International Research Journal of Environment Sciences ISSN 2319–1414
Vol. **3(11), 4**1-46, November **(2014)** *Int. Res. J. Environment Sci.*

Effective Removal of Pesticide (Dichlorvos) by Adsorption onto Super Paramagnetic Poly (styrene-co-acrylic acid) Hydrogel from Water

Tiwari Alka* and Bind Anita
Research Centre, Department of Chemistry, Govt.V.Y.T.PG. Autonomous College, Durg, C.G.-491001, INDIA

Available online at: www.isca.in, www.isca.me
Received 21st September 2014, revised 26th October 2014, accepted 19th November 2014

Abstract

The removal of pesticide "dichlorvos" from aqueous solution by adsorption onto superparamagnetic nano iron oxide loaded poly (styrene-co-acrylic acid) hydrogel was studied by batch and column method. The adsorbent hydrogel was characterized by FTIR, XRD and TEM analysis techniques. The efficiency of the poly (styrene-co-acrylic acid) hydrogel was studied by measuring the maximum uptake of dichlorvos at fixed pH, concentration and time. The batch and column studies were carried out under varying experimental conditions such as contact time, initial pesticide concentration, adsorbent dose, pH, bed height and flow rate. The adsorption data was applied to Langmuir isotherm equation.

Keywords: Adsorption, hydrogel, Dichlorvos, Nano iron oxides, Isotherm.

Introduction

A wide range of pesticides has been extensively used by modern agriculture practices[1]. There are major routes thought which pesticides reach into the environment, either by application, disposal, runoff or a spill[1]. Environmental contamination due to the excessive use of pesticides has become a great adverse effect on human health and environment[2]. The excessive use of pesticides to control the crop destroying insects has gained momentum in last two to three decades. Due to their widespread usage, they easily contaminate different media i.e. soil, air and ground water. Their residues may remain in soil which decreases the biodiversity in the soil and they may also enter into the ground waters by eroding soil[3]. Many Organophosphate compounds are currently being used as pesticides have been of great concern due to their persistence, bioaccumulation as well as their toxicological effects on human health and the environment[4]. Pesticides are hazardous and toxic in nature and persist in the aquatic environment for many years after their application[5].

Most of the developed countries have banned many of the pesticides due to their potential neurological effects to man and ecosystem. In many developing countries, the use of organophosphate pesticide have banned because they do not readily break down, they pollute the air, soil, river, lakes and ultimately marine ecosystem[6]. Organophosphate pesticides are organic micro pollutants of great environmental concern due to their toxicity, persistent nature and highly adverse effects on animals and human beings[7]. Dichlrvos is a highly toxic organophosphate insecticide widely used in developing countries. Dichlorvos is highly toxic to mammals and human beings. The signs of intoxication are salivation, lachrymation, diarrhea, tremors and terminal convulsions with death occurring from respiratory failure. Many developing countries applying the combination of a number of chemical, biological and physical processes for decontamination of water. Adsorption as one of the processes has evolved almost effective physical methods for pesticide removal[8].

Adsorption is a surface based process in which adsorbate is held onto the surface of adsorbent by Van der waals forces. It may also occur due to electrostatic attraction and chemical bonding. It is one of the well-known methods used in the removal of such hazardous compounds from polluted waters[9-11]. There are many conventional methods consists of coagulation, flocculation, sedimentation, sand-multimedia filtration, disinfection, photo catalysis and adsorption etc. Among these techniques, adsorption has proved to be the most appropriate method to treat the effluents offering advantages over conventional process[12].

The goal of this study is to determine the sorption capacity of super paramagnetic nano iron oxide loaded poly (styrene- co-acrylic acid) hydrogel as adsorbent in removing "Dichlorvos" insecticide from aqueous solution. The effectiveness of poly (styrene-co-acrylic acid) to remove pesticide can be used an alternative medium to treat the contamination from water environment or wastewater.

Material and Methods

Material: The monomer acrylic acid, styrene, N,N- methylene-bis -acrylamide (cross-linker), potassium per sulphate (initiator), 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 PSA hydrogel: To a mixture of styrene and acrylic acid in 1:1 ratio, the cross linker (N, N-methylene-bis-acrylamide) and initiator (potassium per sulphate) were added and the mixture was heated at 70^0C in an electric oven for 1hr. The co-polymeric hydrogel so formed was washed with distilled water and cut into small uniform size pieces. For insitu magnetization, these pieces were equilibrated in an aqueous solution of ferrous chloride and ferric chloride for 24hr. followed by the addition of concentrated ammonia solution and kept overnight. The nano iron oxide loaded co-polymeric hydrogel was then washed thoroughly with distilled water, dried, crushed into a fine powder and stored.

Preparation of stock solution*:* The stock solution of dichlorvos of 1000 µg/ml^{-1} concentration was prepared by dissolving 0.1g of pesticide in 100ml of alcohol. Working solutions were prepare each experiment by diluting the above solution.

Analytical technique*:* An aliquot of standard solution containing 10-100µg of dichlorvos was evaporated to 0.5ml in a water bath then kept in ice cold water and 0.5 ml of 1M sodium hydroxide solution was added. This solution was left for 15-20 minutes for complete hydrolysis followed by the addition of 1ml phloroglucinol solution and kept in a boiling water bath for 15 minutes. Then in ice was kept in ice cold water and the volume was made up to 25ml with 0.01M Sodium hydroxide solution to get a colored dye .The absorbance of dye was measured at 475nm against a reagent blank.

Adsorption experiment: The concentration of pesticide before and after adsorption was determined spectrophotomatrically (Cary 60 UV/Vis spectrophotometer) by following method. The adsorbed amount of pesticide was determined by the following equation.

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

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

Where C_0 and C_e (µg /mL^{-1}) are initial and equilibrium concentration of dichlorvos solutions respectively, V_{sol} (mL) is the volume of the dichlorvos solution subjected to sorption and m sorb (g) is the weight of sorbent.

Fixed bed column studies: The pesticide solution was collected at different time intervals and its concentration was determined spectrophotomatrically.

The total amount of pesticide sent to the column (m_{total}) is calculated by 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:

$$removalf\ \% = \frac{q_{total}}{m_{total}} X100 \quad (4)$$

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

Results and Discussion

FTIR Analysis: Fourier Transform Infrared spectroscopy (FTIR) of super paramagnetic PSA Hydrogel as shown in figure 1 indicated the peak at 2930.55cm-^{1}, assigned 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 due to acrylic acid were observed at 1725 cm-^{1}, and 1449 cm-^{1} due to C=O, and C-O, stretching of the carboxylic (-COOH) group and at 3446.24 cm-^{1} due to –OH stretching of (-COOH) group. The characteristic peak at 566.69 cm-1 relates to Fe-O group, which indicates the loading of iron –oxide particles on PSA Hydrogel because the surface of iron oxide with negative charges has an affinity towards PSA Hydrogel, the magnetite nano particles could be loaded into protonated copolymer by the electrostatic interaction and chemical reaction through N,N-methylene-bis-acrylamide cross linking.

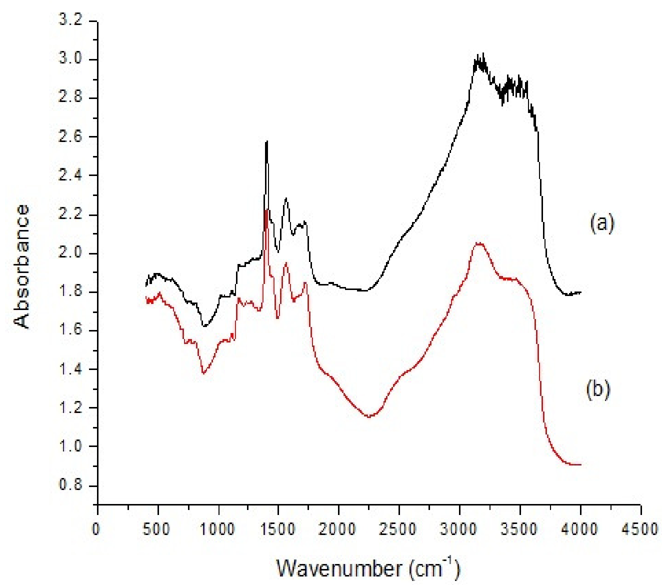

Figure-1
FTIR spectra of super paramagnetic poly (styrene-co-acrylic acid) Hydrogel

XRD Analysis*:* The XRD pattern of Supermagnetic PSA Hyrdogel showed five characteristic 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 in finger. 2 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 –

$$2FeCl_3 + FeCl_2 + 8NH_4OH \rightarrow Fe_3O_4 + 8NH_4Cl + 4H_2O \quad (5)$$

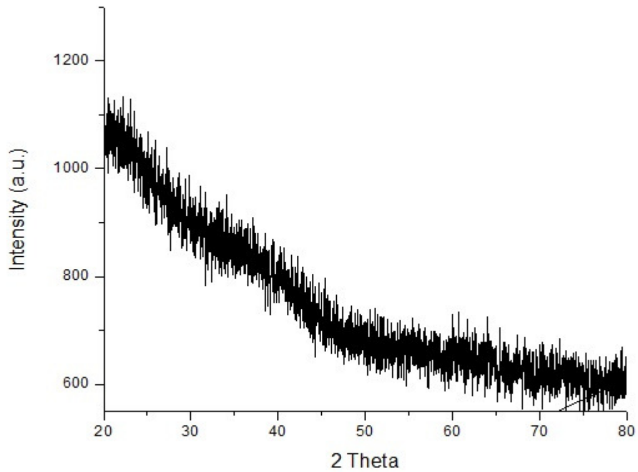

Figure-2
XRD pattern of super paramagnetic poly (styrene-co-acrylic acid) hydrogel

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 10nm, as shown in figure 3. 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 sizes of individual nano particles seem to be 1-10nm, whereas majority of nano particles exhibit smaller size i.e. 5 and 8 nm.

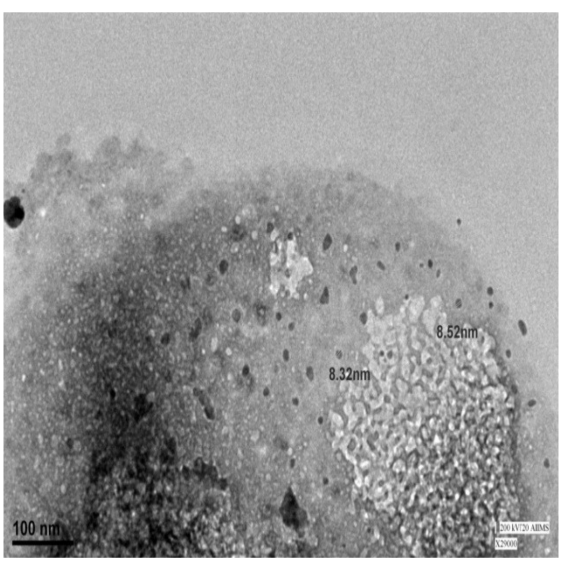

Figure-3
Transmission Electron Micrograph of iron oxide nanoparticles

Batch adsorption studies: Batch adsorption performance of the poly styrene-co-acrylic acid hydrogel for the adsorption of dichlorvos was investigated by various operating parameters such as effect of dichlorvos concentration, effect of pH, effect adsorbent dose and time.

Effect of pH: In order to determine the effect of initial pH on pesticide removal from aqueous solution, batch adsorption experiment was performed at various pH values that ranging from 2 to 8 by keeping all other experimental conditions constant (i.e. concentration of pesticide 50µg/mL^{-1}; temperature 30±1^{0}C; adsorbent dose 0.4g; contact time 60min.). Lower sorption efficiency observed at basic pH range (pH 7-11) might be attributed to the increase in hydroxyl ions leading to the formation of aqua-complexes thereby retarding the sorption[16]. At basic pH values the dissociation degree of groups at the adsorbent surface is high and both, the adsorbent and solutes occur in their negatively charged forms. Consequently, the adsorption is disfavored due to the presence of electrostatic repulsion between the molecules and the surface of adsorbent. The maximum uptake of pesticide was achieved at pH 4, as shown in figure 4 which was optimized for further investigations.

Figure-4
Effect of pH variation on the dichlorvos removal thought poly styrene-acrylic hydrogel = 0.4g, time = 60mintes, temp. =28±0.2^{0}C

Effect of initial concentration: Effect of pesticide concentration on the adsorption was evaluated by varying pesticide concentration (10-60µg/mL^{-1}) by employing uniform operational conditions [adsorbent dose 0.4g; contact time 60min.; temperature 30 ±1^{0}C; pH 3]. The equilibrium sorption capacity of pesticide was found to increase with the increase in sorbate concentration up to a certain concentration and remained constant with additional increase in concentration, as shown in figure 5 which may be attributed to the increase in concentration gradient and thus indicating the saturation of sorption sites.

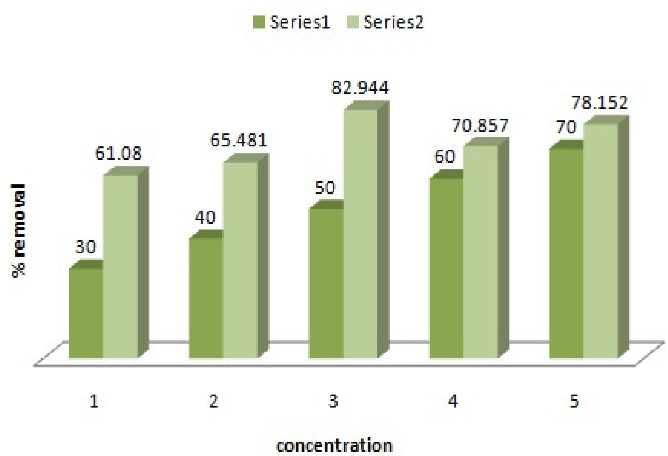

Figure-5
Effect of concentration variation on dichlorvos pesticide removal though superparamagnetic PSA hydrogel =0.4g, pH = 4, temp. = 28±2^{0}C

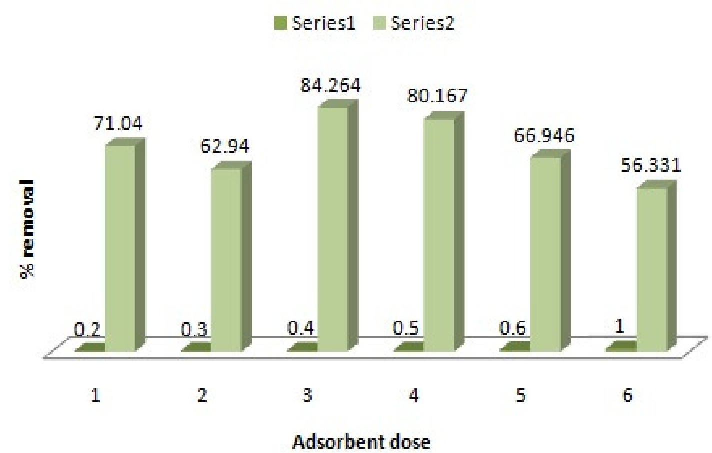

Figure-6
Effect of adsorbent dose variation on dichlorvos pesticide removal thought poly styrene –co-acrylic acid hydrogel pH = 4, time = 60minutes, temp. = 28± 0.2^{0}C

Effect of adsorbent dose: Adsorbent dose is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dose on the removal of pesticide was studied by varying the dose of adsorbent in the range of 0.2-1g at fixed pesticide concentration.

Effect of contact time: In order to determine the equilibrium time for maximum uptake 0.4 g of adsorbent was shaken with 20ml 0f 50µg/mL^{-1}pesticide for different time intervals (10 to 120 min), 60 minutes time was found sufficient to attain equilibrium sorption showing the maximum uptake up to 80.16% as shown in figure 7.

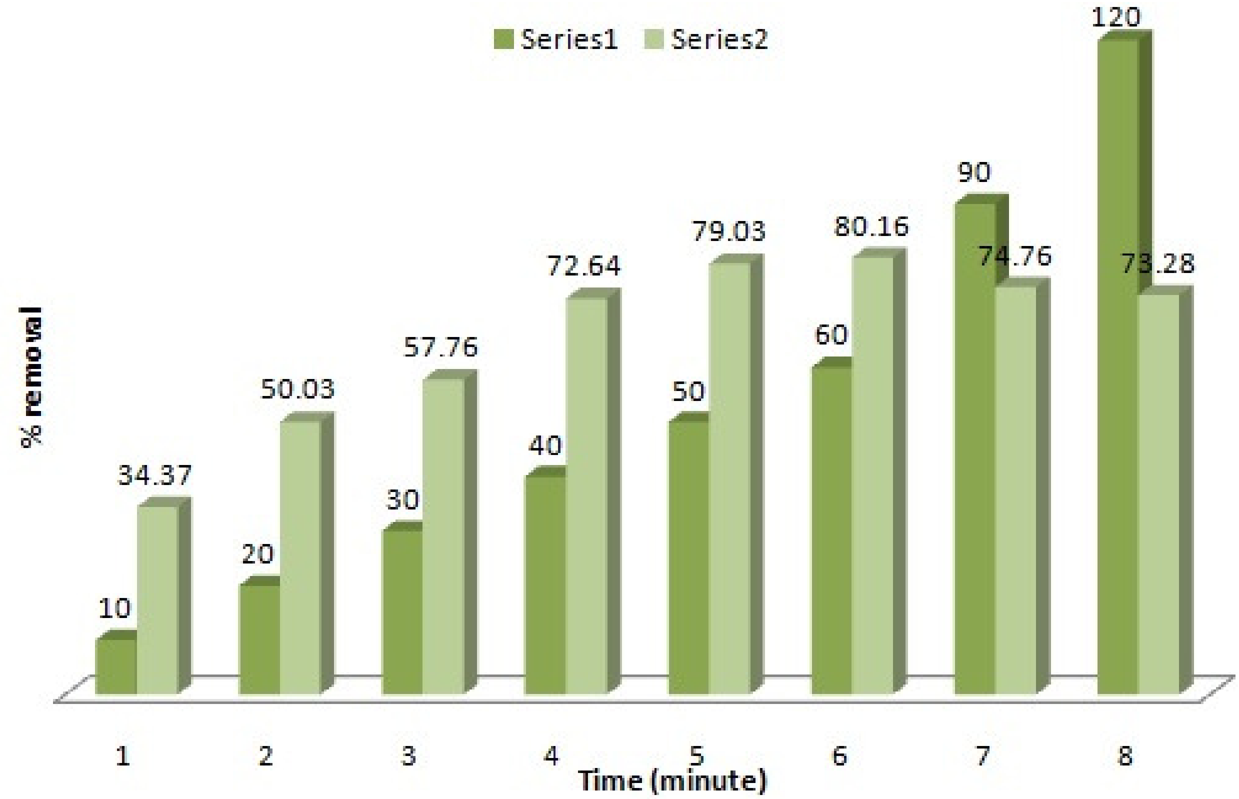

Figure -7
Effect of time on dichlorvos pesticide removal of thought poly styrene- co-acrylic acid hydrogel = 0.1g, pH = 4, time = 60 mintues

Adsorption isotherm: The parameters obtained from the different model provide important information on the adsorption mechanism and at surface properties of the adsorbent. The most widely accepted surface adsorption models are Langmuir model.

Langmuir isotherm: The Langmuir isotherm was applied for adsorption equilibrium study which is based on the assumption that maximum adsorption corresponds to monolayer of adsorbate molecules on the adsorbent surface that the energy of adsorption is constant and that there is no transmigration of adsorbate on the plane of the surface. The Langmuir equation is tested in the following linearised form:

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

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 ($\mu g/mL^{-1}$). The values of 'Q' (mmol g^{-1}) are calculated from slope of the linear plots whereas the values of 'b' are estimated from the intercept of the plot .shown in figure 5.

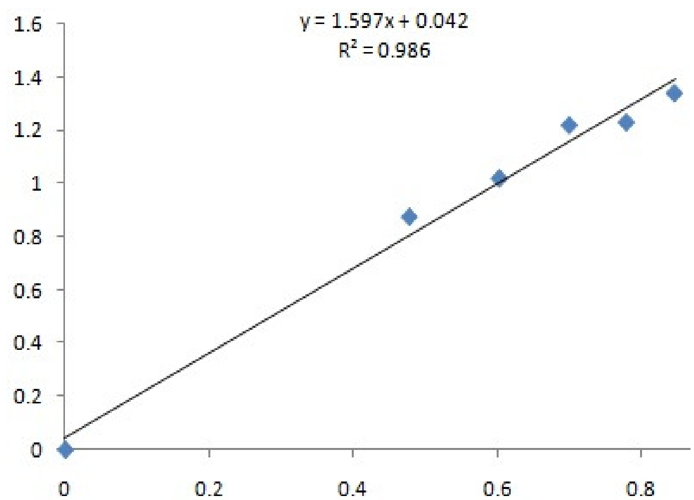

Figure-8
Langmuir sorption isotherm of dichlorvos pesticide on poly styrene- co- acrylic hydrogel

Fixed bed column studies: The column performance of the poly styrene-co-acrylic acid hydrogel for the adsorption of dichlorvos was investigated by various operating parameters such as effect of dichlorvos concentration, effect of flow rate and effect of bed height. The changes in the concentration gradient affect the saturation rate and breakthrough time and the diffusion process is concentration dependent.

Effect of flow rate:-Adsorption of pesticide "Dichlorvos" in columns was operated with different flow rates (1, 2 and 3mL/min.) until no further pesticide removal was observed as shown in table-1. The breakthrough curve for a column was determined by plotting the ratio of C_e/C_0 (C_e and C_0 are the pesticide concentration of effluent and influent respectively) against time. The column performed well at lowest flow rate (1mL/.min.) With the increase of flow rate from 1 to 3ml/min, the breakthrough and exhaustion time was increased. The Breakthrough time decreased as the volumetric flow rate increased.

Table-1
Results of breakthrough curve at different flow rates for adsorption of dichlorvos (pesticide) onto styrene-co-acrylic acid hydrogel

Bed height (cm)	Flow rate	t total (min)	m total (mg)	q total (mg)	q_{eq}
4	1	210	21	16.119	10.5
4	2	150	15	11.36	15.00
4	3	145	11.4	21.94	21.75

Effect of bed height: In order to study the effect of the bed height on the adsorption performance and the breakthrough curves, fixed-bed experiments were conducted at different bed heights (2.0 ,4.0 and 6.0cm) as shown in table 2 with an inlet pesticide concentration of $50\mu g/ml^{-1}$ and a volumetric flow rate of 1.0 ml/min. It has been noticed that the breakthrough time corresponding to the bed height of 2.0, 4.0 and 6.0cm are 85, 135, 145 min. respectively. It was observed that when the bed height increases, the number of binding sites is higher, thus increasing the adsorption area of the adsorbent. In this situation, the adsorbate has more time to diffuse through the pores of the adsorbent.

Effect of initial pesticide concentration: The influence of the initial pesticide concentration on the shape of the breakthrough curves was studied at inlet concentration of 30, 40 and 50 $\mu g/ml^{-1}$, at a constant flow rate (1.0ml/min) and bed height of 4.0 cm. It was observed that when the initial pesticide concentration increased from 40 to $50\mu g/ml^{-1}$, the breakthrough time decreased.

Table 2
Results of breakthrough curve at different bed height of adsorption of dichlorvos onto styrene-co-acrylic acid hydrogel

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	135	7.75	4.856	6.75
6	1	165	7.5	3.946	8.00

Table 3
Results of breakthrough curve at different concentration for adsorption of dichlorvos (Pesticide) onto styrene-co-acrylic acid hydrogel

Bed height (cm)	1	Different concentration (ppm)	t total (mg)	m total (mg)	q Total (mg)	q_{eq}
4	1	40	160	6	3.924	6.4
4	1	50	210	21	16.119	10.00
4	1	60	150	6	3.924	9.00

Conclusion

The magnetic nano particles loaded ploy (styrene-co-acrylic acid) hydrogel has been found to be very effective adsorbent for the removal of dichlorvos from aqueous solution. By batch method the maximum removal of dichlorvos was noticed at pH between 3 to 4 at 28^0C in 60 minutes. In flow method the breakthrough time and shape of the breakthrough curve were conditioned by the tested operation conditions such as volumetric flow rate, bed height and inlet pesticide concentration.

Acknowledgments

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

References

1. Adachi A., Ikedia C, Takagi S, Fukao N, yoshie E and Okano T, Efficiency of rice bran for removal of Organochlorine compounds and benzene from industrial waste water, *J. of agri. food chem.,* **49**, 1309-1314 **(2001)**
2. Bakour EI, Morillo H, usero J and ooassini A, Natural attenuation of pesticide water contamination by using ecological adsorbents, application for chlorinated pesticide included in European water framework directive, *J. of Hydro.,* **364**, 175-181 **(2009)**
3. Shukla G., Kumar A., Bhanti M., Joseph P.E. and Taneja A, Organochlorine pesticide contamination of ground water in the city of Hyderabad, *Environ. inter.,* **32**, 244-247 **(2006)**
4. Monirith I., Uneno D, Takahashi S, Nakata H, sudryanto A, Subramanian A, karupiah S, ismail A, Muchtar M, Zhehg J, Richardson B.J., Prudente M, hue N.D., Jana T.s., Tkalin A.V and Tanabe S, Asia –pacific mussel Watch : Monitoring contamination of persistent Organochlorine compounds in coastal water of Asian countries, *Mar. pollu. Bull.,* **46,** 281-300 **(2003)**
5. Radan B.D, Pennigton D.W., Eckley N. and Boethling A, *Environ. Sci. Technol.,* 33-3482 **(1999)**
6. Philip H.H, Michalenko E.M, Jarvis W.F, Basu D.K., Sage G.W, Meyland W.M., Beauman J.A and Gray D.A., Handbook of Environmental fate and Exposure Data For oganic chemicals, Lewis, Chelse, MI, **3, (1991)**
7. Memon G.Z., Bhanger M.I., Akhtar M., Talpur F.N. and Memon J.R., Adsorption of methyl parathion pesticide from water using watermelon peels as a low cost adsorbent, *J. Chem. Eng.,* **138,** 616–621 **(2008)**
8. Zhang S.J., Shao T., Bekaroglu S.S.K., Karanfil T., The impacts of aggregation and chemistry of carbonano tubes on the adsorption of synthetic organic compounds, *Environ. Sci. Technol.,* **43,** 5719–5725 **(2009)**
9. Sheha R.R. and Metwally E., Equilibrium isotherm modeling of cesium adsorption onto magnetic materials, *J. Hazard. Mater.,* **143,** 354–361 **(2009)**
10. Gupta V.K. and Imran A., Removal of DDD and DDE from waste water using baggasses fly ash sugar industry waste, *Water Res.,* **35**, 33e-40 **(2001)**
11. Gupta V.K., Jain C.K., Imran A. and Chanda S., Removal of Lindane and malathion from waste water using baggaaae fly ash : A sugar industry waste, *Water Res.,* **3,** 2483e-2490 **(2002)**
12. Zweiner C, weil L and Niesser R, Atrazine and parathion-methyl removal by UV and UV/O_3 in drinking water treatment, *Inter. J. of analy. Chem.,* **58,** 247-264 **(1995)**
13. Agarwal S and Nayak A, Comparative investigation on adsorption performance of mesoporous activated carbon prepared from waste rubber tire and activated carbon for an azo dye, *J. of Hazarad. Mater.,* 186-891 **(2011)**
14. Chen G.C., Shan X.Q., Pei Z.G., Wang H.H., Zheng L.R. and Zhang J. et al., Adsorptionof diuron and dichlobenil on multiwalled carbon nanotubes as affected bylead, *J. Hazard. Mater.,* **188**, 156–163 **(2011)**
15. Kundu Snigdha, Modeling phenol adsorption in Water environment using artificial neutral network, *Inter. Res. J. of Environ. Sci.,* **2(7),** 39-43**(2013)**
16. Tiwari Alka and Kathane Prerna, Supper paramagnetic PVA-Alginate Microspheres as Adsorbent for cu2 ions removal from Aqueous systems, *Inter. Res. J. of Environ. Sci.,* 2(**7**), 44-53 **(2013)**
17. Mohan Raj V., Padmavathy S. and Sivakumar S., Water quality Parameters and it influences in the Ennore estuary and near Coastal Environment with respect to Industrial and Domestic sewage, *Inter. Res. J. of Environ. Sci.,* **2(7),** 20-25 **(2013)**
18. Dubey Savita, Analysis of Physico-Chemical Parameters of Kshipra river Water at Ujjain, India *Inter. Res. J. of Environ. Sci.,* **2(7),** 1-4 **(2013)**
19. Zaker Y., Hossain M.A. and Islam T.S.A., Effect of Various Factors on the Adsorption of Methylene Blue on Silt Fractionated from Bijoypur Soil, Bangladesh, *Inter. Res. J. of Environ. Sci.,* **2(6),** 1-7 **(2013)**