Removal of pesticide (Monocrotophos) from aqueous solution using nano iron oxide loaded poly (styrene-co-maleic anhydride) co-polymer by batch and fixed bed column method

Anita Bind and Alka Tiwari

Abstract-Removal of Monocrotophos from aqueous solution using PSMA Hydrogel was studied by batch and column adsorption experiments. The effects of adsorbent dose, contact time, concentration and pH on the adsorption processes were systematically studied in batch sorption experiment.The results showed that the maximum adsorption was 95% of 10µg/ml manocrotophos adsorbed onto PSMA with contact time of 120min. at pH 8.The adsorbent polymer was characterized by FTIR, XRD and TEM analysis techniques. Equilibrium adsorption data was applied to Langmuir and Freudlich isotherm. Column experiments were carried out at different influent pesticide concentration, flow rate and bed height.

Keywords: adsorbent, pesticide, adsorption, Langmuir, monocrotophos

1. Introduction:-In recent years, rapid industrialization and a dramatic increase in the human population, the chemical substances (fertilizers,herbicides, pesticides, heavy metals and organic contaminates) have become the most significant environmental pollutants [1]. Pesticides enter surface and ground water primarily as runoff from crops and are prevalent in agricultural area [2]. The use of pesticide is helpful in improving the production of food grams & vegetables etc but also shows adverse effects on the environment & human health [3]. Pesticides are one of the main causes of water pollution and some being the persistent organic pollutants;contribute to soil contamination [4].

Pesticides are very dangerous and harmful because of their tissue degradation and carcinogenic nature.Monocrotophos [dimethyl – (E) -1- methyl -2 (methyl carbamoyl) vinyl phosphate]is an organophosphursinsecticide with nonspecific systemic and acricide action used for the protection of various cash crops[5-6].It is principally used in agriculture as a relatively cheap pesticide and it is water soluble, thus weakly sorbed by soil particles and quickly penetrates into the plant tissues[7-8]. Hence,it is necessary to decrease the pesticides concentration from water leading to clear and safe ecosystem.

Waste water treatment methods include precipitation, coagulation, floatation, sedimentation, filtration, membrane process, electrochemical techniques, ion exchange, biological process and chemical reactions;each method has its own merits and limitations in applications [9]. Most of the pesticides present in surface water are removed or transformed during physical / chemical treatment

processes and environmentally compatible technologies for the removal of pesticide from agricultural waste water[10].Inagricultural field, polymers are widely used for many applications [11].Adsorptionis a surface phenomenon in which adsorbate is held onto the surface of adsorbent by van der waals forces and saturation is represented by equilibrium point. It is well known methods used in the removal of such hazardous compounds from polluted waters [12]. Recent attention of the scientists has been devoted to the study of different types of low cost materials such as fertilizer waste [13] walnut shell [14] bagases[15] cornwood[16] , bleaching earth[17] red mud [18], gas concrete material [19],industrial waste [20]. Among these adsorbent magnetic PSMA hydrogel showed highest removal efficiency of pesticides.In the present paper the magnetic adsorbent(PSMA) hydrogel and its use for decontamination of water. Poly styrene-co-maleic anhydride is a synthetic co-polymer of hydrophilic maleic anhydride and hydrophobic styrene having interesting chemical and biological properties. The presence of hydrophilic polymer "maleic anhydride" may promote better diffusion of aqueous solution through the porous structure of polymer and also provides a strong electron accepting ability. TheNanoparticlesof iron oxide have a tendency to aggregate due to the strong magnetic dipole-dipole attractions. In order to avoid this problem, nano particles were impregnated into the co-polymer matrix by insitu method which providesthem better stability. For comparing the adsorption capacity of PSMA hydrogel with and without impregnation of iron oxide nanoparticles the experiments were carried out by batch method which showed the removal of monocrotophos as 94.5% and 65% respectively. Thus by encapsulation role of nanoparticles of iron oxide into the co-polymer i.e. metric, it could increase is to enhance the removal capacity of the above adsorbent.

2. Material and methods

***Material*:** The monomer maleic anhydride, styrene, N,N- methylene- bis -acrylamide (cross-linker), potassium per sulphate (initiator), ammonia, anhydrous ferric chloride and ferrous chloride tetra hydrate were purchased from Molychem, Mumbai, India. Double distilled water was used throughout the experiments.

Synthesis of super paramagnetic PSMA co-polymers:To a mixture of styrene and maleic anhydridein 1:1 ratio the cross linker (N, N-methylene-bis-acrylamide) and initiator (benzoyl peroxide) were added and heated at 70^0C in an electric oven for 1hr. The co-polymeric SMA polymer so formed was washed with water. For insitu magnetization, the co-polymer was equilibrated in aqueous solution of ferrous chloride and ferric chloride for 24hr., followed by the addition of concentrated ammonia solution and kept overnight. The magnetic co-polymer was then washed thoroughly with water, dried crushed into a fine powder and stored.

Preparation of stock solution:The stock solution of monocrotophos of 1000mg dm^{-3} concentration was prepared by dissolving 0.1g of pesticide in 100ml of alcohol. Working solutions were prepared by diluting the stock solution for each experiment.

3. Adsorption Experiment: (Batch method):

The amount of monocrotophos present in solution (before and after adsorption) was determined by using UV/Vis spectrophotometer and the sorption degree (percentage removal) and sorption capacity of the sorbent was calculated by the following equations –

$$\text{sorptiondgree} = \frac{C_e - C_0}{C_0} \times 100 \quad (1)$$

$$\text{sorptioncapacity} = \frac{C_e - C_0}{m_{abs}} \times V_{sol} \quad (2)$$

Where C_0 and C_e (mg dm^{-3}) are initial and equilibrium concentrations of monocrotophos solutions respectively, V_{sol} (L) is the volume of the monocrotophos solution subjected to sorption and m sorb (g) is the weight of sorbent.

4. Column adsorption experiment: - For fixed bed column adsorption, a column of 10cm height and 1cm diameter was filled with the adsorbent with gaps and then a known concentration of monocrotophos solution was allowed to pass through the bed at a constant flow rate (1 ml /min^{-1}) in down flow manner. The pesticide solution was collected at different time intervals and its concentration was determined spectrophotomatrically.

The total amount of adsorbate sent to the column (m_{total}) was calculated using the following equation:-

$$m_{total} = \frac{C_0 Q t_{total}}{1000} \quad (3)$$

Where C_0 influent concentration, Q and t_{total} are the influent flow rate and exhaustion time respectively.

The adsorbed amount of pesticide in column study was determined by the following equation-

$$removal\% = \frac{q_{total}}{m_{total}} X 100 \quad (4)$$

Where $q_{total}$is sorbed quantity of adsorbat and m_{total} is the total amount of adsorbate sent to the column.

Determination of monocrotophos:-The concentration of monocrotophos in the solution was determined spectrophotometrically using a UV/VIS spectrophotometer cary60 at λ_{max} =240 nm.

5. Characterization of adsorbent: The adsorbent "magnetic SMA polymer" was characterized by XRD, FTIR, and TEM analysis.

XRD analysis:The crystalline nature of the magnetic nano particles loaded SMA co-polymer was studied on a Bruker D8advanced X-ray Diffractometer with scanning range of 20-80^0 (2 Θ) using cu kα radiation with wavelength of 1.5406 (UGC- DAE, Indore ,INDIA) .

FTIR Analysis: FTIR spectra of adsorbent were recorded using Varian Vertex FTIR Spectrometer (UGC-DAE, Indore, INDIA).

TEM Analysis: The average particle size, size distribution and morphology of iron oxide nanoparticles were examined using a TECNAI-G20 TEM at a voltage of 200kv. The solvent dispersion of the particles was drop- cast onto a carbon coated copper grid and the grid was air dried at ambient conditions (25±10 ^{0}C) before loading into the microscope (AIIMS, New Delhi, INDIA).

[Figure 1]

Results and discussions: The adsorbent "magnetic SMA polymer" was characterized by XRD, FTIR, and TEM analysis.

XRD Analysis: The XRD pattern of magnetic PSM co-polymer showed five characterististic peaks (2 =30.09; 35.44, 43.07, 56.96 and 62.55), marked by their indices [(511), (311), (400), (511) and (440), (511), and (440)]. The position and relative intensities of all diffraction peaks match well with those from the JCPDS file No.89-5984 for magnetic (Fe_3O_4) Magnetite particles are obtained according to the following reaction –

$$2FeCl_3 + FeCl_2 + 8NH_4OH \longrightarrow Fe_3O_4 + 8NH_4Cl + 4H_2O \quad (3)$$

[Figure 2]

FTIR Analysis:Fourier Transform Infrared spectroscopy of magnetic PSM co-polymer as shown in figure 3, indicated the peak at 2930.55cm-^{1}, due to C-H bond of methylene group ,at 3050-3000cm-^{1} due to Ar-H stretching, 1600 cm-^{1}(v), 1580cm-^{1}(v),and 1450 cm-^{1} (m)due to C=C stretching respectively. Absorption peaks of maleic anhydrides were observed at 1725 cm-^{1}, and 1780 cm-^{1} due to C=O of anhydride group .The characteristic peak at 566.69 cm-1 relates to Fe-O group, which indicates the loading of iron –oxide particles on PSM co-polymer .

[Figure 3]

TEM Analysis: The shape, size and morphology of iron oxide nano particles were determined through TEM imaging. The TEM images of nano particles show almost cubic iron oxide particles with an average size of less than 10 nm. It should be noted, however,

that the majority of the particles were scattered, a few of them showing aggregates indicate stabilization of the nano particles. The size of individual nano particles seems to be 1-10 nm, whereas majority of nano particles exhibit smaller sizes i.e. 5 and 8 nm**.**

6. Batch adsorption studies: Theadsorption experiments were carried out by varying pH, contact time, adsorbent dose, and adsorption concentration.

Effect of pH: - In order to evaluate the effect of initial pH on removal of pesticide from aqueous solution; batch adsorption experiments were performed at various pH values ranging between 2 to 8 by keeping all other experimental conditions constant (concentration 10µg/dm^{-3}; temperature 30±1^{0}C; adsorbent dose 0.1g L^{-1}; contact time 120min).A variation of the pH affects the ionization degree and solubility of the solute as the surface charge of the adsorbent[20]. When solution pH is below 4, the cationic species of pesticides are dominant in solution and the overall surface charge on the adsorbent both are positive Therefore, the electrostatic repulsion forces predominant, resulting in the lower adsorption capacity.At higher pH values the anhydride moieties of the adsorbent gethydrolyzed, hence the adsorbent surface becomes negatively charged,while the surface of adsorbate becomes more positively charged, leading to an electrostatic attraction between them.The maximum uptake of pesticide was achieved at pH 8, which was optimized for further investigation.

Effect of adsorbent dose: - The effect of adsorbent dose on the removal of pesticides was studied by varying the dose of adsorbent from 0.1 to 2g/ml. The experiment was carried out at fixed pesticide concentration at 10µg/ml, at a fixed temperature of 45^{0}C and pH 8. Initially, the amount of pesticide adsorbed was found to be rapid from 0.005 to 0.1g/ml. Further increase of adsorbent dose resulted in very less increase in adsorption. Hence0.1 g/ml was considered the optimum dose.

Effect of contact time:- Effect of contact time in the range of 10-150min. on the percent sorption of monocrotophos onto SMA co-polymer. Percent sorption increases with increasing agitation time and acquires equilibrium at 120min, which was taken as optimized value for further investigations.

Effect of concentration:-The effect of initial pesticide concentration was studied on the adsorption to styrene-co-maleic anhydride co-polymer under the determined optimum conditions. By increasing the initial analyte concentrations more pesticides is left unabsorbed in the solution due to the saturation of the binding sites [21].

7. Adsorption Isotherm: -The Langmuir and Freudlich adsorption isotherm models are widely used to describe adsorption data in waste water applications.

The Langmuir model- This isotherm represents the equilibrium distribution of sorbate between solid and liquid phases and represents monolayer sorption on a set of distinct localized sorption sites having the same sorption energies and no interaction between sorbed molecules.[22]. The Langmuir equation is tested in the following linearised form:

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \qquad (6)$$

Where 'Q' is the maximum sorption capacity indicating a monolayer coverage of the sorbent with sorbate while 'b' represents the enthalpy of the sorption, independent of temperature. C_e is the equilibrium pesticide concentration ($\mu g/mL^{-1}$) in water sample. The values of 'Q' (mmol g^{-1}) are calculated from slope of the linear plots whereas the values of 'b' are estimated from the intercepts of the plots.

Freudlich isotherm: This isotherm gives an empirical expression encompassing the surface heterogeneity and the exponential distribution of energies [23]. The linearized Freudlich model can be described by the following equation:

$$Inq_e = \left(\frac{1}{n_f}\right) InC_e + InK_f \qquad (7)$$

Where K_f is the Freundlich constant related to the binding energy and adsorption capacity (mg/g) and $1/n_F$ is the heterogeneity factor. From the plot of q_e vs. C_e from experimental data, K_F and $1/n_F$ can be evaluated from the intercept and slope of the linear regression, respectively.

8. Adsorption kinetics:

The Lagergrene's pseudo-first –order and pseudo-second-order models were used to test adsorption kinetics data in order to investigate the mechanism of adsorption. The value of correlation R^2 for the pseudo-second-order model is relatively high (>0.99) and the adsorption capacities calculated by the model are also close to those determined by experiments. However, the values of R^2 for pseudo-first-order model are not satisfactory. Therefore, it has been concluded that the Lagergrene's pseudo- second-order adsorption model is more suitable to describe the adsorption kinetics of the pesticides.

Fixed bed adsorption dynamics: -The operation parameters such as inlet concentration (c_0), volumetric flow rate (Q) and length of the bed (L) have a great influence on breakthrough and saturation times and on the dynamics of the column. In thisstudy, the effect of these parameters on the breakthrough curves of the monocrotophos was investigated.

Effect of initial influence concentration: -At a fixed bed height of 2cm.and a flow rate of 1ml/min effect of 5, 10 and 20ml/min solution concentration on poly SMA by monocrotophos was studied. It was observed that the increase in influent concentration was directly proportional to the sorption capacity [24]. This was attributed to increase in driving force (concentration gradient or mass transfer) for the adsorption process. [Table 1]

Effect of bed height:-Increase in bed height of adsorption column leads to an extension of breakthrough point as well as the exhaustion time of adsorbent [25]. This is due to increase in the amount of adsorbent in the column which translates to increase in service area. Bed height containing poly SMA of 0.5, 1 and 2cm for monocrotophos adsorption was varied at a fixed flow rate of 1ml/min and 10µg/mL, it was observed that sorption capacity increase can be attributed to sufficient residence time of monocrotophos solute in the column adsorption region which provided. [Table 2]

Effect of flow rate:-Reduction in exhaustion or column saturation and residence time due to unsatisfactory utilization of adsorption bed is a common phenomenon whenever higher flow rates of solution are used in column adsorption processes [26]. An increase in sorption capacity was observed when solution flow rate was increase from 1 to 3 ml/min, the sorption capacity decreased for adsorbent. This was attributed to intense competition for the limited active sites of the adsorbent by the numerous adsorbates molecules present in higher flow of solution.

[Table 3]

9. Conclusion: Magnetic nano particles of iron oxide loaded Styrene-co-maleic anhydride co-polymer has been found to be very effective adsorbent for the removal of monocrotophos from aqueous solution. By batch method the maximum removal of monocrotophos was noticed at pH between 7 to 8 at 45^0C in120min.In the flow method breakthrough time and shape of the breakthrough curve were conditioned by the tested operation conditions such as flow rate, bed height and inlet pesticide concentration. The novelty of this work is that the above adsorbent is cost effective, non toxic, can easily synthesized.

10. Acknowledgments

The authors would like to thank to UGC-DEA consortium of Scientific Research, Indore, India for FTIR analysis and AIIMS New Delhi, India for TEM , XRD ,SEM analysis.

References-

[1] P. Duchnowicz, P.Szczepaniak, M. Koter 2005. Erythrocyte membrane protein damage by phenoxyacetic herbicides and their metabolites j. of pesti. Biochem. Physiol. 82 59-65

[2] A. Begum 2008. Cost effective method of removal of fluoride from waste wate Inter. soci. of environ. botanist, Environews, 15-6

[3] N.P.Agnihotri, G. Kulshresthra, V.T.Gajbhiye ,S.P. Mohapatra& S.B. Singh 1996. Oraganochlorine insecticide residues in agricultural soil of the Indo-Gangetic plan, Environmental monitoring and assessment Enviro. Moni. and assess. 40 (3) 279-288

[4] A.M. carro, R.A.Lorenzo, 2001. Simultaneous optimization of the solid-phase extraction of organochlorins and organophosphorus pesticides using the desirability function j. of analyst. 126 1005-1010

[5] S. Senthikumar, S.K.Krishna, P. Kalamani, C.V.N.Subramaniam, Ganapathi 2001. Adsorption of organophosphorus pesticide from aqueous solution using "Waste" jute fibre carbon Mode. Appli. Scie.4 (6)

[6] A.M. Carro, R.A. Lorenzo 2010. Simultaneous optimization of the solid-phase extractionof organochlorine and organophosphorus pesticides using the desirability function j. of Analyst 126: 1005–10109

[7] D. De Almeida Azevedo, S. Lacorte, T. Vinhas, P. Viana, D. Barceló 2000. Monitoring of priority pesticides and other organic pollutants in river water from Portugal by gas chromatography–mass spectrometry and liquid chromatography–atmospheric pressure chemical ionization mass spectrometry J. of Chromato. A 879 13–26

[8] S.M. Gitahi, D.M. Harper, S.M. Muchiri, M.P. Tole, R.N. Ngàngà 2002. Organochlorineand organophosphorus pesticide concentrations in water, sedimentand selected organisms in Lake Naivasha (Kenya) j. of Hydrobi. 488 123–128

[9] W. Li, S.-P. Qiu, Y.-J. Wu 2008. Triazophos residues and dissipation rates in wheat crops and soil J. of Ecotoxi. and Environ. Safety 69, 312–316 9

[10] M. Akhtar, S.M. Hasany, M.I. Bhanger, S. Iqbal 2007. Low cost sorbents for the removal of methyl parathion pesticide from aqueous solutions j.of Chemosphere 66 1829–1839

[11] G.Z. Memon, M.I. Bhanger and M. Akhtar, Peach –nut shells-an effective and low cost adsorbent for the removal of endosulfan from aqueous solution.

[12] A. Saeed, M. Iqbal 2003. Bioremoval of cadmium from aqueous solution by black gram husk (Cicerarientinum) Water Research 37 3472–34809

[13] S.Chowdhury, P. Saha, 2010. Sea shell powder as a new adsorbent to remove Basic Green 4 (malachite Green) from aqueous solution, Equilibrium, kinetic and thermodynamic studies J. chem, Eng. 164 168-173

[14] G, Annadurai, R.S, Juang, D.J, Lee 2002. Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. J.Hazard. Mater. 92 263–274 .

[15] V.K, Gupta, I, Ali 2008. Removal of endosulfan and methoxychlor from water on carbo slurry J. of Environ. Sci.Technol. 42 766–770

[16] V.K,Gupta, I, Ali, V.K.Saini 2004. Removal of chlorophenols from wastewater using red mud: an aluminum industry waste J. of Environ. Sci. Technol. 38 4012–4018

[17] Wu, F.C., R.L,Tseng,R.S. 2001. Adsorption of dyes and phenols from water on the activated carbons prepared from corncob wastes J. Environ. Technol. 22: 205–213 9

[18] C, Xia, F, Zhou, Y, Chen, L, Zhang 2011. Removal of lead from aqueous solution by sewage sludge carbon adsorbent j. of Adv.Mater. Res. 239, 242.

[19] J.S.Noh, J .A Schwarz 1989. Stimation of the point of zero charge of simple oxides by mass titration. J. of colloid Interface Sci.130: 157-164

[20] H. Freundlich 1926. Colloid and Capillary Chemistry, Methuen, London, pp. 397–414,

[21] I. Langmuir 1918.The adsorption of gases on plane surface of glass, mica and platinum J.of the Chemical Society 40: 1361–1403

Captions of figures:-

Figure 1 Transmission Electron Micrograph of iron oxide Nanoparticle

Figure 2 XRD pattern of super paramagnetic poly (styrene-co-maleic anhydride) co-polymer.

Figure 3 FTIR spectra of super paramagnetic poly (styrene-co-maleic anhydride) co-polymer.

Figures

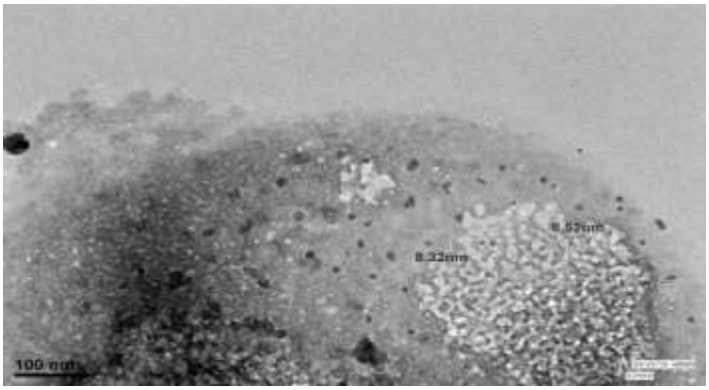

Figure 1

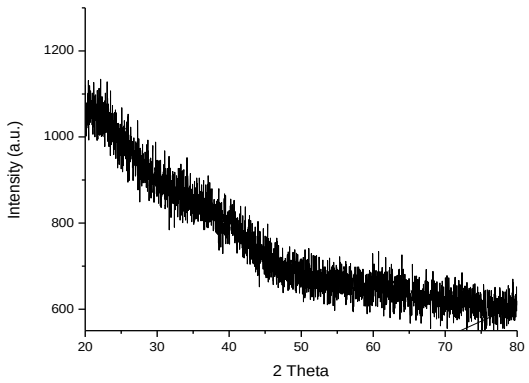

Figure 2

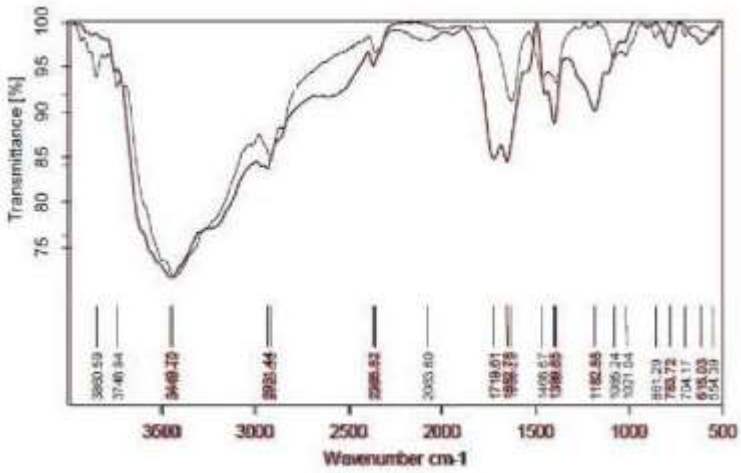

Table 1

Bed height (cm)	Flow rate	t total (min)	m total (mg)	q total(mg)	q_{eq}
2	1	200	21	16.119	10.5
2	2	250	15	11.36	15.00
	3	125	11.4	21.94	21.75

2					

Table 2

Bed height (cm)	Flow rate	t total (min)	m total(mg)	q total (mg)	q_{eq}
2	1	145	7.25	4.314	7.25
4	1	155	7.75	4.856	6.75
6	1	175	7.5	3.946	8.00

Table 3

Bed height (cm)	1	Different concentration (ppm)	t total (mg)	m total(mg)	q Total(mg)	q_{eq}
2	1	5	160	6	3.924	6.4
2	1	10	210	21	16.119	10.00
2	1	20	150	6	3.924	9.00