The sorption behavior of organophosphate pesticide on zeolite

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ABSTRACT studies on restriction of pesticidal movement in contaminted soil and water are reported here . sorption isotherms could be well described by the material. Sorption of Methyl parathion on Bentonite thermodynamic parameters for sorption have also been calculated to predict the mechanism of sorption . the FTIR analysis and thermodynamic studies exhibit the possibility of hydrogen bonding between the substrate and the pesticides molecule.it has been found that varying the sorptive properties of synthetic aluminosilicates results in immobilization of pesticides in a contaminated soil and protection of soil and water by using the aluminosilcates as pesticides carrier in slow release formulations.

Hydrated aluminosilcates can sorb more than 100% of their weight in water and the swelling phenomena influences the ability of soil to supply water and nutrients to growing plants [1]. the sorption behaviour of pesticides in soil mineral s is important in evaluating their possible distribution in environment while desorption characterisitics indicate the potential for reducing their availability to vegetation through which it enters into the human food chain . the bahaviour of pesticidal residue depends strongly on the extent to which they are retained in minerals, which further depends on sorption and desorption of soil mierals sorption and desorption depends on temperature , soil minerals composition and pH [2,5] . after sudying the bahaviour of pasticides in synthetic aluminosilicates , it is possible to synthesize these minerals in a way that helps in the in the degradation of pesticides by holding it for a longer peroid at least till it completely gets degraded[6] . the present studies are devoted to sorption and desorption behaviour of Methyl parathion with Bentonite to control the movement of pesticides in soil .

Experimental-

The aluminosilicates used for the present studies are hydrothermally synthesized by taking aqueous solutions of $Al(No_3)_3$ and Na_2Sio_3 to provide Al, Si, in different stoichiometric ratio which corresponds to their crystalline counterpats. To synthesis the material bentonite , metal ions Al, Si were taken in a motor ratio 6:4 the different aqueous solutions are first prepared in distilled water and then mixed thoroughly to given a paste. The mixture is then transferred to a Teflon lined stainless steel press use vessel & kept in an oven at 150^0C for 72 h. after completion of synthesis period the product was filtered, washed repeatedly with distilled water dried at room temp & kept in a powder form for further use.

X-ray power diffraction pattern of analogues of bentonite radiations source of wavelength 1.54066 A^0, The diffract to gram was recorded in the range $2Q=5$ to 120^0 infrared spectroscopy (FTIR) was used to complement the XRD identification of different aluminosilicates and to confirm the presence of OH group as well as Si-O-Al, Si-O-Al and O-Si-O linkage in the synthesized materials [7]. IR absorption spectra were obtained from KBr pellet using Nicolet – 410 spectrometer.

Batch sorption studies were carried out at desired pH value , contact time different concentration of Methyl parathion and sorbent dosage level in a100 ml and conical flask containing 50 ml of test solution . pH of the solution was maintained by 0.1 M HCL and 0.1 M NaoH as required. 100 mg of sorbent material was then added and content of the flask was shaken for 3 h in an electrically thermostated reciprocating shaker at the rate of 100 strokes /min at 30^0C . As temperature is an important parameter in a sorption studies, all the sorption experiments were performed at different temperature, Viz. 30, 40, and 50± 1^0 C and corresponding thermodynamic calculations were made after attaining the filtered through filter paper and 10ml aliquot of the filtrate was centrifuged at 5000 r.p.m at the same temperature and supernatant solution taken to Estimate the concentration of pesticide in solution spectrophotometrically by ammonium molybdophosphate method the sorbed concentration of methyl parathion on to the synthetic aluminosilicates at equilibrium was calculated by the difference in the amount of methyl parathion.

Results and discussion

The broad peak in case of the material show amorphous nature infrared spectral study provide information about the polyhedral frame work structure of aluminosilicates. The X – Rays power diffraction pattern shows maxima at $2Q = 26.6^0$, 7.02^0 . FTIR spectrum of material show a strong and broad peak at 3600-3800 cm^{-1} for the –OH stretching and strong and sharp peak near 1400 cm^{-1} for -OH bending frequency the absorption bands at 1000-1120 have been ascribed to Si-O-Si, O-Si-O bending vibration respectively amorphous aluminosilicates can act as effective barriers for immobilization of pesticides present as contaminants in soil and water and may also show controlled release of fertilizer to prevent the contamination of the surface and ground water.
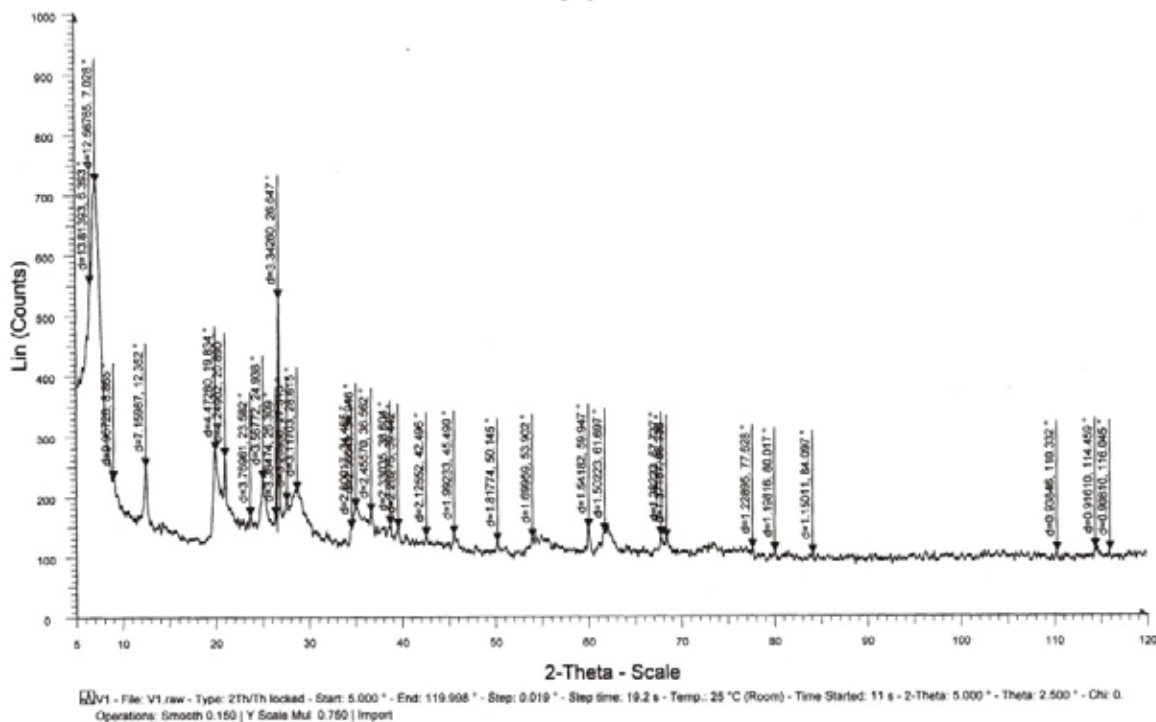
Fig 1- XRD of Bentonite

Sorption isotherm

Sorption of methyl parathion on bentonite which shows that sorption and desorption behavior of pesticide strongly depends on the nature and composition of the material [9,10]. Pesticides are sorbed from aqueous system onto surface of aluminosilicates by a wide variety of mechanisms. The operative mechanism for any perticular reaction depends on the nature and properties of active sites on the material surface , the bulk chemistry of the system (e.g.pH,hydration status, exchangeable inorganic cations) and the chemical nature of the pesticides.[1] the sorption isotherm is generally used for the design of sorption system. The sorption isotherms are studied at pH and temperature (30± 1^0 C). The Freundlich isotherm is the most widely used mathematical description for the sorption of organic molecules present in the solution phase onto solid material surface.

Freundlich equation may be written as,

$C = K C_e^{1/n}$

(Non –linear Form)

$\log C = \log K + 1/n \log C_e$

(Linear Form)

Table 1- thermodynamic parameters for sorption of methyl parathion onto bentonite

| T/^{0}C	T/K	sorption %	Equilibe-rium constant K	G^0 KJ mol^{-1}	H^0 KJ mol^{-1}	S^0 KJ mol^{-1}	lnkc	1/T
35	308	12.6	0.126	-5304.45			-2.07147	0.028571
40	313	12.9	0.129	-5329.32	-0.11608	-93.446	-2.04794	0.025
45	318	16.9	0.169	-4700.39			-1.77786	0.022222
50	323	9.1	0.091	-6436.68			-2.3969	0.02

Where C_e is the equilibrium concentration of methyl parathion in solution in mg mL^{-1} , C is the amount of methyl parathion sorbed onto the aluminosilicates material (mg mg^{-1}) . The value of k can be taken as a relative indicator of sorption capacity , while 1/n shows the energy or intensity of sorption . these are the experimental parameters , which depends on the system of sorbent and sorbate. The values of n represent a favourable sorption [11]. Figure 2 shows the freundlich plot for sorption of methyl parathion by the bentonite.

Effect of temp

Effect of temperature on sorption of methyl parathion on

synthetic aluminosilicates at different temperature (35, 40,45, 50±1^{0}c) has been studied puring the temperature studied, pH of the medium methyl parathion concentration equilibration time i.e., pH7, 0.0100M and 24h respectively were kept constant the decrease in sorption is due to the change in energy of sorption or weakening of or born of vanderwaals forces of attraction between the pesticide and material surface causing in physical sorption of pesticide with a change in temperature [2,13-15].
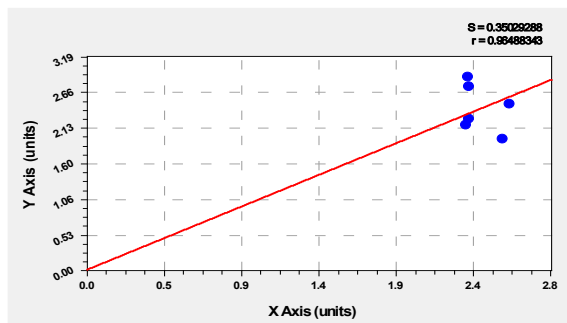
Fig 2 freundlich sorption isotherm for the sorption of methyl parathion onto bentonite.

The Methyl parathion have functional groups capable of engaging in H- bonding and vanderwaals bonding . the presence of C=O bond will result in the overall polarity and also more polar molecules is likely to move closer to charged surfaces increasing the likelihood of vanderwaals interaction . the quality and nature of smaller particle size fraction also contribute to the surface area and hence largely control the overall sorption characteristics of minerals.

Thermodynamic parameter, namely gibbs free energy (G^0) , enthalpy (H^0) , entropy (S^0) changes for the process and apparent equilibration constant K were calculated by using standard thermodynamic equation :

$$\Delta G^0 = -RT \ln k$$

$$\ln (K_1/K_2) = \frac{\Delta H^\circ}{R} \frac{T2-T1}{T1T2}$$

$$\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$$

$$K = C/Ce$$

The values of corresponding thermodynamic parameters (G^0,H^0 and S^0) are given in table1. The value of k have been found higher than unity for all the materials indicating that the patricide has high preference for material the standard free energy change ((G^0) for the sorption process was obtained at 35, 40 , 45, 501^{0}C the values G^0 indicate the degree of spontaneity of sorption whereas negative values reflect a more energetically favorable sorption process. The G^0 values also confirm the feasibility of the sorption. The negative value of overall heat of sorption H^0 indicate exothermic nature of reaction with a strong binding of pesticides molecule on the mineral surface .the low value

of H^0 also show that sorption may occur through covalent bonding mechanism and /or hydrogen bonding[16]. The sorption of pesticides could also be explained as the interaction with exchangeable cations most probably through water molecules corrdinated with cations. Methyl parathion interacts with exchange cations through molecules of coordinated water possible by means of C=O , P-O and P=S group[17].

Effect of pH:-
pH is also an important factor governing sorption of pesticides . In order to optimize the pH for maximum removal /sorption efficiency , experiments were conducted in the pH range of 2-10 at constant temperture (301^{0}C) , 3 h equilibration time ,0.0100 M Methyl parathion concentration and aquous to sorbent ratio 1:1(ML/mg) fig. 3 shows the effect of pH on sorption of Methyl parathion onto the synthetic aluminosilicates . Experimental studies shows that decrease in acidity or increase in pH substantially increases the Methyl parathion uptake onto the synthetic aluminosilicates materials [20,21] .
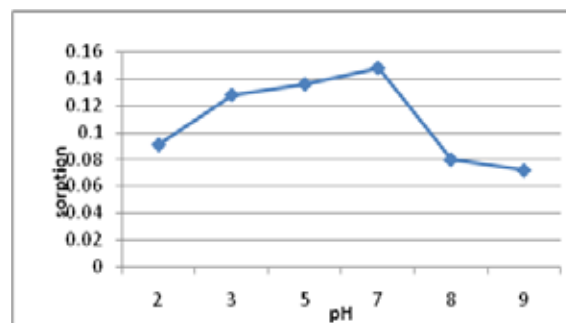

Fig 3- Effect of pH on sorption of Methyl parathion onto Bentonite.

Desorption study:-
The stability of the sorbed pesticide towards double distill water is established by desorption study for period of 3h to 1 day. The desorption data several that the percentage of desorption after 2h is found to be 4 to 60% the desorption data show the capability of materials to hold the pesticide for a long time.

Conclusions –
The synthesized aluminosilicates have been shown to be good retention materials providing a suitable matrix to hold the pesticide for a longer period and minimize the possibility of leaching of pesticide with distil water. Bentonite material could be best utilized for the restriction of methyl parathion. Maximum uptake capacities of both the material ware found to occur at neutral medium and temperature 301^{0}C when 0.0100 M methyl parathion concentration and aqueous to sorbent ratio 1:1(ML/mg) were taken by varying the sorptive properties of alumino silicates, they can be used to immobilize pesticide in a contaminated soil and its removed from contaminated water. These materials may also be used as controlled supplier of nutrients towards plants growth.

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