J. Chem. Soc. Pak., Vol. 35, No.3, 2013

Removal of Paraquat and Linuron from Water by Continuous Flow Adsorption/ Ultrafiltration Membrane Processes

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(Received on 28th August 2012, accepted in revised form 10th December 2012)

Summary: The magnetic activated carbon (MAC) was prepared, characterized and compared with powdered activated carbon (PAC) for its adsorptive parameters. Both adsorbents were then used in combination ultrafiltration (UF) membrane as pretreatment for the removal of paraquat and linuron from water. The comparison of membrane parameters like percent retention, permeate flux and backwash times for PAC/UF and MAC/UF hybrid processes showed that percent retention of paraquat and linuron was high for PAC due to its high surface area. However due to cake formation over membrane surface the decline permeate fluxes and long backwash times for PAC were observed. PAC also caused blackening of pipes and flow meter. MAC (an iron oxide and PAC composite) was removed from slurry through magnet thus no cake formation and secondary problems observed for PAC was not encountered. Also the backwash times were minimum for MAC/UF process.

Keywords: Adsorption, Permeate flux, Percent retention, backwash times, Ultrafiltration.

Introduction

The use of pesticides to maintain the production of crops quality and quantity to satisfy the increasing human population is an essential tool these days. Paraquat and linuron are the widely used herbicides that are used for the selective weed control in a wide range of crops. Chemically paraquat is 1,1'-dimethyl-4,4'-dipyridinium chloride commonly known as methyl viologen and is used as quaternary ammonium herbicide while linuron is 3-[3,4-(dichlorophenyl)-1-methoxy- 1-methylurea]. Linuron kills the herbs by inhibiting the Hill reaction in photosynthetic electron transport which in turn inhibits ATP and NADPH formation [1-4]. As animals do not prepare their food by photosynthesis and are therefore not directly affected by these chemicals. They have low mammalian toxicity and do not build up along food chains. However it is persistent and adsorbed on soil organic matter. The persistence, leaching characteristics and availability for root uptake of linuron are determined from its adsorption on soil organic matter. Paraquat is the most toxic poison if ingested deliberately or accidently. Thus it is marketed in form of blue dye to avoid confusion with beverages like coffee etc. [3, 4].

To protect the human health and environment from the harmful effects of pesticides regulation of these substances in water and effluent is required. A number of classical treatments processes are in use for the removal of pesticides from water. They are broadly classified into two categories; destructive processes like destructive oxidation [5-7] and recuperative processes like adsorption on porous solids [8-10].

Low pressure membrane processes like ultrafiltration (UF) membrane has become well recognized approach for the production high quality drinking water [11-13]. UF membrane has the ability to remove turbidity and microorganisms due to size exclusion. However they do not remove the natural and synthetic organic compounds effectively from water. In order to remove these discrepancies and meet the stringent water quality regulations, powdered activated carbon (PAC) has been used in combination with UF membrane. In such hybrid systems the organic compounds are adsorbed by the adsorbent and the UF membrane act as a positive barrier to particulate matter including adsorbent [14, 15]. However according to Lin [16, 17] and Lee [18] PAC causes a decline in permeate flux and is associated with some other secondary problems like blackening of pipes and other accessories when used in PAC/UF hybrid processes. The cake formed by PAC over the membrane surface causes longer backwash times which leads to water and electric power losses [16-18].

Magnetic adsorbents have been used for the removal of organic and inorganic contaminants from water. The magnetic adsorbents can easily be removed from slurry after treatment through magnetic processes [19-26]. In our previous work we prepared magnetic activated carbon (MAC) from

PAC, iron chloride and iron sulfate through method devised by Oliveira *et al*. [19] and was used for the removal of phenol red from water [27].

In the present study MAC was prepared, characterized and compared with PAC for its adsorptive properties, and was used in combination with UF membrane in a hybrid manner for the removal of linuron and paraquat.

Results and Discussion

Physicochemical Characterization of Adsorbents

The surface area of PAC, MAC and iron oxide was measured by nitrogen gas adsorption method, using automated equipment (Surface area analyzer QS-7), employing multipoint BET isotherm data fitting. The surface area of PAC was high as compared to MAC (PAC/iron oxide composite). This was due to impregnation of iron oxide in micro pores of PAC. The X-ray diffraction pattern of MAC, iron oxide and PAC were determined using Rigaku D/Max-2200/PC, X-ray powder diffractometer (Fig. 1). Usually magnetite, hematite, goethite and maghemite are formed under the described reaction conditions. PAC showed only the goethite peak whereas magnetite, hematite, goethite and maghemite peaks were observed for iron oxide. MAC showed maghemite and goethite peaks. Out of the peaks observed only magnetite and maghemite are attracted by magnet. The presence magnetite and maghemite peak in MAC shows the possibility that it can be separated from slurry through magnet. This was further confirmed by bulk sigma magnetization measurements using Vibrating Sample Magnetometer, VSM (Fig. 2 and 3). The magnetization values for iron oxide and MAC were 62 and 10 $JT^{-1}kg^{-1}$ respectively.

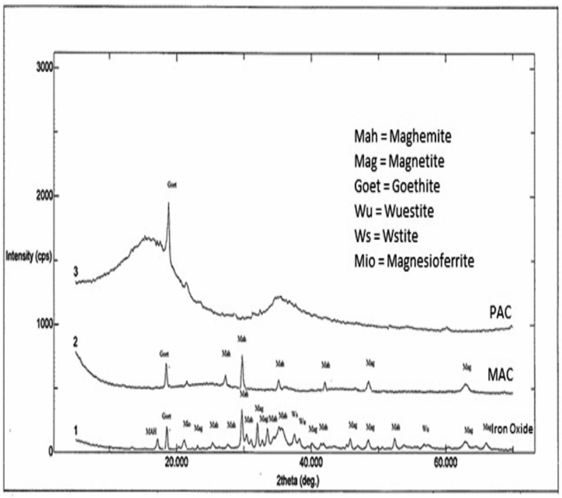

Fig. 1: XRD pattern of PAC, MAC and iron oxide.

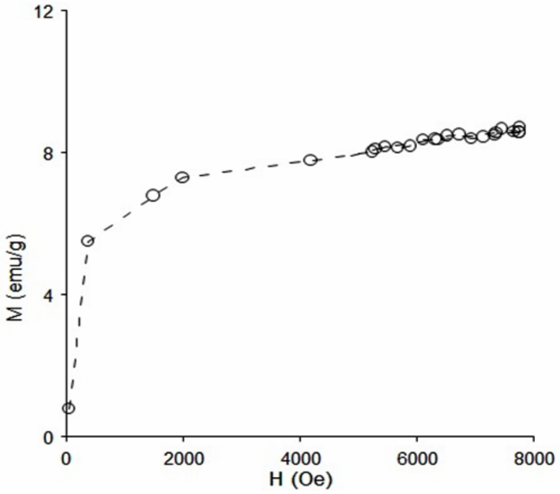

Fig. 2: Bulk Sigma Magnetization for iron oxide.

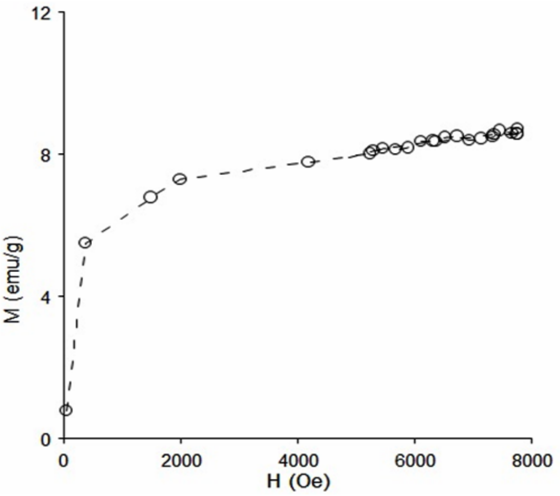

Fig. 3: Bulk Sigma Magnetization for MAC composite.

The isoelectric point (IEP) of adsorbent is an important parameter that determines the interaction between adsorbent and adsorbate at a given pH. A particular adsorbent may act as cation or anion exchanger depending upon the medium pH which finally acquire a net zero charge. This point is called point of zero charge (pzc). At a point when there is no adsorption of ions other than H+ and OH- then IEP = pzc. A number of techniques including acid/base titration and pH drift technique are widely used to determine pzc of an adsorbent [28]. The mass titration results for PAC and MAC are shown in Fig. 4 and 5. From Figures the pzc of PAC and MAC was found to be 8.98 and 8.67 respectively.

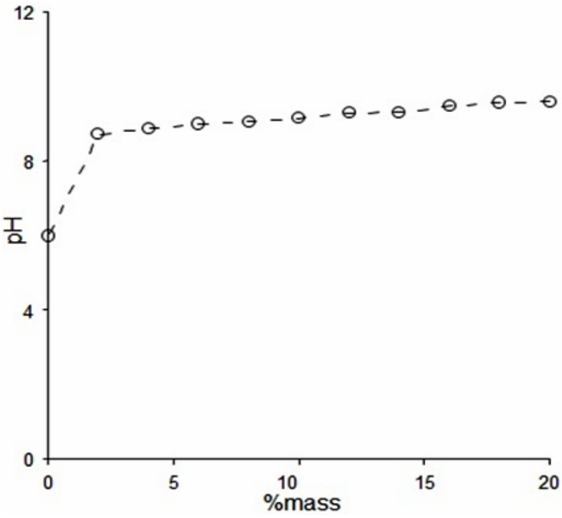

Fig. 4: PAC mass titration graph.

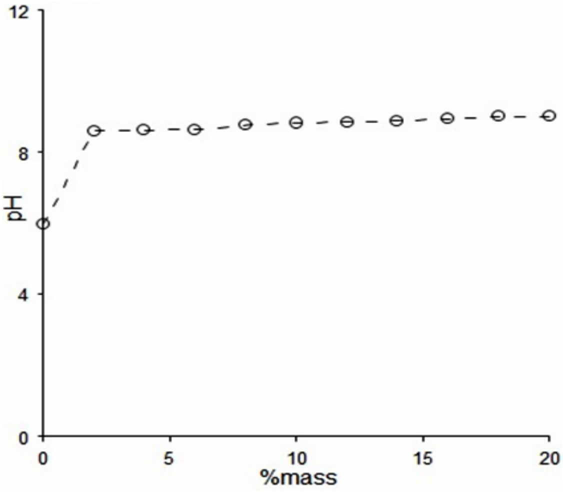

Fig. 5: MAC mass titration graph.

Dry and wet methods of analysis are used to determine surface groups of activated carbons. The wet techniques include Boehm [29] and potentiometric titrations [30, 31]. "Dry" methods include diffuse reflectance FTIR etc. Although FTIR provide qualitative information about the carbon surface, the quantitative insight is not straightforward and requires special mathematical treatment with many approximations used [29]. On the other hand, Boehm and potentiometric titrations provide qualitative and quantitative information on the carbon surface. The FTIR spectrum of PAC and MAC are given in Fig. 6 and 7. Due to black background it is difficult to get a clear picture of adsorbent from FTIR spectrum. The functional groups determined from FTIR strums of PAC and MAC are shown in Table-1 while Boehm titration results are given in Table-2.

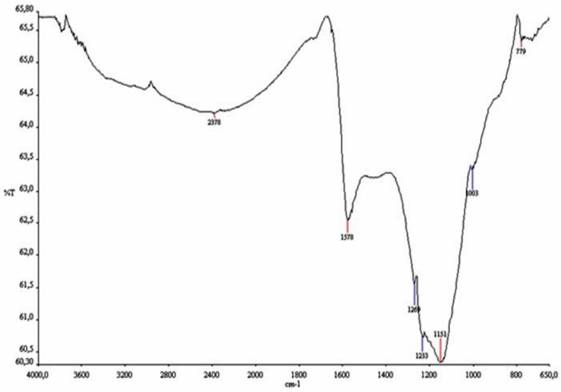

Fig. 6: PAC IR spectrum (ATR method).

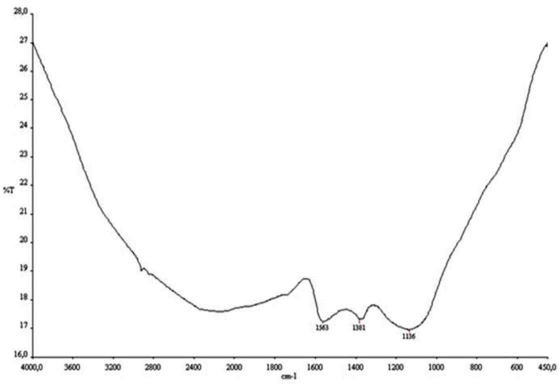

Fig. 7: MAC IR spectrum (ATR method).

Table-1: FTIR analysis of PAC and MAC.

Functional groups	Transmission (%)	
	PAC	**MAC**
N-H (2400-3200 cm^{-1}) Amonium ions	**64.25**	**……**
C=O (1550-1610 cm^{-1}) Carboxylic acid türleri	**62.40**	**17.2**
C-O (1250-1300 cm^{-1}) Carboxylic acids	**61.7**	**17.4**
C-O (1220-1260 cm^{-1}) Aromatic ether	**60.7**	**…..**
C-O (1050-1170 cm^{-1}) Acrylic anhydrides	**60.36**	**17**
C-X (1000-1100 cm^{-1}) Floroalkanes	**63.46**	**…**
Ar-H (750-810 cm^{-1}) m- disubstitute	**65.5**	**…**

Table-2: Boehm titration results.

Adsorbent	Acidic groups (meqg)	Carboxylic acid groups (meqg)	Carboxylic +Lactonic groups (meqg)	Phenolic groups (meqg)	Lactonic groups (meqg)	Basic groups (meqg)
PAC	**21.3525**	**4.5625**	**18.98**	**2.3725**	**14.4175**	**1.0**
MAC	**21.7175**	**3.1025**	**18.25**	**3.4675**	**15.1475**	**0.6**

Sorptive Abilities of Adsorbents

Langmuir [32] and Freundlich [33] adsorption isotherms were used to analyze the experimental data. Both these models are considered to describe the satisfactory the adsorption experimental data. Langmuir isotherm is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and that there is no transmigration of adsorbate in the plane of the surface. The Langmuir adsorption isotherm is mathematically given as:

$$\frac{C}{q} = \frac{C}{Q_0} - \frac{1}{Q_0 b} \tag{1}$$

where q is the amount adsorbed (mg g^{-1}), C is the equilibrium concentration of the adsorbate (mg L^{-1}) and Q_0 and b are Langmuir constants related to maximum adsorption capacity and energy of adsorption respectively.

The Freundlich adsorption isotherm is basically empirical and is especially useful for the description of adsorption onto adsorbent surfaces with heterogeneous energy distribution, when the energy term 'b' of Langmuir isotherm varies as a function of the surface coverage strictly due to variations in the heat of adsorption. The linear form of Freundlich isotherm is given as:

$$lnq = lnK + \frac{1}{n} lnC \tag{2}$$

where C is the equilibrium concentration (mgL^{-1}), q is the amount adsorbed (mgg^{-1}). K and n are Freundlich constants related to adsorption capacity and adsorption intensity respectively. The Freundlich and Langmuir isotherm constants along with correlation coefficients are given in Table-3.

Table-3: Equilibrium adsorption parameters for the adsorption of paraquat and linuron on PAC and MAC.

Isotherm	**PAC**		MAC	
Langmuir:	**paraquat**	**Linuron**	**paraquat**	**Linuron**
Q_0 (mg g^{-1})	**139.14**	**298**	**116.7**	**261**
b (L mg^{-1})	**0.046**	**1.03**	**0.0067**	**0.07**
R^2	**0.976**	**0.988**	**0.94**	**0.95**
Freundlich:				
K	**2.85**	**158.5**	**3.07**	**142.3**
1/n	**0.89**	**0.23**	**0.83**	**0.16**
R^2	**0.909**	**0.96**	**0.96**	**.94**

Adsorption kinetic study is important as it depicts the uptake rate of adsorbate, and controls the residual time of the whole adsorption process. In this study two adsorption kinetic models, pseudo-first order [34] and pseudo-second order [35] kinetic models were used to describe the adsorption kinetic data. The pseudo-first order equation can be expressed in a linear form as

$$\ln(q_e - q) = lnq_e - k_a t \tag{3}$$

where q_e and q (mg g^{-1}) are the amount of sorbed pesticides at equilibrium and time t respectively and k_a (min^{-1}) is the rate constant. The values of k_a and R^2 are given in Table-4.

Table-4: Kinetics parameters for the adsorption of paraquat and linuron on PAC and MAC.

Adsorbent	**Compound**	**Pseudo-first order kinetic model**		**Pseudo-second order kinetic model**	
		k_a (1/min)	**R^2**	**K_2 (min .g mg^{-1})**	**R^2**
PAC	**Linuron**	**0.032**	**0.960**	**5.2×10^{-3}**	**0.99**
	Paraquat	**0.072**	**0.874**	**2.7×10^{-2}**	**0.98**
MAC	**Linuron**	**0.030**	**0.903**	**5.0×10^{-3}**	**0.98**
	Paraquat	**0.097**	**0.952**	**2.2×10^{-1}**	**0.99**

A linear form of pseudo-second order equation is shown in equation (4)

$$\frac{t}{q_t} = \frac{1}{K_2 q^2} + \left(\frac{1}{q}\right) t \tag{4}$$

where K_2 (g mg^{-1} min^{-1}) is the rate constant of adsorption, q (mg g^{-1}) is the amount of pesticides adsorbed at equilibrium and q_t at time t. The values of rate constant K_2 and R^2 are given in Table-4.

The best fit of the data was obtained with pseudo-second order kinetic model as the correlation coefficient values for this model were higher than pseudo-first order kinetic model.

Adsorption/UF Membrane Filtration Studies

UF membrane was integrated with adsorbents PAC and MAC for water treatment containing pesticides paraquat and linuron. The setup is shown in Fig. 8. The UF was used in dead end flow mode and, membrane parameters like decline in permeate flux, percent retention and backwash times were determined for the integrated system. Usually natural organic matter is responsible for fouling in UF membrane processes. However synthetic organic matter as pointed out by Crozes *et al.* [36], are smaller than the pore size of membrane can lead to significant irreversible fouling. The percent retention of paraquat and linuron by UF membrane are shown in Fig. 9. The retention of the solute depends on its size and configuration relative to the pore size of the membrane. Chemical interactions of the solution and membrane like adsorption, concentration polarization, and fouling are also important [37, 38]. The improved percent retention for the integrated systems PAC/UF and MAC/UF are shown in Fig. 10 and 11. The percent retention of paraquat and linuron were for PAC/UF process as compared to MAC/UF system. This was due to the fact that PAC has large surface area as compared to MAC.

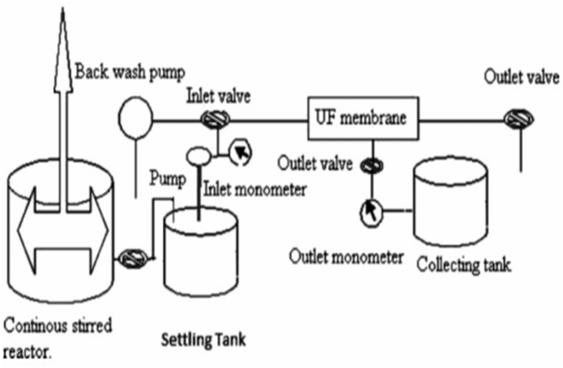

Fig. 8: Diagram of pilot plant.

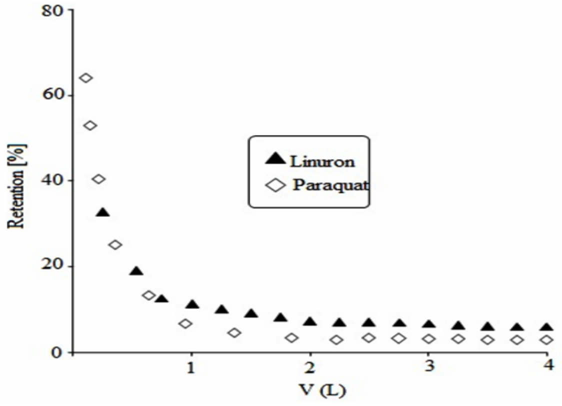

Fig. 9: Percent retention of paraquat and linuron by UF membrane.

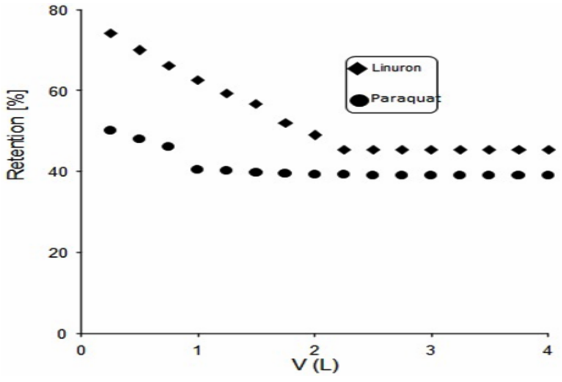

Fig. 10: Percent retention of paraquat and linuron by UF membrane in presence of PAC.

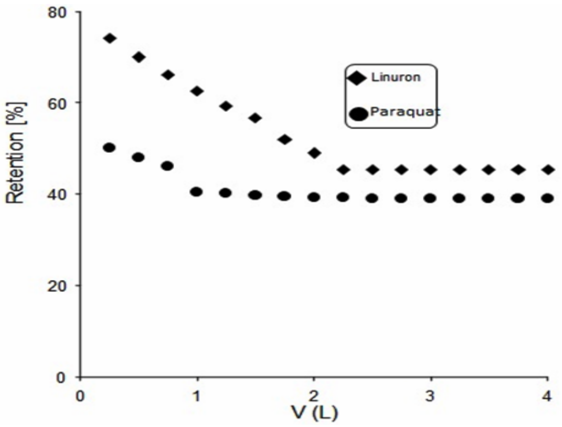

Fig. 11: Percent retention of paraquat and linuron by UF membrane in presence of MAC.

The molecular weights of these two pesticides are smaller than the molecular weight cut off of the UF membrane used in this study. These were supposed to pass freely from membrane and permeate concentration should be equal to bulk concentration. However inspite of low retention a decline in permeate flux was observed for these substances (Fig. 12). The improved permeate fluxes for PAC/UF and MAC/UF systems are shown in Fig. 13 and 14. Inspite of the low surface area of MAC almost similar fluxes were observed for both PAC/UF and MAC/UF systems. This was due to the fact that MAC was removed from slurry in the settling tank by magnetic process and was stopped from being entering into membrane. PAC has long settling time and enters into membrane system where it forms cake over membrane system which causes a decline in permeate flux. For MAC no such cake formation over the membrane surface was observed.

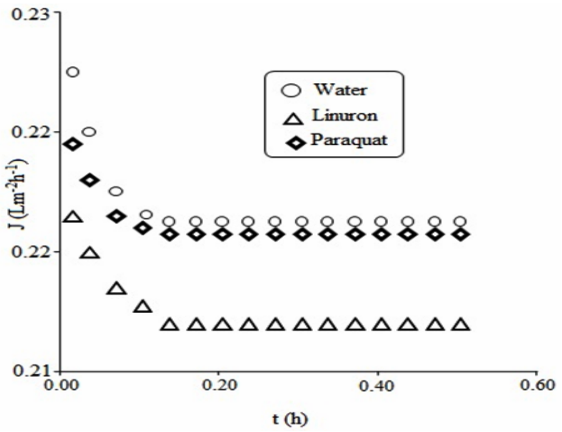

Fig. 12: Effect of paraquat and linuron on permeate flux.

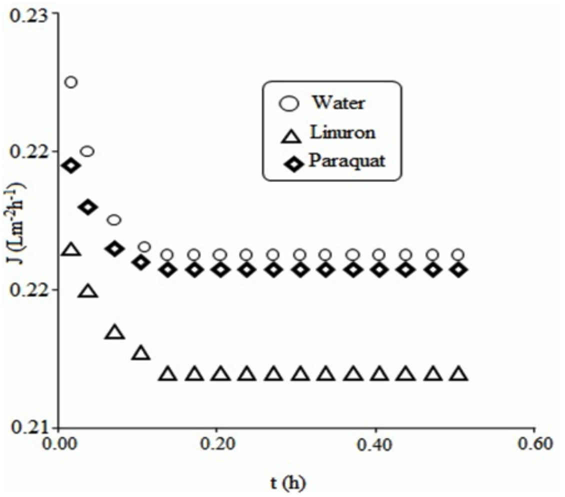

Fig. 13: Effect of paraquat and linuron on permeate flux in presence of PAC.

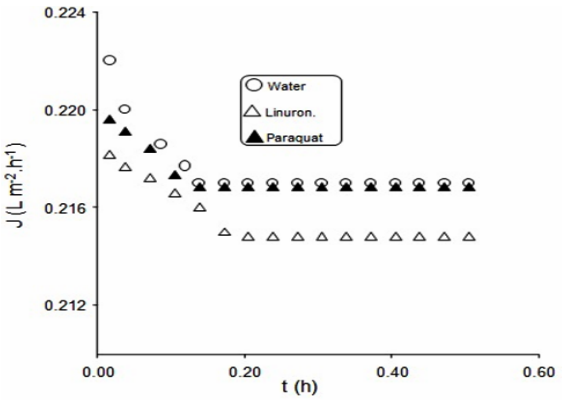

Fig. 14: Effect of paraquat and linuron on permeate flux in presence of MAC.

After each 30 minute cycle backwashes with distilled water was applied. For MAC/UF system the backwash time was lesser as compared to PAC/UF system. This was due to the fact that the cake formed by PAC over membrane surface took more time to detach from the surface while for MAC as mentioned earlier no such cake formation was encountered. The backwash time are important from economical point of view in membrane processes as longer backwash times leads to large electric power and water losses. Thus it is concluded that the use of MAC in membrane hybrid processes is an economical in terms of electric power and water losses.

Experimental

Materials and Characterization

A single batch of commercial charcoal based activated carbon was obtained from Norit. The characteristic physical properties of activated carbon are given in Table-5. The activated carbon was washed with distilled water and subsequently dried in oven at 110^{0}F for 4 hours before use. Two pesticides paraquat and linuron were selected in this study and were bought from Sigma Aldrich. Iron chloride and iron sulfate were obtained from Sigma Aldrich. Polyether UF membrane were purchased from IMT, Netherland. The characteristics of UF membrane are listed in Table-6.

Table-5: Physical properties of PAC, MAC and iron oxide.

Parameter	PAC	MAC	Iron oxide
BET surface area	**1150 m^2/g**	**868 m^2/g**	**64 m^2/g**
Micropore volume	**0.335 (cm^3 g^{-1})**	**0.212 (cm^3 g$^{-)}$**	**0.07 (cm^3 g^{-1})**
Mesopore volume	**0.085 (cm^3 g^{-1})**	**0.065 (cm^3 g^{-1})**	**.......**
Apparent density	**0.51 g/mL**	**0.63 g/mL**	
Particle size			
d10	**4 µm**	**2 µm**	**.......**
d50	**24 µm**	**21 µm**	**.......**
d90	**90 µm**	**93 µm**	**.......**
Ash	**12% Max**	**.......**	**.......**
Chloride (acid extracts)	**0.1%**	**.......**	**.......**
pH	**Alkaline**	**alkaline**	**.......**

Table-6: UF membrane parameters.

Parameter	Specification
Matterial	**Polyethersulfone**
Type	**Capillary multibore *7**
Diameter bores ID	**0.9 mm**
Diameter fibre OD	**4.2 mm**
MWCO	**100 kD**
Surface area	**50 m^2**
Maximum temperature	**40 ^{0}C**
Maximum pressure	**7.5 bar**
Membrane back wash pressure	**0.5-1 bar**
Maximum	**2.5 bar**
Operation pH range	**3-10**
Back wash pH range	**1-13**
Disinfection chemicals	
Hypochlride (NaOCl)	**50-200 mg L-1**
Hydrogen peroxide (H_2O_2)	**100-200 mg L-1**

MAC was prepared by mixing 200ml each of iron chloride and iron sulfate with known quantity of PAC. The mixture was heated to 70^{0}C and 100ml of NaOH was added to it drop wise. The resulting product was washed with distilled water till its pH reached to 6.5. It was dried in oven at 100^{0}C for 6 hours. Iron oxide was prepared by same procedure as described above. The physical parameters of MAC and iron oxide are given in Table-5. PAC, MAC and iron oxide were characterized by XRD (Rigaku D/Max-2200/PC). PAC and MAC were also characterized by FTIR and Boehm titration. The infrared spectra of the PAC and MAC were recorded in the range 4000–400 cm^{-1} on a BioRad FTS 175C spectrophotometer using a pellet technique. The samples were prepared mixing 1mg of material with 100mg of spectroscopy grade KBr. Point of zero charge was determined for MAC and PAC. Iron oxide and MAC were by bulk sigma magnetization

(Vibrating Sample Magnetometer, VSM). The BET surface area of PAC, MAC and iron oxide were determined by a surface area analyzer QS-7 by standard N2 adsorption at 77 K.

Batch Adsorption Studies

The paraquat and linuron stock solution were prepared in distilled water and diluted to required initial concentration (10-100mgL^{-1}). 100ml of each these solutions were contacted with 0.01g of PAC and MAC for 12 hours and 250rpm agitator speed at room temperature in thermostat cum shaking assembly. The amount of paraquat and linuron adsorbed by PAC and MAC were determined by UV-visible spectrophotometer (Thermo Electron corporation Heγios γ UV-Visible spectrophotometer) at 257 and 210.5nm respectively. The concentration of paraquat and linuron retained in the adsorbed phase was calculated by using following formula;

$$q_e = \frac{(C_0 - C_t)V}{W} \qquad (5)$$

where C_0 is initial pesticide concentration, C_t is concentration at any time t, V is volume of solution and W is weight of adsorbents in gram.

For kinetic studies, a specially designed container of 12L capacity was used. Mixing was provided by a blade. A motor was used to drive the impeller. The top surface of the vessel was open to atmosphere. Experiments were performed at the agitation rate of 250 rpm and 25^{0}C. Samples were withdrawn at different time intervals using syringe and were analyzed by UV-Visible spectrophotometer.

Pilot Plant Studies

A schematic pilot scale dead end-flow UF rig used in the experiment is shown in Fig. 8. The set consists of UF membrane, pumps, flow meter, monometers, settling tank etc. The membrane used is made up of semipermeable polyether with a molecular cut off of 50kda. First the membrane parameters like percent retention, permeate flux and back wash times were determined for paraquat and linuron. The membrane was then used in combination with PAC and MAC, and the membrane parameters were determined. The percent retention of the pesticides by membrane alone and in hybrid processes was determined by using formula:

$$R = 100\left(1 - \frac{C_p}{C_b}\right) \qquad (6)$$

where Cp is the concentration of solute in permeate and Cb is the solute concentration in bulk.

Membrane flux averaged over time of filtration was calculated as follow:

$$j = \frac{1}{A}\frac{dV}{dt} \qquad (7)$$

where A is the membrane area and V is the permeate volume at time t.

Conclusions

In this study a comparison was made between powdered activated carbon and the prepared magnetic activated carbon. The magnetic activated carbon encountered no cake formation over membrane that result in improved permeate fluxes while for powdered activated carbon inspite of high surface area the cake formed over membrane cause a decline in permeate fluxes. The blackening of pipes and flow meter encountered in case of powdered activated carbon were not observed for magnetic activated carbon. The backwash times for magnetic activated carbon were comparatively shorter than for powdered activated carbon. The backwash time are important from economical point of view in membrane processes as longer backwash times leads to large electric power and water losses. Thus magnetic activated carbon can be used as alternative to powdered activated carbon in membrane water treatment hybrid reactors.

Acknowledgement

The study was supported by research fund of Istanbul University Turkey. Project NO: 3822.

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