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Rad.C-8 Recovery of Waste Dyes, Pesticides and Detergents by Using Hydrogels Prepared by Gamma Irradiation.

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ABSTRACT

Hydrogels have been prepared by Irradiation acrylic acid and glycerol using methanol and water as solvents. Another sample was prepared with methanol only. The application of the prepared two hydrogels used for recovery of some reactive, acid and direct dyes and also recovery two different pesticides and detergents from wastewater were studies. The hydrogels complexes with different pollutants have been isolated and

methanol and water as solvent during polymerization has a great adsorption towards dyes, pesticides and detergents than sample containing methanol only. The adsorption isotherm capacity of the two hydrogels was studies by the effect of temperature (20,30,40 ^{0}C) on the adsorption capacity through the kinetic studies of adsorption. The adsorption capacity increase with rising temperature and thermodynamic parameters ΔH, ΔS and ΔG were determined. Also, the adsorption capacity is considerably affected by pH values (3,7 and 10). It was found that the adsorption capacity increases in acid medium and decreases towards the alkaline medium for both dyes and pesticides, while the irreversible results was shown in case of anionic detergents. Frundlich equation of adsorption isotherm was applied in this work.
Keywords: Radiation polymerization, Removal of dyes, Pesticides, Detergents .

INTRODUCTION

Crooslinked hydrophilic polymers capable to absorption large volumes of water are termed hydrogels. Hydrogels have found widespread applications in the fields of bioengineering, biomedicine, pharmaceutical, veterinary, food industry, agriculture and others. It is used as controlled release systems of drugs for production of contact lenses as adsorbents for removal of some agents in environmental applications and also as carrier mater, pesticides and fertilizer in agriculture[1-7].

In our previous studies, adsorption of some cationic dyes and some heavy metal ions by acrylamide-maleic acid hydrogel, acrylic acid, acrylonitryle-acrylamide with rubbers powder, for the recovery of different metal ions, have been investigated.[3,8,9]

The present paper is aimed to study a convenient method for removing some dyes, pesticides and detergents from water by adsorption on a new adsorbent of acrylic acid/glycerol hydrogels and prepared by irradiating gamma - rays. The hydrogels were used in adsorption of some water soluble dyes, such as reactive blue dye, acid red dye, and direct orange dye and two pesticides such as larvine and dursbane, and two detergents such as comperlan and dehydroquart.

EXPERIMENTAL

Materials & Techniques:

Materials:

Acrylic acid (AAc) was of pure grade (Merck, Germany) and Glycerol was also of pure grade. Pure grade solvents were used also.

Techniques:

Preparation of the hydrogels:

The first hydrogel was prepared by mixing acrylic acid to glycerol by the ratio of (1:1) mol. Using methanol and water (5:5) ml. For each mole as solvents. The second hydrogel was prepared by mixing acrylic acid with glycerol by the same ratio with 5 ml methanol only. The previous components were subjected to Co-60 gamma source at irradiation dose of 20 kGy at a dose rate 8.8 KGy/h.

Application

The hydrogels were used for recovery of reactive, acidic and direct dyes and also recovery of pesticides, Larvine (carbamite) and Dursbane (organophosphorous) and anionic detergents, Comperlan and Dehydroquart from wastewater.

Characterization:-

Determination of water uptake percent:

A known weight of the non-soluble hydrogel (W_1) was soaked in bidistilled water for 24 hrs. at room temperature. The sample was then removed and blotted on a filter paper to remove the excess of water on the surface (W_2). The water uptake was calculated using the following equation:

$$\text{Water uptake (W.U.) \%} = W_2\text{-}W_1/W_2 \quad 100$$

Where

W_1 : initial weight of the hydrogel

W_2 : final weight of the swelled hydrogel

Instrumentation

1-Gamma irradiation source.

The irradiation process was carried out using gamma cell facility at National Center for Radiation- Research and Technology, Nasr city Cairo, Egypt.

2- X-ray Diffraction :

The x-ray diffraction patterns of prepared hydrogels were measured by a shimadza diffractometer XD-DI series which is operated fully automatically. The X-ray copper target tube was operated at 40kv and 30mA. All the diffraction patterns were examined at room temperature with scanning speed of 2°C in 20 min^{-1} (20 mm/min).

3- U.V. spectrophotometer :

The instrument with the double beam U.V- visible sp.200, PYE-Unicam, England The concentration of each pollutant solutions was determined by measuring absorbance at characteristic wavelengths; 594 nm for reactive blue dye, for acid red dye, 528 nm for direct orange dye; also 498 nm & 283 nm for dehydrogel detergents .

4- Thermal Analysis:

Shimadzu TGA system of type TGA-50 was used for measurement of TGA. Nitrogen flow was kept at constant rate of about 50 ml/min to prevent thermal oxidation processes of the polymer samples.

RESULT and DISCUSSION

Characterization of the hydrogels:

Water uptake and the effect of organic solvents towards the two hydrogels were investigated as shown in Table (1). It can be observed that the hydrogel containing methanol and water as solvents have greater water uptake percent than the hydrogel containing methanol only. The swellibility as the prepared hydrogels in different organic solvent were investigated. It is found that both hydrogels have great affinity to polar solvents than non polar solvents. Also, hydrogel containing a mixture of solvent methanol and water has less swelling in organic solvent than the hydrogel containing methanol only.

Table (1): Behaviour of the hydrogels towards different solvents.

Solvent	PAAc/Gly. (MeOH)	PAAc/Gly. (MeOH + H_2O)
	Uptake %	*Uptake %*
Water	88	100
Methanol	69	51
DMF	30	18
Acetone	18	12
Chloroform	5	4
Toluene	2	2
Benzene	0	0
Cyclohexane	0	0

Chemical stability of the two hydrogels against Acid and Alkali:

The prepared two hydrogels were treated with 1% dilute sodium hydroxide. However, such treatment dose not resulted in obtaining the sodium salt. On the contrary, a gelatinous product has been formed. This behavious may be attributed to the destruction of the crosslinks in which decrease in the crosslink density leads to obtain a gelatinous product of the hydrogels. On the other hand, it was found that HCl has no adverse effect on the hydrolysis of the crosslinks and practically no change in the chemical structure was observed. However, it has been found that the addition of dilute 1% HCl leads to a slight increase in the swelling equilibrium of the two hydrogels.

Thermogravimetric analysis

The TGA thermogravimetric of acrylic acid / glycerol / methanol (I) which is illustrated in fig. (1) show that the thermal decomposition of the hydrogel is occurred in the two steps. It is clear that the hydrogel in the first step losses about 35 % of its weight, 90% decomposed during the second steps at 420°C. The TGA thermogram of acrylic acid /glycerol /methanol / water (II) shows that the thermal decomposition of the hydrogel also is occurred in two steps. It is losses 22% of its weight in the first step, 67% during the second step at 445°C. Moreover, it can be observed that the hydrogel (II) has better thermal stability than the hydrogel (I)

Infra red spectroscopy:

Hydrogel was characterized by IR in previous[10]

Adsorption isotherm for removing the different pollutants.

Kinetic adsorption isotherm

In figs (2-5) show that the relation between the time of adsorption (hour) and the removal percent.

$$\text{Removal \%} = C_o\text{-}C_i / C_o \quad 100$$
$$\text{or } \Delta C / Co \quad 100$$

where C_o initial concentration mg/L

C_i final concentration after absorption mg/L

In general trends, it was found that the adsorption capacity for the two hydrogels increases with increasing the temperature. In fig. (2) hydrogel contain (MeOH) at constant pH = 7 gives 80 % removal for reactive blue dye, 60 % for acid red dye and 57 % for direct orange dye and the steady state was achieved after about 8 hours where the equilibrium state of adsorption was become constant. Fig. (3) using the same dyestuffs with other hydrogel (MeOH + H_2O), it shows the decreasing in removal percent for reactive blue dye than in hydrogel (MeOH) where gives 70 % removing percent but the other dyes gave 80% and 78 % removal in acid red dye and direct orange respectively. The factor make reactive blue dye have lower affinity to be absorbed on to the hydrogel (MeOH + H_2O) then hydrogel (MeOH) was due to net work crosslinking of hydrogel and the physicochemical structure of the dye.

Figs. (4, 5) show the removal percent of pesticides (Larvine and Dursban). It was found that Larvine has more affinity to be adsorbed than Dursban compound in both hydrogels. This is due to the aliphatic nature of Larvine compound to the aromatic nature of Dursban. Also, it was found that hydrogel (MeOH + H_2O) has more ability to adsorb the two pesticides more than hydrogel (MeOH), it gives at pH = 7 and 40 °C (77 %, 62%) for the first hydrogel while the second gives (60 %, 52%) for the second hydrogel without water for both Larvine and Dursban respectively.

Figs. (4, 5) also illustrate the removal percent of detergents (comperlan and dehydroquart) anionic detergent. They show high affinity to be adsorbed onto the hydrogels than dyes and pesticides, it gives removal percent in hydrogel (MeOH + H_2O) (96% and 80%) and in hydrogel (MeOH) gives (70% and 60%) for both comperlan and dehydroquart respectively. This can be explained in the light of the high charge in an anionic detergents, which has very high affinity towards the active crosslinkage in hydrogels.

The adsorption isotherm was followed thermodynamically according to the data tabulated in table (2). In both hydrogels, the pollutants were adsorbed onto the network structure and the penetrated through the pours. The heat of adsorption of all pollutants onto hydrogels hand a negative sign which indicated that the adsorption process through these hydrogels was exothermic
Reaction, where ΔH is negative values and ΔH was calculated from the following equation.[4]

$$(\Delta H_{ads}) = R \ln C_2/C_1 /(1/T_1 \quad 1/T_2)$$

C_1 concentration at first temp T_1
C_2 concentration at second temp T_2

The entropy change (ΔS_{ads}) was measured by the equation .

$$\Delta S_{ads.} = \Delta H_{ads.}/T$$

It was found that all the value of $\Delta S_{ads.}$ for all the pollutants onto the hydrogels are very small negative fraction limited to zero which represented that the reaction at equilibrium state was ordered reaction .

Also the free energy change ($\Delta G_{ads.}$) of the adsorption was measured and it is found that the batch adsorption technique is spontaneous reaction where all the values are negative values .

$$\Delta G = \Delta H - T\Delta S$$

Equilibrium adsorption isotherm

Figures(6,7) show the relationship between the effect pH on the maximum adsorption capacity . It was found that for both dyes and pesticides, the maximum adsorption increase with decreasing pH value (acid medium) and decrease with increase the pH value (alkaline medium). In case of anionic detergents the opposite results was obtained where the maximum adsorption increase at pH= 10 (alkaline medium) and decreases at pH = 3 (acidic medium).

Also, it was found from figs (6a,7a) that reaction blue dye was more adsorbed at pH =3 than the other dyes red and orange (80% , 63% and 41%) for hydrogel (MeOH) and (85%, 80% and 73%) for hydrogel (MeOH + H_2O) respectively . Pesticides larvine is more than dursbane 78% and 60% at pH =3 for hydrogel (MeOH) and (85% and 70%) for hydrogel (MeOH + H_2O). In case of detergents comperlane was more affinity towards the hydrogels in pH =10 90% and 73 % for hydrogel contain (MeOH) and (98% and 84%) for hydrogel (MeOH + H_2O) respectively.

The effect of pH can be attributed to three interrelated causes: the hydrophobicity of pollutants, the solubility of the pollutants and the ions of the buffer solution. This show that the effect of pH on the adsorption capacity was much better than the effect of temperature. The fact that the adsorption capacity

indicated that the ions of the buffer solution interact with the hydrogels and the pollutant molecules.

X-Ray Diffraction

X-ray diffraction data of both the two hydrogels before and after adsorption by different pollutants (dyes, pesticides and detergents) are shown in table (3). This technique is used to represent their morphological structure and the change in its crystal form due to the effect of swelling and interaction of pollutant compounds onto the hydrogel polymer structure. Table (3) shows the angle between incident and diffracted ray (2θ) Viz intensity I/Io (peak light) for hydrogels (MeOH) and hydrogel (MeOH + H_2O) before adsorption process. It was found that 2θ was 20.1 degree and 64.3 degree and the interplanar distance was 4.4°A and 1.4°A, respectively. It is illustrated that there are a wide change between the two hydrogels, therefore the hydrogel (MeOH + H_2O) has more 2θ than hydrogel (MeOH) by three times. This can be represente the more swelling character of hydrogel prepared with water than that prepared without water. Also, the interplanar distance decrease from 4.4 to 1.45°A and this decrease is three times too. The interplanar distance changes can be explained by the formation of new crosslinkage between the polymeric chains by the formation of intermolecular hydrogen bonding.

It was also found that integrated int.(counts) are taken as indication of the amorphous and crystallinity percent of the polymer according to the area under the peak obtained from the sharts of the x-ray diffraction patterns, when integrated int. (counts) is increased, the crystallinity is also increased .

It was shown from table (3) that the hydrogel contains water-methanol as solvent is an amorphous one while hydrogel containing methanol only was found to be crystalline. This phenomena was due to the free mobility of the polymer chain containing water molecule, which is considered as a good swelling agent for poly acrylic acid, and probably due to the break down of the hydrogen bonding net work structure, caused by the incorporation of such dyes, pesticides and detergents towards the activity of new action polar sits excess in hydrogel (MeOH + H_2O) than the other prepared without H_2O

CONCLUSION

In this work , the hydrogel prepared with water give more swelling and also more adsorption capacity for the uptake of all pollutants used. The structure of two hydrogels are confirmed by x-ray, IR and TGA analysis. It was found that the adsorption is physical adsorption at different temperature 20, 30 and 40 °C and it is exthothermic reaction, ordered at equilibrium and spontaneous. Also, the pH effect at 3, 7 and 10 was measured and it was found that the effect of pH for removing the pollutants is very important factor than the temperature effect.

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Table (2) : Thermodynamic parameters such as Heat of adsorption (ΔH), the entropy at equilibrium state (ΔS) and free energy change of adsorption prossess (ΔG) of different pollutants onto different hydrogel.

Pollution	Sample	AAc/Gy (MeOH) I			AAc/Gy (MeOH + H_2O) II		
		$-\Delta H_{ads.}$ KJ/mol	$-\Delta S$ KJ/mol	$-\Delta G$ KJ/mol	$-\Delta H_{ads.}$ KJ/mol	$-\Delta S$ KJ/mol	$-\Delta G$ KJ/mol
Dyes	Reactive Blue	7.7	0.027	0.05	6.9	0.02	1.24
	Acid Red	6.8	0.02	1.14	7.3	0.025	0.225
	Direct Orange	5.2	0.018	0.1	7.0	0.024	0.208
Pesticides	Dursban	4.2	0.014	0.238	3.0	0.010	0.17
	Larvine	4.8	0.016	0.272	3.7	0.013	0.021
Detergents	Comperlane	3.9	0.013	0.221	4.8	0.016	0.272
	Dehydquant	2.1	0.007	119	2.8	0.009	0.253

Table (3) X-ray diffraction measurments of two different prepared hydrogel befor and after uptaking onto them by different dyes, pesticides and detergents.

Pollution	AAc/Gy (MeOH) I				AAc/Gy (MeOH + H_2O) II			
	Sample	2 θ (deg.)	d(A°)	Integrated int. Counts	Sample	2 θ (deg.)	d(A°)	Integrated int. Counts
Dyes	Blank	20.1	4.4	11913	Blank	64.3	1.5	57
	Reactive Blue	81.3	1.2	304	Reactive Blue	20.1	4.4	8626
	Acid Red	20.6	4.3	8101	Acid Red	20.4	4.4	9059
	Direct Orange	21.6	4.1	16734	Direct Orange	63.4	1.47	125
Pesticides	Dursban	46.1	1.97	2424	Dursban	22.3		3680
	Larvine	17.9	4.9	11071	Larvine	27.4		23576
Detergents	Comperlan	22.8	3.9	6464	Comperlan	21.6	4.1	5009
	Dehydquart	20.6	4.3	8960	Dehydquart	19.9	4.5	4205

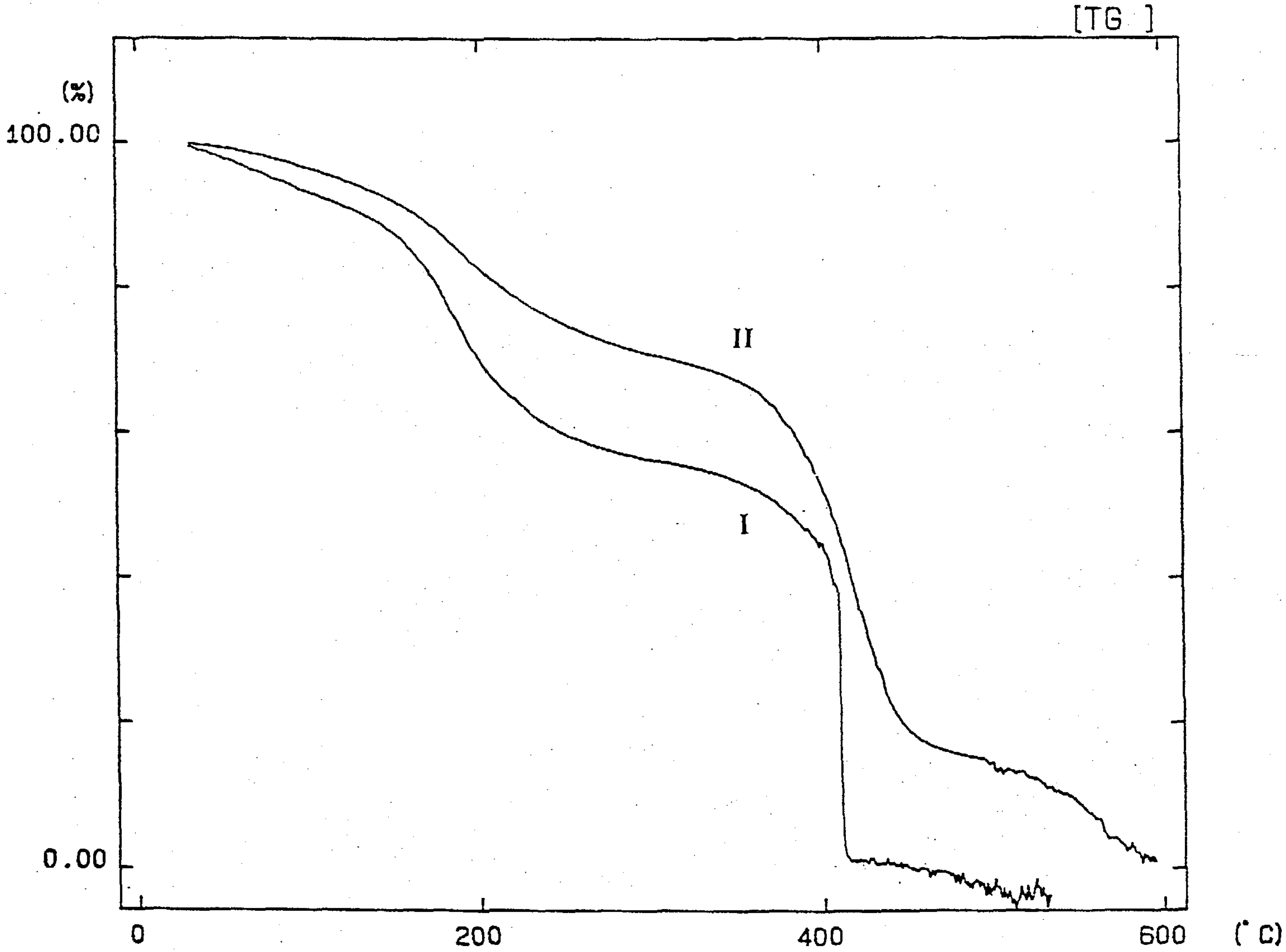

Fig. (1) : TGA curve of Acrylic acid / Glycerol / Me hydrogel (I).

TGA curve of Acrylic acid / Glycerol / Me / H_2O hydrogel (II).

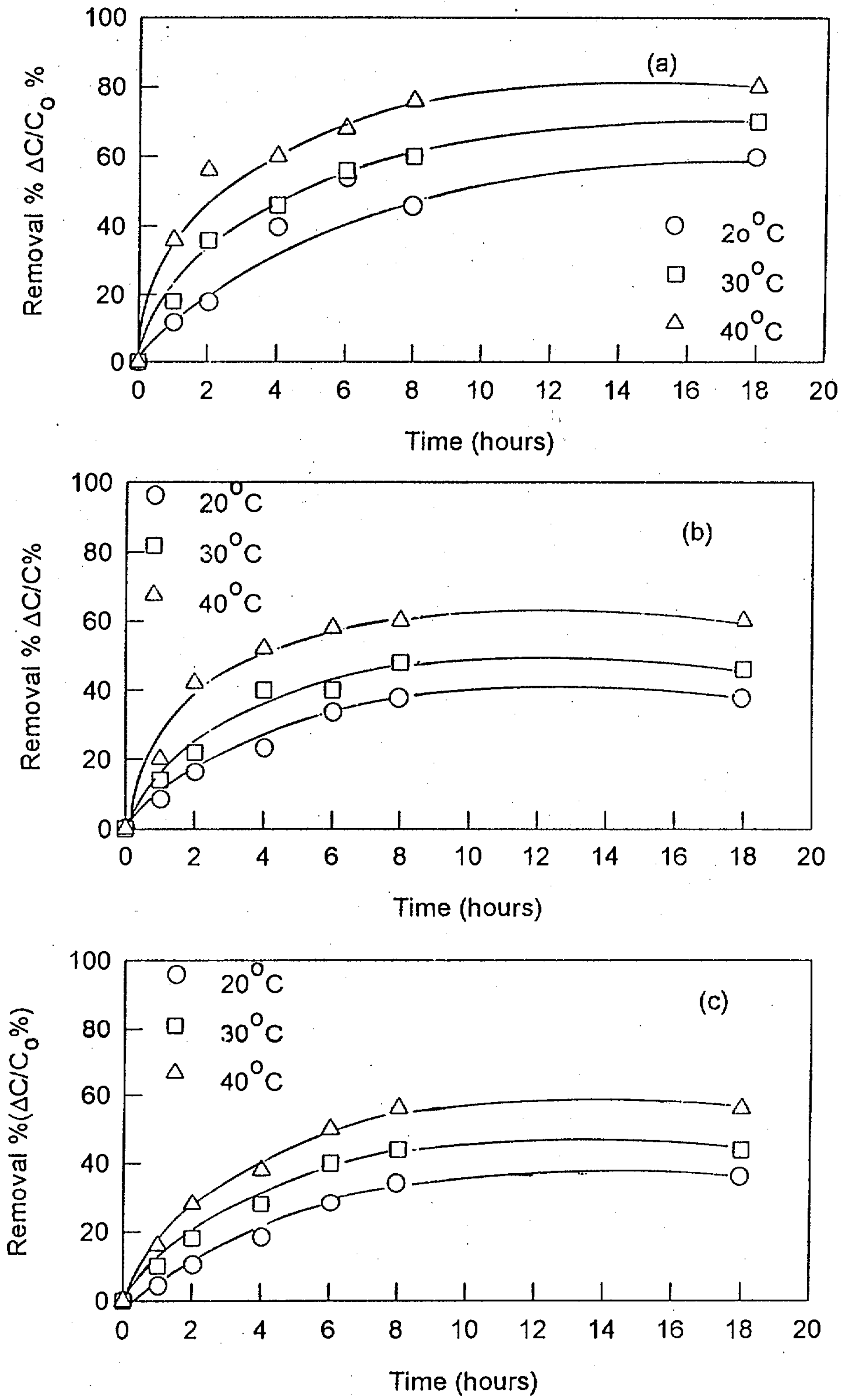

Fig. (2) : Effect of Temperature on the Adsorption of Reactive Blue(a), Acid Red(b) andDirect orange(c) Dye on Acrylic Acid/ glycerol Hydrogel in methanol at constant pH=7

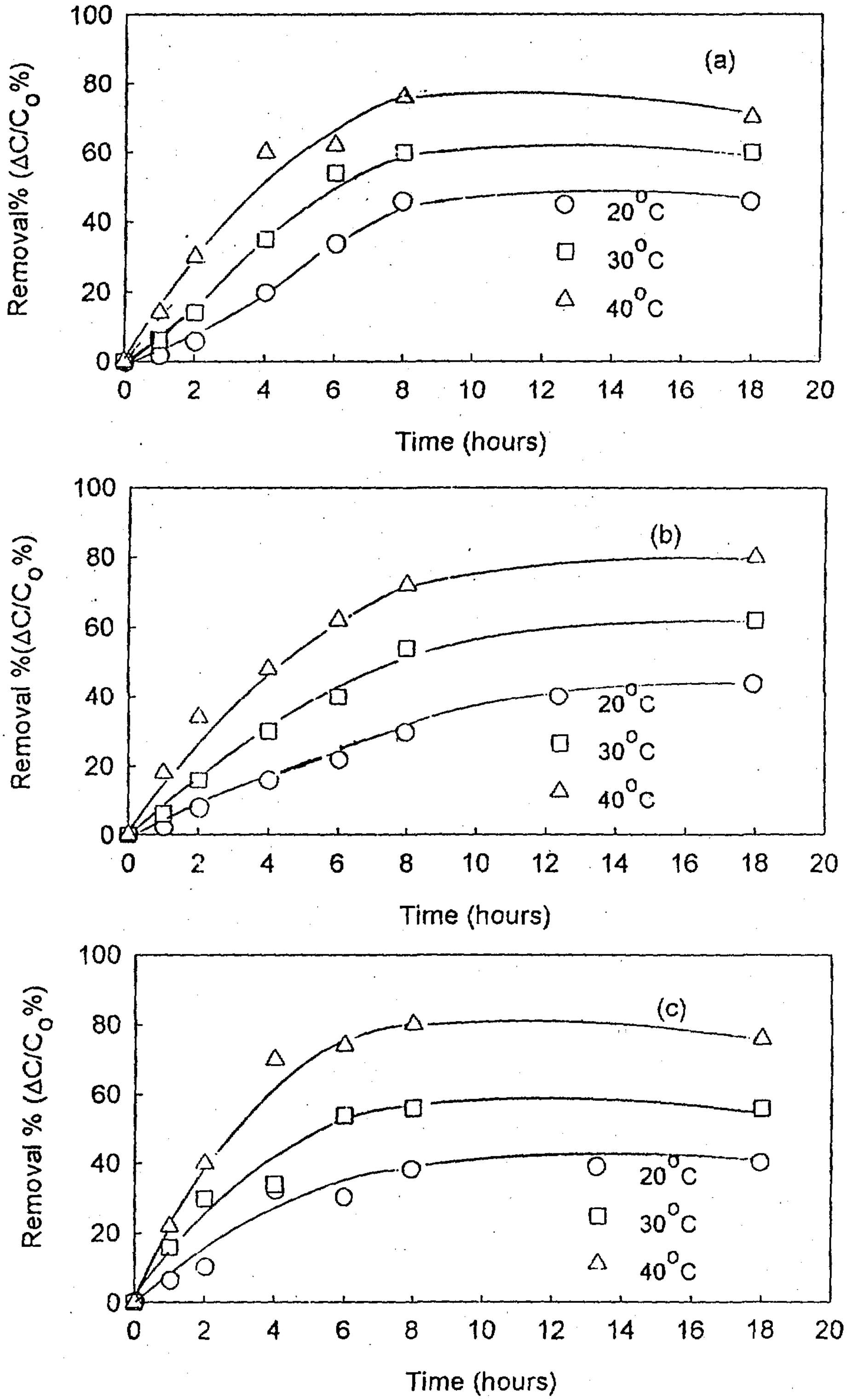

Fig. (3): Effect of temperature on the Adsorption of reactive blue (a), Acid red(b) and Direct orange (c) dyes on Acrylic acid/glycerol Hydrogel in methanol and H_2O at constant pH=7

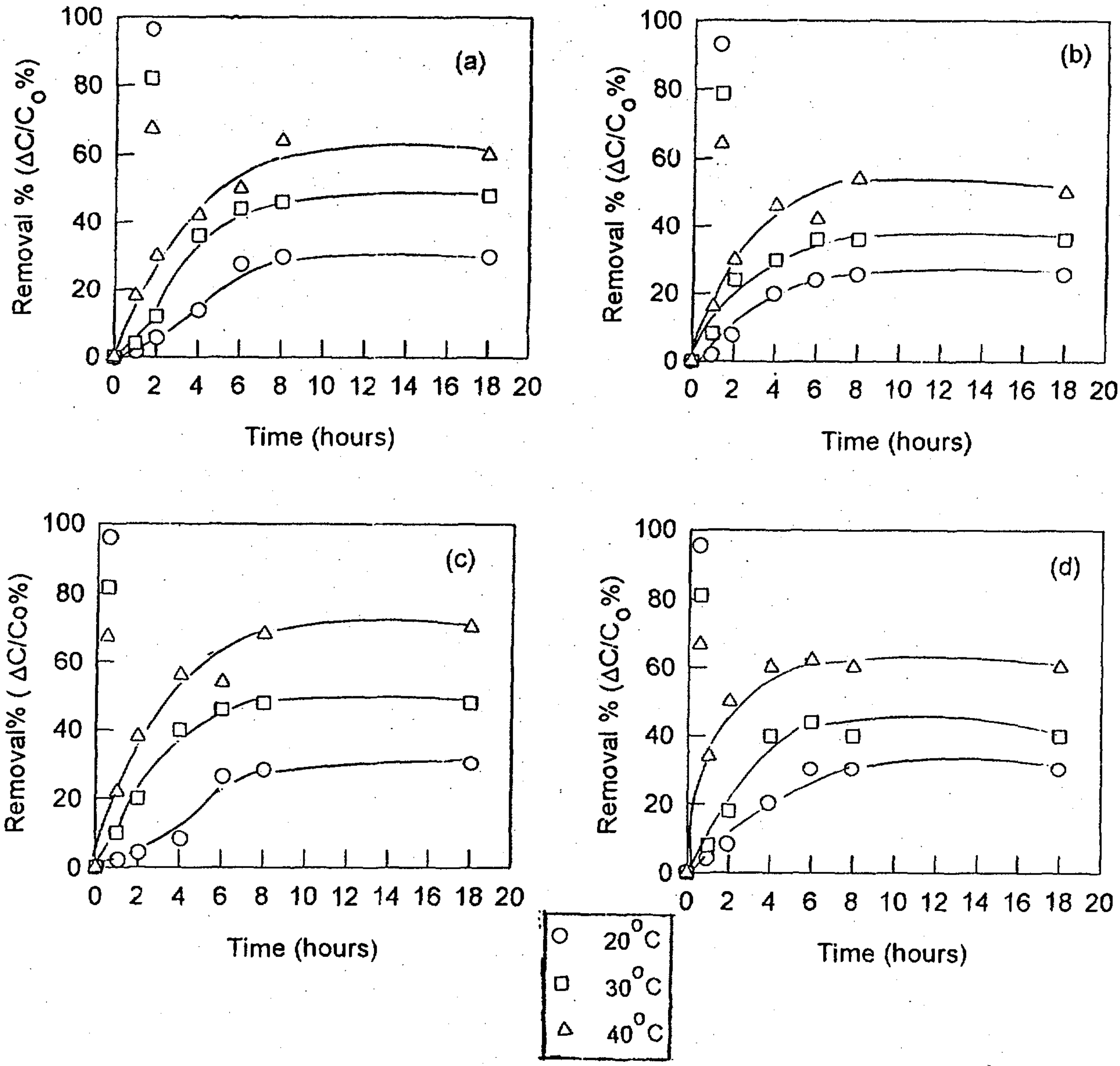

Fig. (4): Effect of Temperature on the Adsorption of Larvine(a),Dursbane (b), Comperlan (c) and Dehyquart (d) on Acrylic acid/glycerol Hydrogel in methanol at constant pH = 7

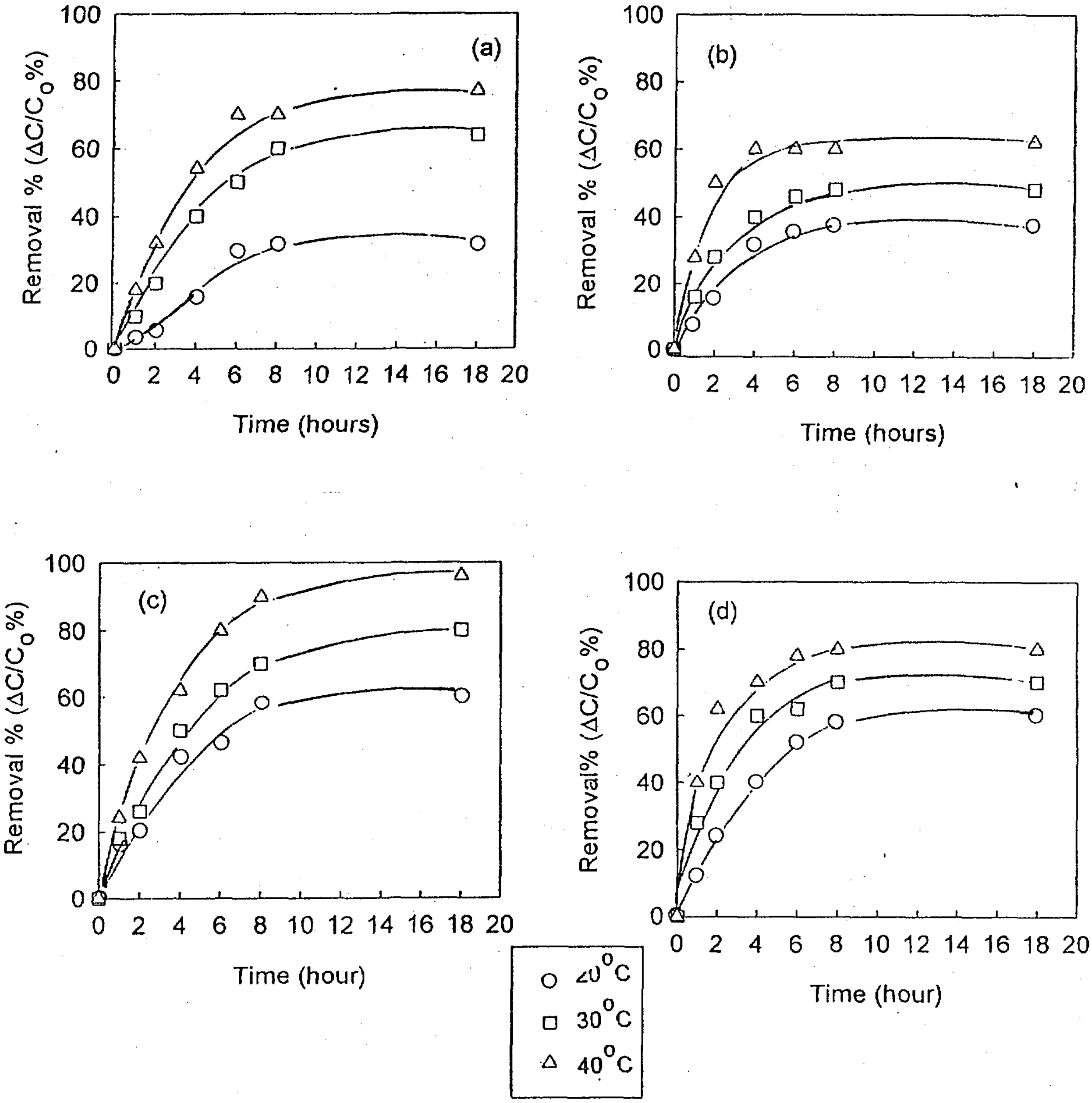

Fig. (5): Effect of Temperature on the Adsorption of Larvine(a),Dursbane (b), Comperlan (c) and Dehyquart (d) on Acrylic acid/glycerol Hydrogel in methanol and H_2O at constant pH = 7

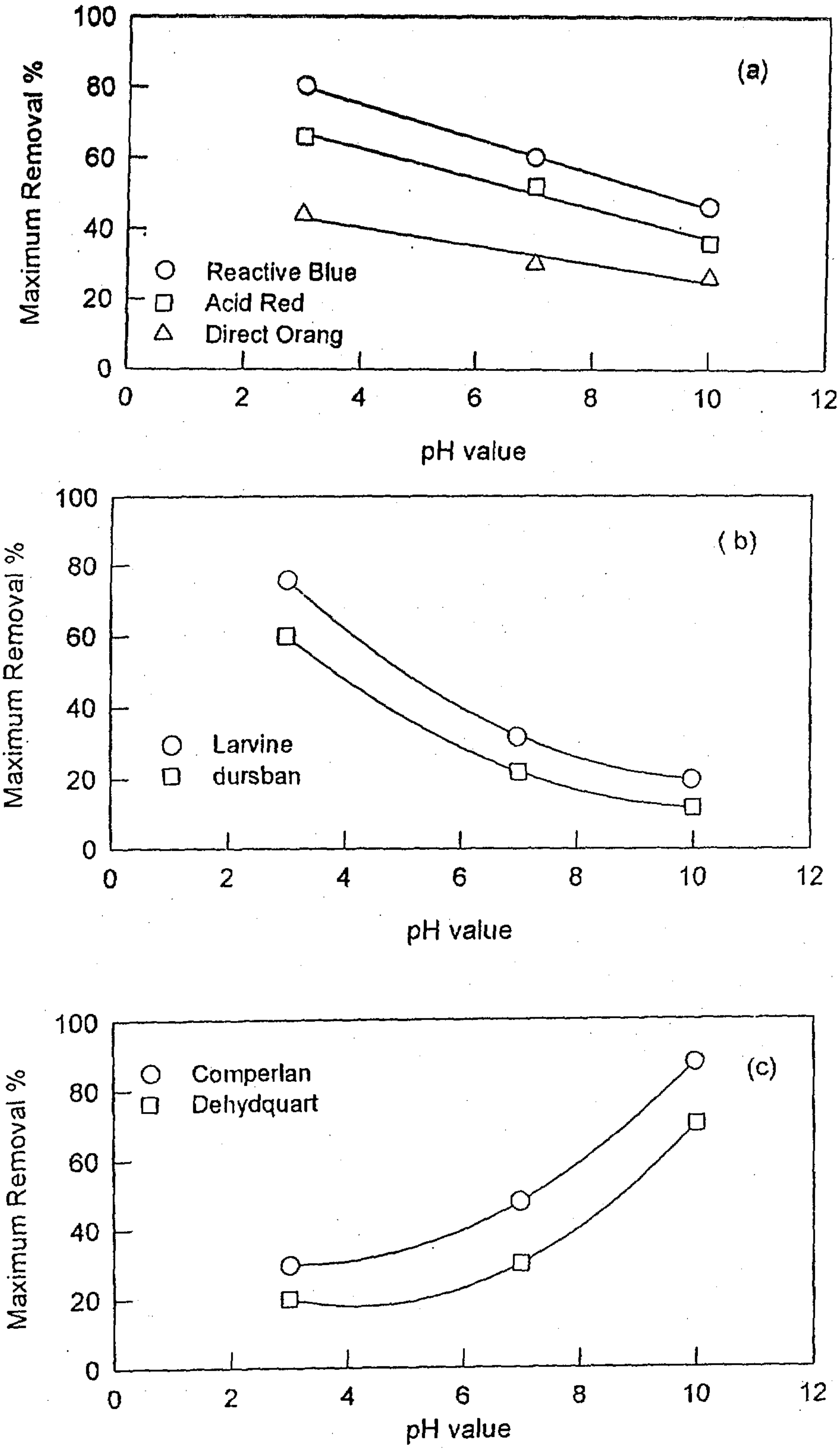

Fig. (6): Effect of pH on the Adsorption of Anionic Detergents(a), Pesticides(b) and different(c) dye on Acrylic Acid / glycerol Hydrogel in methanol at constant temperature 20°C

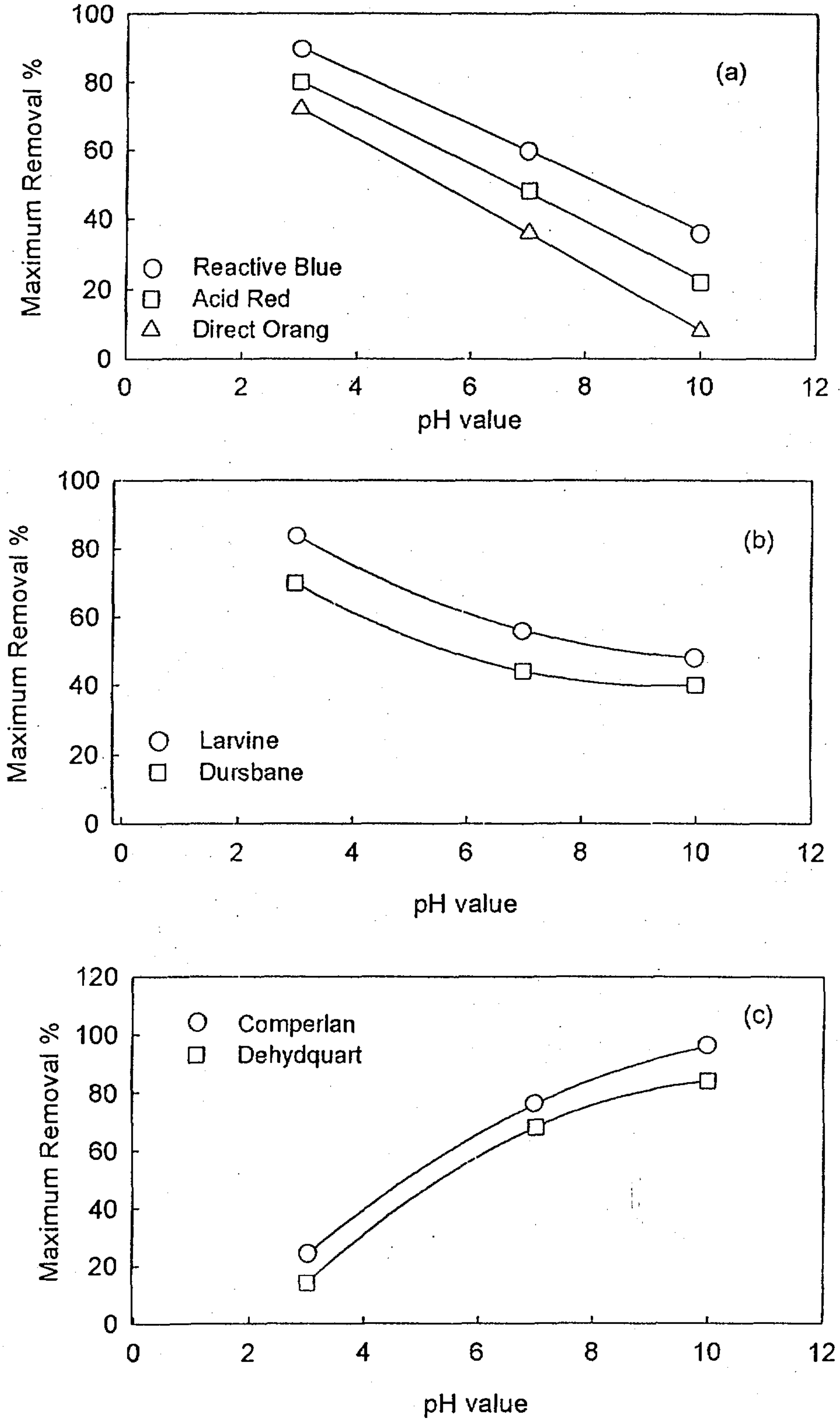

Fig. (7): **Effect of pH on the Adsorption of different dyes (a), Pesticides (b) and Anionic detergents (c) on Acrylic acid / glycerol Hydrogel in methanol and H_2O at constant temperature 20 °C**