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LIQUID ABSORPTION AND DEGRADATION STUDY OF SUPERABSORBENT POLYMERS (SAP)

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ABSTRACT

Absorption behaviors of varied masses of superabsorbent polymers (SAPs) were studied. 1.4g of SAP was in 40ml of SAP and was found to increase in weight to 41.5g after absorption in distilled water. Effect of saline solutions on absorption behavior of SAP was also studied. Decrease in absorption was observed with increase in saline concentration. The effect of temperature on the absorption behavior of the SAP was also investigated. It was observed that there was rapid increase in absorption with increase in temperature from 20°C – 100°C. The effect of pH investigated recorded maximum absorption at a pH 8. Staphylococcus aurous was found to degrade 0.1g of the SAP to 0.0017g.

Keyword: Sodium poly-acrylate, SAP, Liquid Absorption and Degradation

INTRODUCTION

It is noticeable that there are many water absorbing materials such as pulp, paper, cotton etc. Those materials absorb water by its capillarity hence their water absorption capacity is usually less than 20g water/g absorbent. Another property of these materials is that the absorbed water can be squeezed out by an externally applied pressure. Down memory lane (1960), researchers developed cross linked polyacrylamide which had the properties of absorbing up to 15-75 times of body fluids and retaining it under pressure of up to about 2.5p.s.i called it Hydro-colloidal Absorbent (Harmon and Plains, 1972). Later, due to low absorption capacity was still low, new material was developed which could absorb more than 1000 times of its weight of water, and was termed superabsorbent polymer (SAP) (Fanta *et al.*, 1970; Meshram *et al.*, 2020). Chemically speaking, Superabsorbent polymers (SAPs) or hydrogels are loosely cross-linked, three-dimensional networks of flexible polymer chains that carry dissociated, ionic functional groups (Fanta *et al.*, 1970; Meshram *et al.*, 2020). In modern polymer technology, they are regarded as fascinating materials which can Not only are they of high fluid absorbing capacity, but the absorbed fluid is hard to absorb fluids of greater than 15 times their own dried weight (Meshram *et al.*, 2020). Recently, the leading market for SAPs are the hygiene (baby diapers and adult care articles), water reservoirs in agriculture, Body Water Retainers, Stomach Bulking Agents, Devices for Controlled Drug Delivery, Scaffolds for Regenerative Medicine, and Wound Dressings etc. (Robiul *et al.,* 2011). They are polymers which are characterized by hydrophilicity containing carboxylic acid, carboxamide, hydroxyl, amine, imide groups and so on, insoluble in water, and are cross-linked polyelectrolytes (Meshram *et al.*, 2020). Because of their ionic nature and interconnected structure, they absorb large quantities of water and other aqueous solutions without dissolving by solvation of water molecules via hydrogen bonds, increasing the entropy of the network to make the SAPs swell tremendously (Meshram *et al.*, 2020). The factors that supply absorbing power to polymers are osmotic pressure, based on movable counter-ions, and affinity between the polymer electrolyte and water. The factor that suppresses absorbing power, in contrast, is found in the elasticity of the gel resulting from its network structure.

release, as they merely immobilize the fluid by entrapment rather than by holding it in the structure. The Water absorption capacity (WAC) of SAP however, is the most important characteristic in understanding the hydrogel. Usually, the WAC is measured using volumetric method, gravimetric method, spectroscopic method and microwave method. From a morphological, material resources and preparation method point of view SAP can be divided into particle; powder; spherical; fiber; membrane; emulsion and natural macromolecules, semi-synthesized polymer; and synthesized polymers; graft polymerization; cross-linking polymerization; networks formation of water-soluble polymers and radiation cross-linking respectively (Meshram *et al.*, 2020). Buchholz (1994) has elaborated the uses of super absorbents based on cross-linked, partially neutralized poly (acrylic acid) and graft copolymers of starch and acrylic acid. In another review, the synthesis of cross-linked acrylic acid-*co*-sodium/potassium acrylate has been described (Buchholz, 1994). The solution and suspension polymerization techniques used for preparing the acrylate super absorbents yielded best result (Dayal *et al.,* 1999). In a further assessment study by Bagheri and Afrasiab (2013) on the yield and yield constituent of the plant irrigated by saline water using SAP wrap up produced no considerable benefits (Bagheri and Afrasiab, 2013). Their finding implies that Salinity in the irrigation water enhances bulk density, dwindles porosity and hydraulic conductivity as there is a less scope of water absorption in an ionic water medium and as a result SAP should not be used with saline water (Bagheri and Afrasiab, 2013). The use of superabsorbent polymer was revealed to be effective means for corn production under arid conditions of northern China (Robiul *et al.,* 2011; Mahalleh *et al.*, 2011; Oraee and Moghadam, 2013). El-Hady and a colleague in 2006 have established that, SAP can be used for conserving irrigation water and increasing the agricultural potentialities of sandy soils under the severe conditions of deserts (El-Hady and Wanas, 2006). Contained by an industrial production viewpoint, a positive profile has been published about acrylic SAPs by the Stanford Research Institute, SRI (Chin and Dayel, 1985). Climatic conditions affect the absorption rate of superabsorbent polymers. It is evident that weather condition of countries in the world varies, so the same quantity of superabsorbent polymers when subjected to a liquid at various degrees of temperatures shows different rate of absorption (Meshram *et al.*, 2020). Thus, the research is to study liquid absorption behaviours of Superabsorbent polymers in various saline concentrations at different temperatures.

EXPERAMENTAL

Materials

Synthetically Superabsorbent polymers were purchased and accurately weight for the study, distilled water, NaCl, $MgCl_2$, $CaCl_2$, HCl, NaOH, measuring cylinder, sieve, thermometer, glass funnel, volumetric flask 500ml, beakers and stopwatch.

Methods

Treatment and Experimental Design

Two sets of experiment were conducted. The first constituted of liquid absorption of the polymers when they are subjected to saline solutions at different concentrations, their responsiveness to pH and their effect at various degrees of temperature ranges. The second constituted of the degradation study of the superabsorbent polymers after the introduction of microorganisms.

Procedures

The SAP samples were accurately weighed as 0.2g; 0.4g; 0.6g; 0.8g; 1.0g; 1.2g; and 1.4g. All the samples weights remained constant throughout the period of the study except in pH study which was varied.

Effect of SAP absorption in Distilled Water

The accurately weight samples of the SAP were subjected to 40mls of distilled water for 2 minutes each, monitored with a stopwatch and filtered with a sieve, the increased in weights were recorded and absorption was studied using the following equation

$$Abs = (Wf - Wi) / Wi$$

Where Abs = Absorption Wi = Weight of SAP after absorption Wf = Weight of SAP before absorption

Effect of salt solution on SAP Absorption

Saline solutions of NaCl, $CaCl_2$, and $MgCl_2$ of 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4% W/V concentrations were prepared.

Effect of temperature on superabsorbent polymers absorption

The effects of temperature on superabsorbent polymers were also studied. Superabsorbent polymers were subjected to 40mls of distilled water at varying temperatures ranging between 20 - $100^{O}C$ with a difference of $20^{O}C$. Times of absorptions were recorded. The increased weights of the superabsorbent polymers were also recorded.

Effect of pH on superabsorbent polymers absorption

A constant mass of the dry superabsorbent polymer of 0.1g was used; 0.2M HCl and 0.2M NaOH were prepared and were adjusted to desired pH for the study. There absorptions were calculated from the relation below;

$$\text{Absorption} = (W_f - W_i) / W_i$$

Where W_f = final weight or weight of swollen gel and W_i = initial weight or weight of dry gel sample

Degradation of superabsorbent polymers

The absorption of the samples that were subjected to the above solution were recorded and tabulated. The sample with the highest or better absorption in distilled water and the sample with the poorest absorption in saline solutions were used for the degradation study from the results obtained. Microorganisms from microbiology laboratory of the department of microbiology, Bayero University Kano were subjected to these samples for two weeks for the degradation of the superabsorbent polymers, after two weeks, the difference in weight was obtained and recorded.

FTIR Spectroscopy

The dry SAP was characterized by functional group using Fourier transform infrared (FTIR) spectrophotometer. Absorption of Bands was identified from the Infrared correlation table.

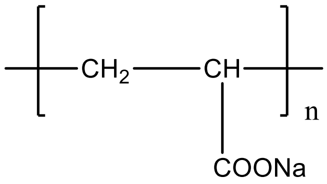
Scanning electron microscopy (SEM)

The Surface Morphology of dry SAP sample was investigated with a scanning electron microscopy machine.

RESULTS AND DISCUSSION

FTIR Spectroscopy

Functional group characterization by Infrared spectroscopy was carried out to confirm the chemical structure of the sodium poly-acrylate SAP, some of the most important peaks were identified, the absorption peak at $3347cm^{-1}$ is for O-H of the carboxylic acid group, the $1544cm^{-1}$ is for C=O of the carboxylate salt and finally C-O band at $1233cm^{-1}$.



$$\left[-CH_2-\underset{\displaystyle COONa}{\underset{|}{CH}}- \right]_n$$

Scheme 1: Structure of sodium poly- acrylate

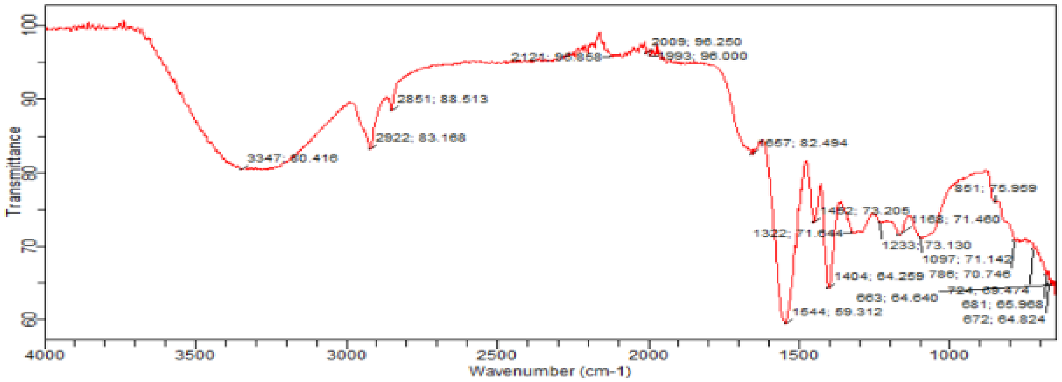


Figure 1: FTIR of sodium poly-acrylate

Effect of SAP absorption in Distilled Water

When SAP were subjected to the distilled water, the result shows that the water absorption capacity increases with increasing weight of the dry polymer, because the neutralized chains contains charges that repel each other, overall neutrality is maintained as the negative carboxylate groups balance the positive sodium ions. When they are contact with water, the sodium ions become hydrated and can move freely within the network but can't escape from the network because they are still weakly attracted by the negative carboxylate ions, this contribute to the osmotic pressure within the gel, the driving force for swelling is the difference between the osmotic pressure inside and outside of the gel. So, maximum swelling occurs in deionised water, this is why absorption increased with increasing weight of the dry SAP. Similar results were obtained by Foster and Keever (1990). Table 2 below displays that, the increased in weight slightly varies because 40mls of water was subjected to the samples which proved not their maximum swelling capacity.

Table 2: Absorption of SAP in distilled water

Dry weight (g)	0.2	0.4	0.6	0.8	1.0	1.2	1.4
Increased in weight (g)	39.2	39.5	40.2	40.4	40.7	41.4	41.5
Weight increase (g)	39	39.1	39.6	39.6	39.7	40.2	40.1

Effect of salt solutions on the SAP at various concentrations.

Table 3, it shows that, NaCl has the highest absorption followed by $MgCl_2$ and finally $CaCl_2$, because of the increasing ionic strength, the absorption tends to decrease. The decrease of the swelling capacity of the hydrophilic polymer is due to the screening effect and a loss of the osmotic pressure difference between the hydrogels and the fluids. The perfect anion-anion repulsion of the carboxylate groups is prevented by the M^{n+} cations that shield the carboxylate groups, so the swelling capacity is decreased. Multivalent cation decreases drastically the swelling capacity. The carboxylate ions do not keep cations in their vicinity, so the charge screening effect is not very effective. The salt type and concentrations can be expressed in terms of ionic strength; the effect of ionic strength on water absorbency can be expressed by Flory's equation (Ichikawa and Nakajima, 1996).

$$Q^{5/3} = [(i/2V_uS^{*1/2})^2 + (1/2 - X_1)/V_1] / (Ve / Vo) \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where Q is the degree of swelling i/V_u is the charge density of polymer, S* is the ionic strength of solution, $(1/2 - X_1)/V_1$, is the polymer-solvent affinity, Ve / Vo is the crosslinking density. According to Eq. (1), when the ionic strength of saline solution increases, the water absorbency decreases. The ionic strength of the solution depends on both the mobile ions and their valence or oxidation state. Small quantities of divalent or trivalent ions can drastically decrease the swelling values. The decreases are more significant by Mg^{2+}or Ca^{2+} ions, which can be additionally caused by the complex formation ability of carboxylate groups including intramolecular and intermolecular complex formations, or because one multivalent ion is able to neutralize several charges inside the gel. Consequently, the crosslink density of the network increases while water absorption capacity decreases (Castel *et al.*, 1990).

Table 3: Absorbances of 0.4%, 0.6%, 0.8%, 1.0%, 1.2%, and 1.4% WV^{-1} NaCl, $MgCl_2$ and $CaCl_2$

% W/V	Wi	NaCl	Abs	$MgCl_2$	Abs	$CaCl_2$	Abs
0.4	0.2	15.6	77.00	12.7	62.50	9.1	44.50
	0.4	22.7	55.75	19.9	48.75	13.8	33.50
	0.6	31.7	51.83	29.8	48.67	21.7	35.17
	0.8	38.7	47.38	36.7	44.88	30.8	37.50
	1.0	40.1	39.10	39.2	38.20	38.1	37.10
	1.2	40.3	32.58	40.2	32.50	40.2	32.50
	1.4	40.4	27.86	40.4	27.86	40.4	27.86
0.6	0.2	8.8	43.00	5.8	28.00	4.5	21.50
	0.4	17.3	42.25	14.6	35.50	13.4	32.50
	0.6	25.5	41.50	19.5	31.50	16.6	26.67
	0.8	33.1	40.38	30.3	36.88	23.5	28.38
	1.0	38.7	37.70	37.6	36.60	36.2	35.20
	1.2	40.4	32.67	40.1	32.42	37.6	30.33
	1.4	40.6	28.00	40.6	28.00	40.5	27.93
0.8	0.2	8.4	41.00	5.3	25.50	3.9	18.50
	0.4	16.5	40.25	10.3	24.75	7.7	18.25
	0.6	23.4	38.00	16.4	26.33	10.9	17.17
	0.8	31.1	37.88	23.5	28.38	16.7	19.88
	1	35.8	34.80	32.8	31.80	22.9	21.90
	1.2	41	33.17	39.8	32.17	28.1	22.42
	1.4	40.8	28.14	40.4	27.86	33.8	23.14
	0.2	8.1	39.50	4.9	23.50	3.7	17.50
	0.4	13.4	32.50	9.4	22.50	6	14.00
	0.6	20.9	33.83	13.7	21.83	9.6	15.00

Table 3 Cont.

	0.8	28.8	35.00	19	22.75	14	16.50
	1.0	31.4	30.40	25.9	24.90	18.1	17.10
	1.2	39.8	32.17	33.1	26.58	23	18.17
	1.4	40	27.57	39	26.86	27.9	18.93
1.2	0.2	7.9	38.5	3.3	15.50	2.6	12.00
	0.4	12.9	31.25	8.9	21.25	4.4	10.00
	0.6	19.6	31.67	12	19.00	7.3	11.17
	0.8	25.5	30.88	16.8	20.00	10.3	11.88
	1.0	31.0	30.00	21.5	20.50	13.6	12.60
	1.2	40.0	32.33	27.8	22.167	17	13.17
	1.4	41.1	28.36	34.4	23.57	21.5	14.36
1.4	0.2	7.2	35.00	2.7	12.50	2.2	10.00
	0.4	12.5	30.25	8.4	20.00	2.8	6.00
	0.6	19.9	32.17	10.8	17.00	7.2	11.00
	0.8	23.9	28.88	13.2	15.50	10.1	11.63
	1.0	30.9	29.90	18.6	17.60	11.8	10.80
	1.2	34.5	27.75	23.3	18.42	13.7	10.42
	1.4	41	28.29	34.0	23.29	16.8	11.00

Abs= Absorption, W_i = initial weight of SAP Wf= final weight of SAP

For the sample SAP at various concentrations of the tabulated data above, the increased in weight of the hydrogel that shows the absorption of each of the SAP samples were represented graphically, refer to appendix for details.

Effect of Temperature on superabsorbent polymers

When the weighed samples of the SAP were added to distilled water at various degrees of temperature, there is rapid absorption. Table 9 shows that with increasing temperature, the dissociation of the ionic functional groups tends to occur very fast. The increased in weight is negligible and tend to differs because the water at a very high temperature is destroying the hydrogel, however upon cooling it turns to form a gel.

Table 9: SAP absorption at 20^0C, 40^0C, 60^0C, 80^0C, and 100^0C

	20^0C		40^0C		60^0C		80^0C		100^0C	
Dry Weight	**Time**	**S. Weight**	**Time**	**S. Weight**	**Time**	**S. Weight**	**Time**	**S. Weight**	**Time**	**S. Weight**
1.4	00:19.85	41.0	00:11.58	39.8	00:06.85	38.9	00:05.40	39.7	00:03.90	39.9
1.2	00:20.51	40.7	00:12.66	39.8	00:70.05	38.7	00:05.67	39.2	00:04.06	39.9
1.0	00:22.86	40.7	00:13.42	39.4	00:07.86	38.9	00:05.74	39.4	00:04.69	39.9
0.8	00:26.42	40.4	00:15.95	38.9	00:07.91	38.9	00:06.59	39.2	00:06.54	39.7
0.6	00:30.23	40.5	00:20.19	38.9	00:11.08	38.8	00:07.36	38.9	00:08.50	39.8
0.4	00:45.22	40.3	00:26.49	38.8	00:17.93	38.5	00:10.45	38.1	00:09.68	39.4
0.2	01:48.74	40.1	01:10.85	38.7	01:00.80	37.9	00:29.29	38.4	00:25.85	38.8

Effect of pH on superabsorbent polymers Absorption

The hydrogel polymer contained sodium poly-acrylate groups; these are groups that are very acidic and fast ionizable. The swelling of the hydrogel shows a very low swelling in very acidic conditions i.e. at pH of 2.6, this may be attributed to the screening effect of the counter ions, i.e. Cl$^-$, shields the charge of the carboxylate anions and prevent an efficient repulsion.

With increasing pH, i.e. at pH of 4 and 6, the ionic strength of the solution (i.e. shielding effect of Cl$^-$ is decreased and the swelling increased. However, at the pH of 8, the high the anion-anion repulsive electrostatic forces of carboxylate groups, the high swelling will be. At Higher pH (i.e. basic) pH 9and 10, there is decreased in swelling, this is due to the screening effect of the counter ions, i.e. Na$^+$, Shields the charge of the carboxylate anions and prevents an efficient repulsion, (Mahdavinia *et al*., 2004; Chen and Zhao, 2000; Flefel *et al*., 2002.)

Table 12: Effect of pH on SAP absorption

pH	2.6	3	4	5	6	7	8	9	10
Increased in weight	1.1	1.7	5.6	4.8	5.3	5.7	7	6.2	5.5

Biodegradation of superabsorbent polymers

Scanning electron microscopy (SEM) which gives the surface morphology of the superabsorbent polymer shows that pores are present on the surface of the SAP, those pores are site or region for water penetration.

From the above figures 2(a) and (b), figure (a) is a 0.1g of the samples with the highest water absorption and (b) for the sample with poor absorption in salt, after the subjection of microorganisms, there is decreased in weight indicating that the microorganisms have acted on the SAP. As seen in figure (c) and (d). The microorganism used was Bacteria specie (*Staphylococcus aureus*).

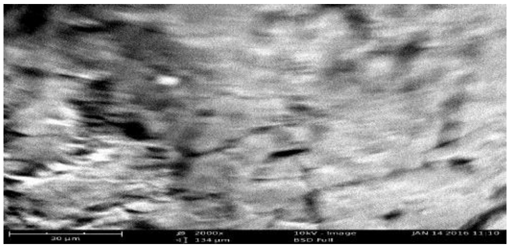
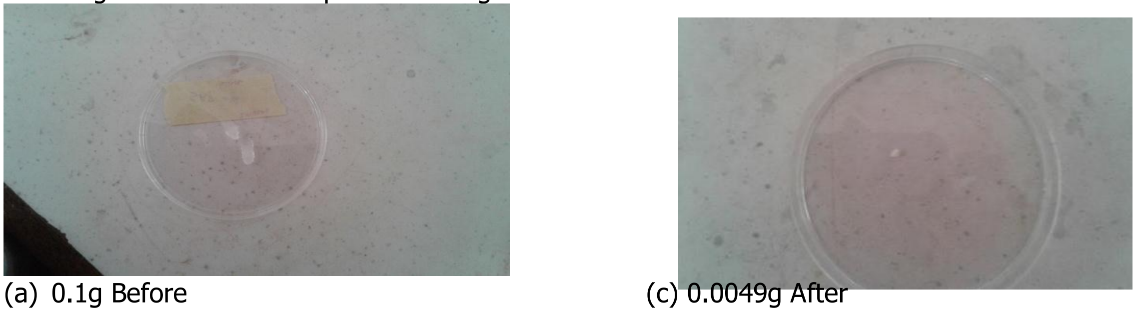


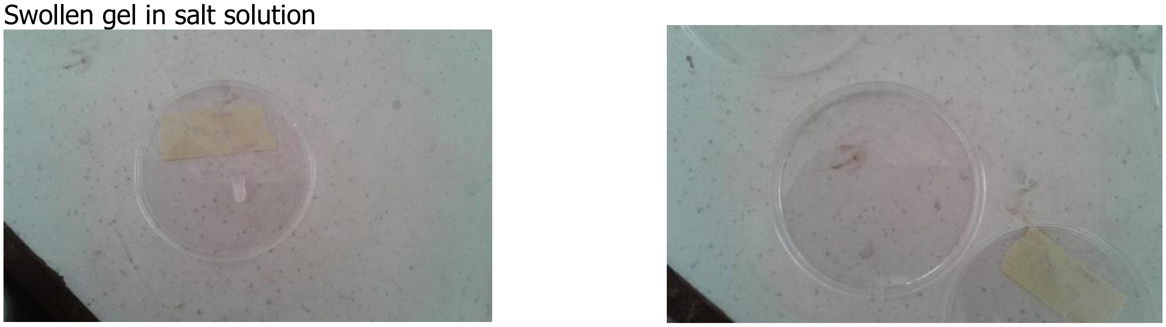
Figure 1: Surface morphology dry SAP samples

Figure 2 below shows the image of the weight samples before and after introduction of microorganisms to the samples Swollen gel in distilled water



(a) 0.1g Before (c) 0.0049g After

Swollen gel in salt solution



(b) 0.1g Before (d) 0.0017g After

Figure 2: Swollen SAP samples in salt and distilled water

CONCLUSION

Salt solution decreases drastically the water absorption capacity (WAC) of superabsorbent polymers with increase in concentration, rapid absorption takes place with increasing temperature and lower absorption capacity at acidic pH, at a pH 8 there is maximum liquid absorption capacity, and finally as basic pH increases, the liquid absorption capacity decreases. Pores present in the SAP surface are regions for water penetration. It would be more important if researchers can consolidate assessing the effect of SAP absorption on liquid sample collected from ocean, and oil samples at temperature below 20^0C to see the effect of absorption on SAP.

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APPENDIX

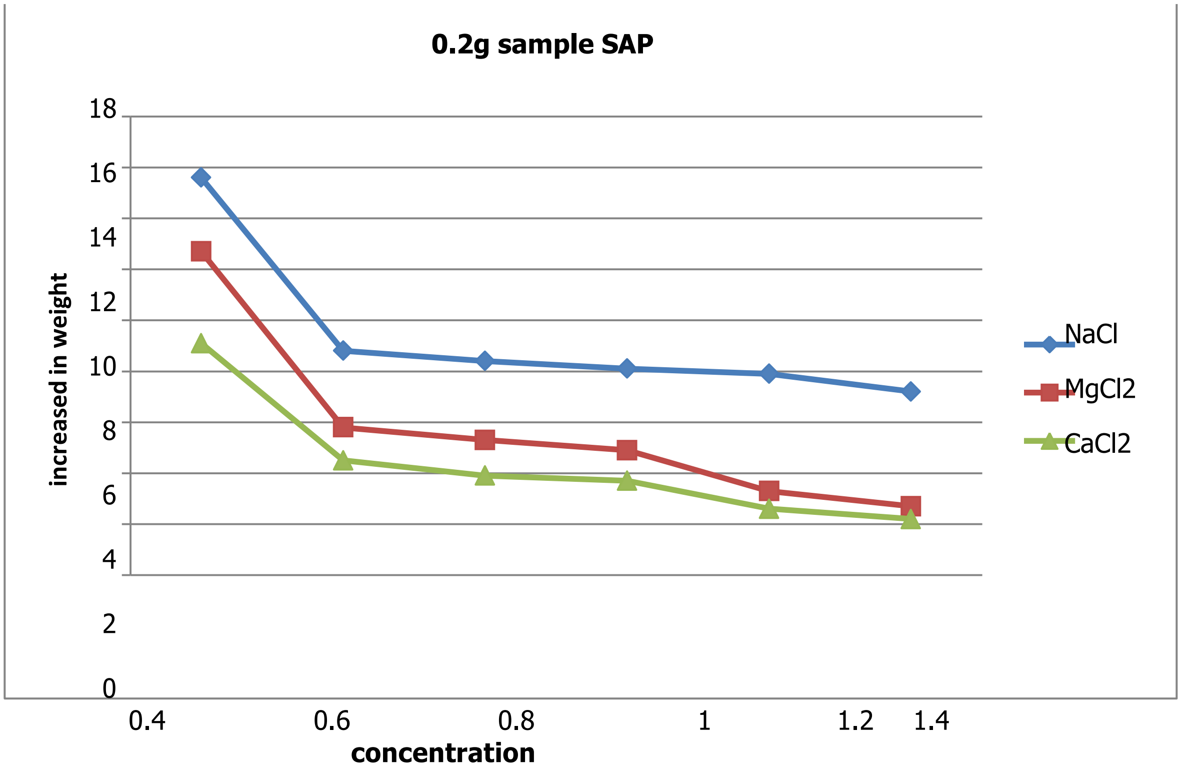

Figure 2: Absorption pattern of 0.2g SAP in various solutions

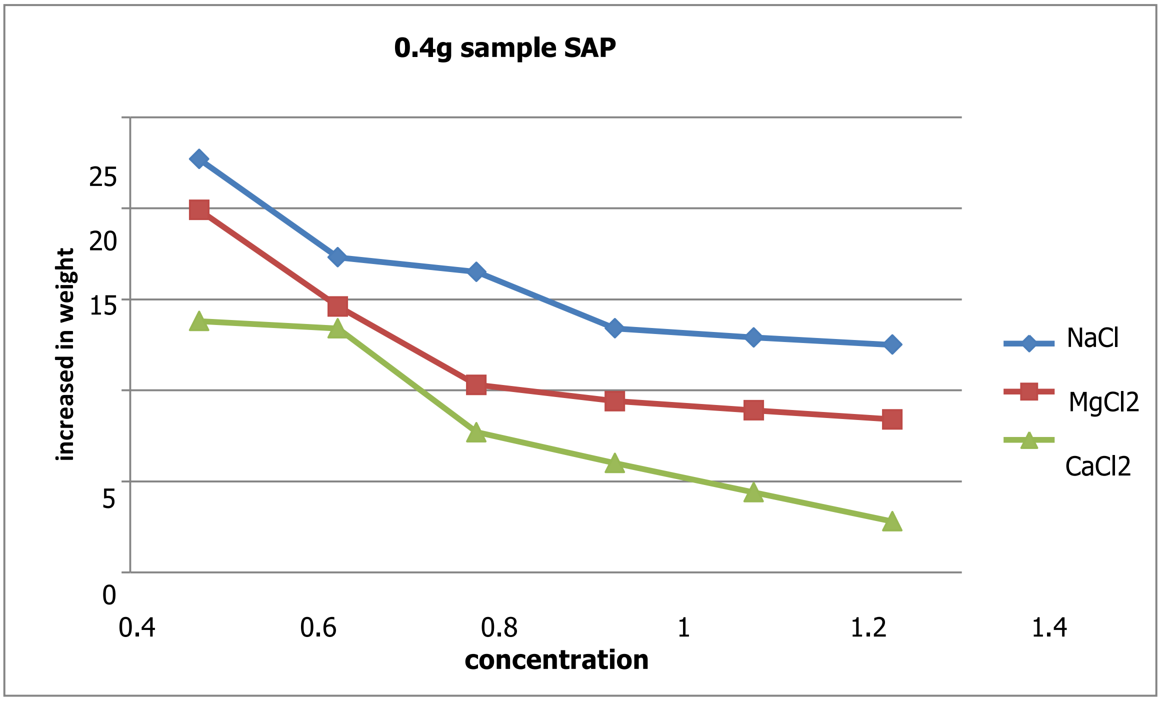

Figure 3: Absorption pattern of 0.4g SAP in various solutions

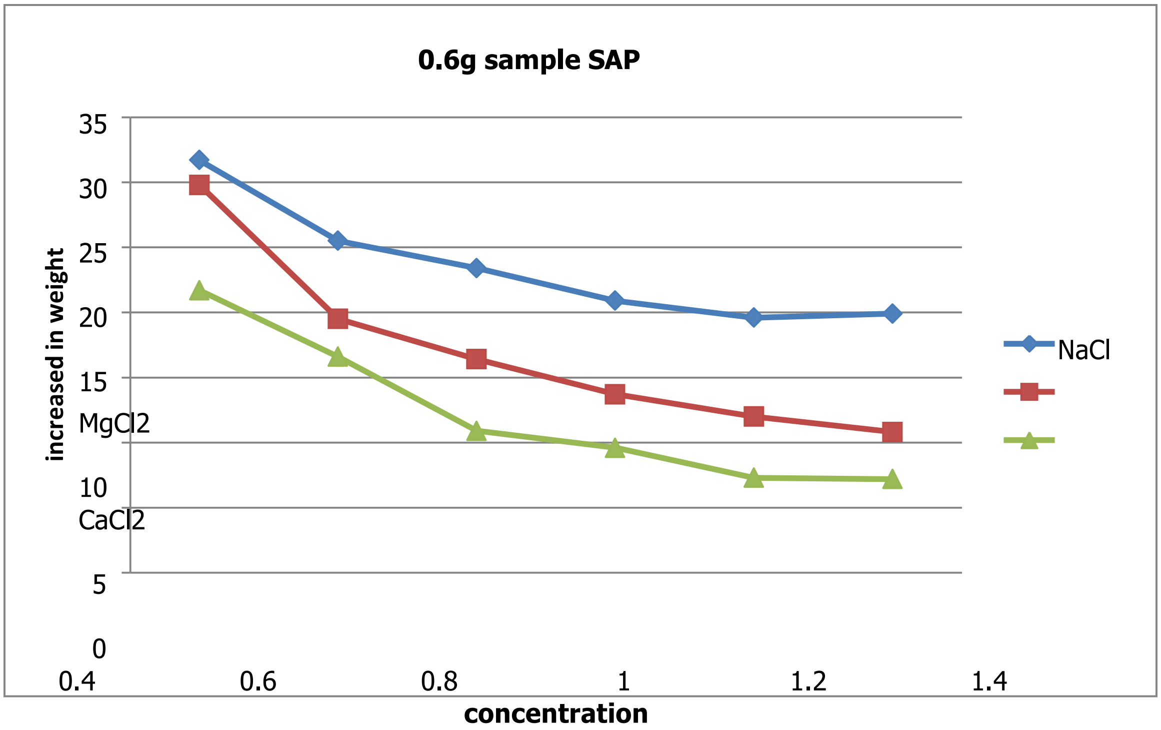

Figure 4: Absorption pattern of 0.6g SAP in various solutions

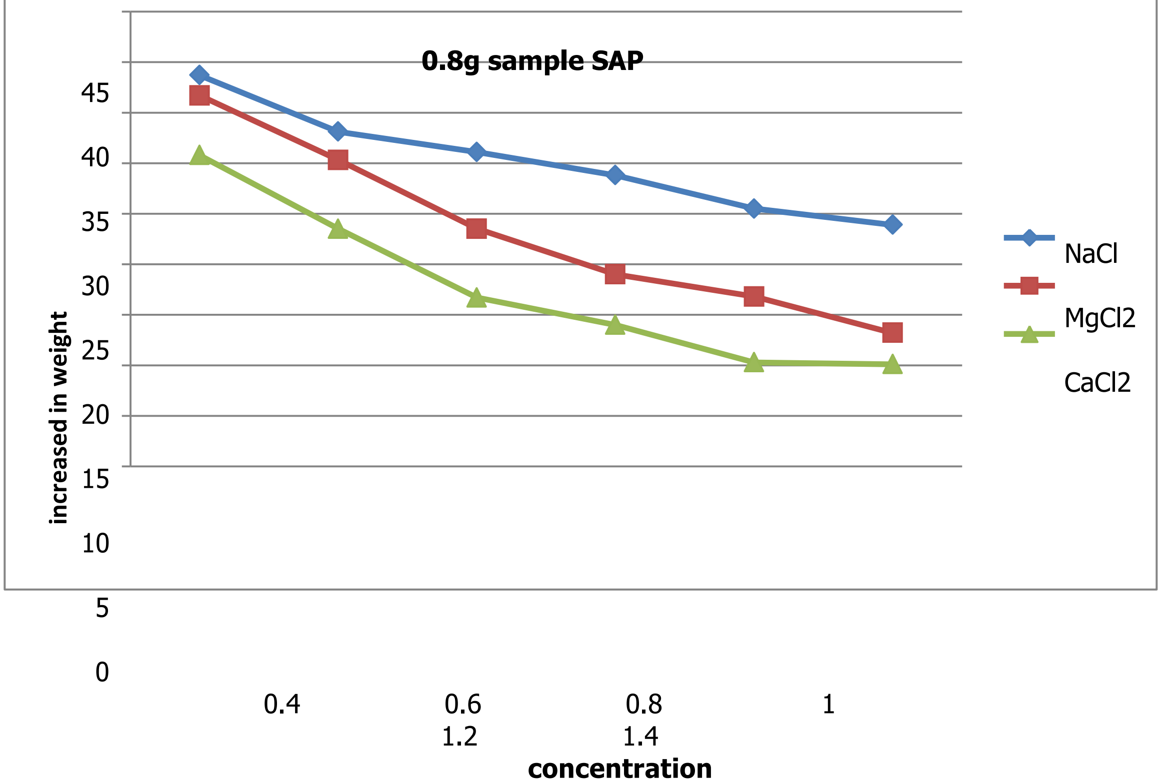

Figure 5: Absorption pattern of 0.8g SAP in various solutions

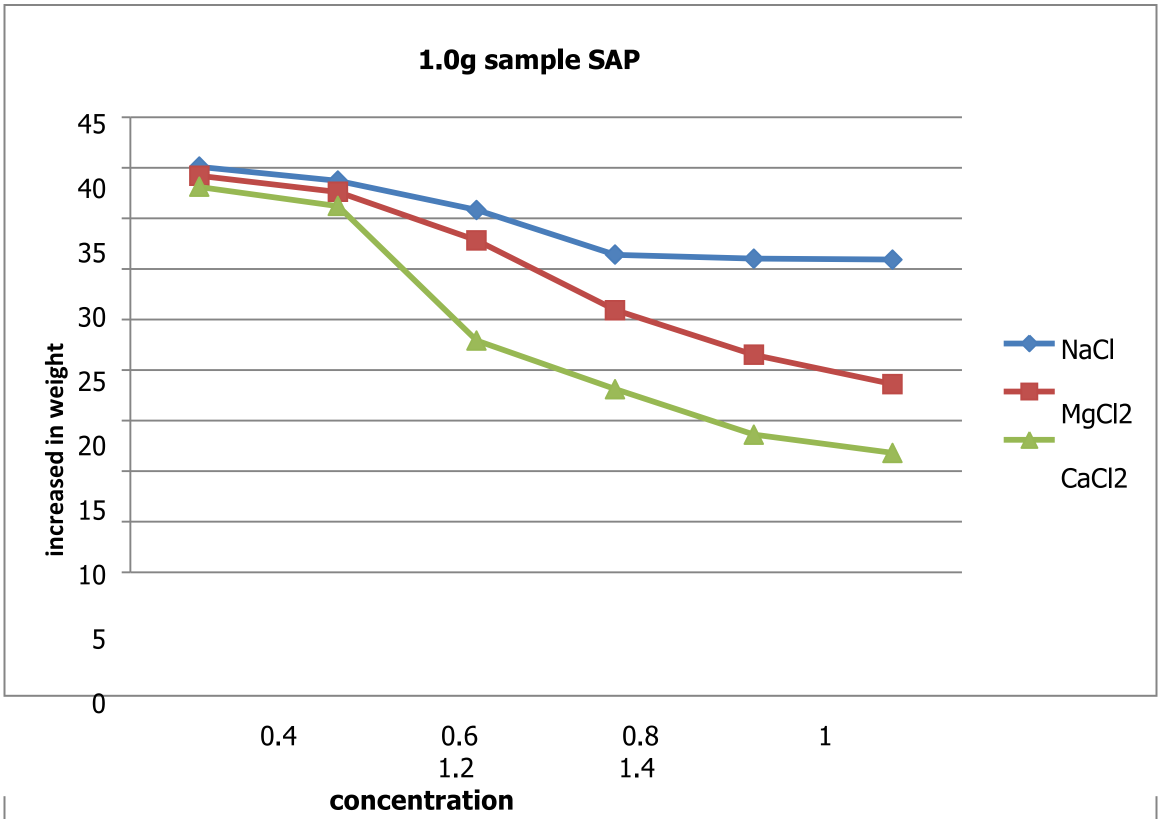

Figure 6: Absorption pattern of 1.0g SAP in various solutions

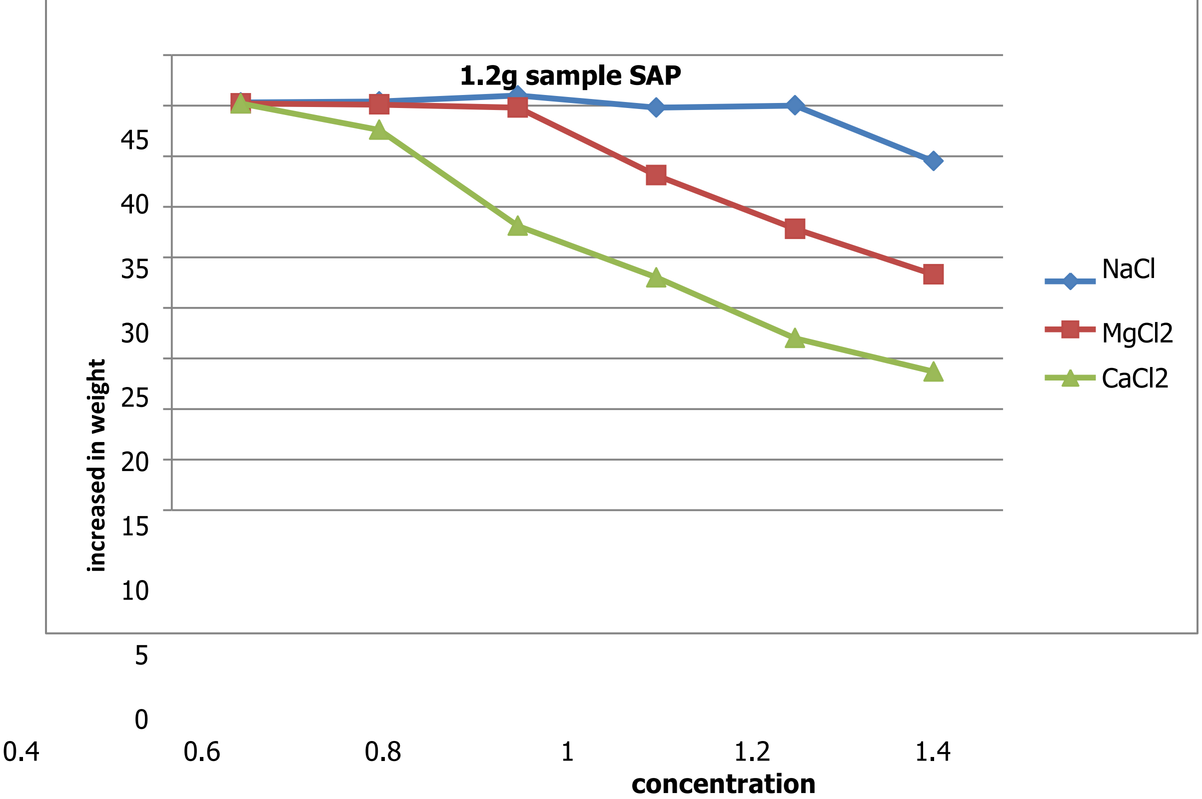

Figure 7: Absorption pattern of 1.2g SAP in various solutions

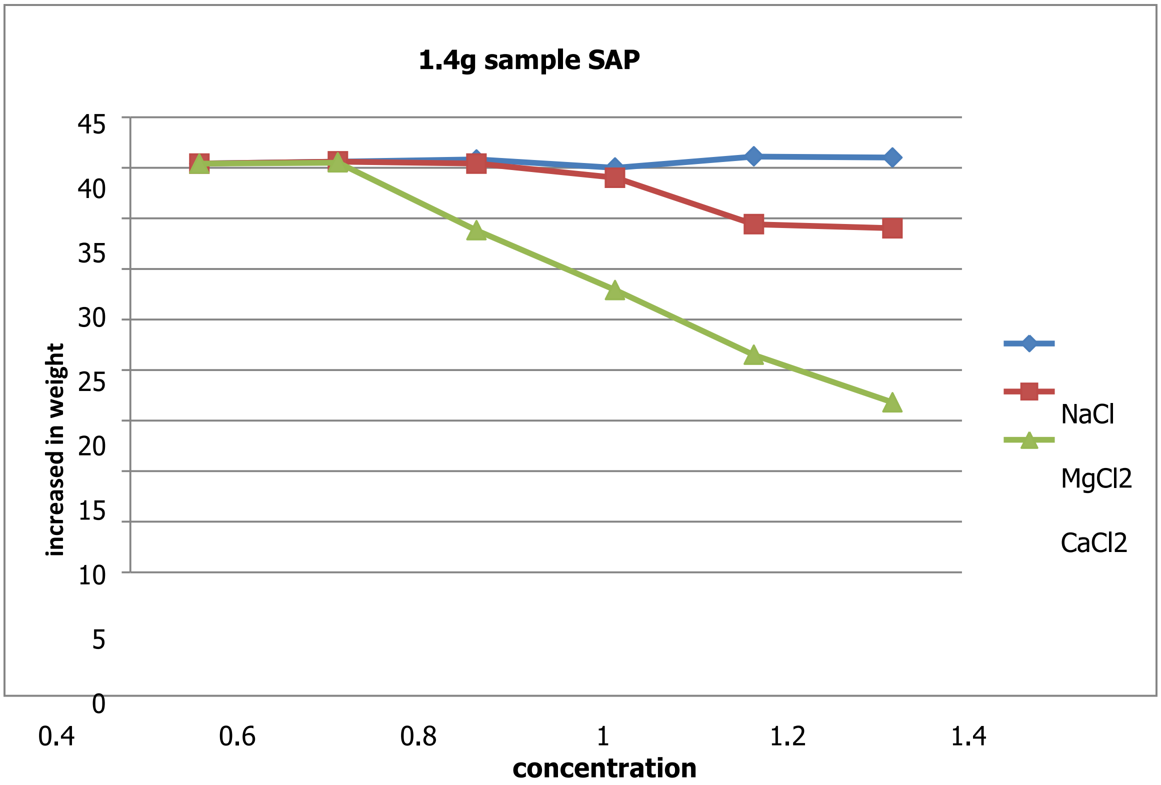

Figure 8: **Absorption pattern of 1.4g SAP in various solutions**

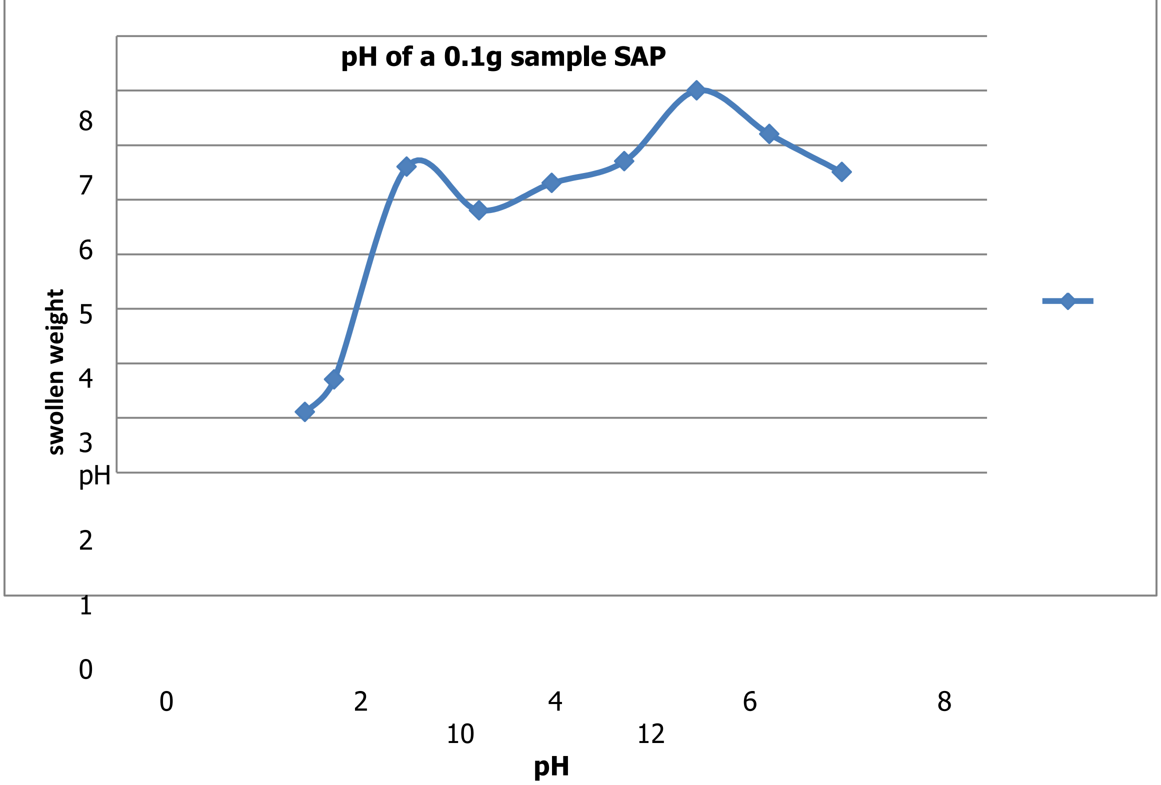

Figure 9: SAP Absorption at varying pH