contact time * Adsorbent dose	4.922	1	4.922	.468	.040
Concentration * pH * Contact time * Adsorbent dose	42.851	1	42.851	4.072	.061
Error	168.371	16	10.523		
Total	216612.718	32			
Corrected Total	2412.866	31			

a. R Squared = .930 (Adjusted R Squared = .865)

Conclusion

The present study shows that organo modified fuller`s earh can be effectively employed as an adsorbent for the uptake of FPE from water samples with better adsorption capacity (200.22 mg g^{-1}). The results showed that adsorption of FPE herbicide is affected by change in pH and at pH 6.0, higher adsorption was achieved. The adsorption was found to increase with contact time and equilibrium was established in 60 min. Likewise, with increase in dose of adsorbent, more sites are available for adsorption of

FPE and thus it increases. The kinetic data followed pseudo-second-order kinetics. The equilibrium data was found well fitted into Freundlich model. The adsorption process was found to be affected by more than one parameter as indicated by intraparticle diffusion model. In statistical evaluation, the individual as well as the interaction effect of various factors on adsorption was investigated and it was observed that concentration, pH and adsorbent dose are the significant factors with p values of 0.0001, 0.004 and 0.006 respectively, while contact time was found statistically insignificant having p value greater than 0.05. The coefficient of determination (R^2=0.930) shows that % adsorption is highly dependent on the studied factors and their interactions. Fuller's earth is readily available in different parts of the world and can be effectively used for the removal of metal ions, pesticides and dyes.

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