THE EFFECT OF RICE HUSKS ON THE ACIDITY
AND ALKALINITY OF TREATED AQUEOUS SOLUTIONS

دراسة تأثير سرمة الارز على حامضية وقلعدية المحاليل المائية المعالجـــــة

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ملخص البحث :

أختيرت سرمة الارز ، والتى تعتبر واحدة من المخلفات الزراعية الرئيسية لتوظيفها فى العديد من عمليات التحكم فى تلوث البيئة مثل معالجة مياه الصرف الصناعية وغيرهـــا ، وقد أعطيت مراجعة عن سرمة الارز تتضمن الانتاج والتركيب والاستخدام وصعوبات الاستخدام

ونظرا لما هو معلوم من تأثير الاس الهيدروجينى على عمليات الازالة للعديــــد من المواد من المياه المعالجة فإن البحث الحالى يعتنى بدراسة تأثير السرمة علـــى الاس الهيدروجينى للمحاليل التى تستخدم السرمة فى معالجتها ، كما تبحث الدراســـة فى امكانية ازالة الايونات الموجبة والسالبة من المحاليل المعالجة من خلال عمليـــات الاستـــزاز على سطح السرمة ، وقد تم دراسة تأثير القيمة الاولية للاس الهيدروجينـــى على قيمة التغيير ،وتركيز السرمة المستخدم فى المعالجه ،وتأثير زمن المعالجة ، وقـــد تم معالجة محاليل حامضية وقاعديه ومتعادلة ، وقد أوضحت الدراسة أن السرمة قـــد أثرت بدرجة كبيره على الاس الهيدروجينى للمحاليل الحامضية والقاعدية المعالجــــة وأن أيونات الهيدروجين والهيدروكسيل قد أزيلت من هذه المحاليل على الترتيب نتيجـــة عمليات المعالجة ، ووجد أن كمية الايونات المزاله تعتمد على قيمة الاس الهيدروجينـــو، للمحلول المعالج وكمية السرمة المستخدمة فى المعالجة وزمن المعالجة ومثالا على ذلك:

عند معالجة محاليل ذات أس هيدروجينى يساوى ٣ وجد أن زمن التقليب اللازم للوصول الى حالة التعادل هو ٢ ساعة وأن أقصى تغيير فى قيمة الاس الهيدروجينى لكل جرام من السرمه هو ٤, ٢ عند تركيز للسرمة يساوى ١٢ جرام / لتر وتم تطبيق معادلتـــى لانجماير وفريتندلتـــس على عمليات الامتزاز من المحاليل الحامضية،ووجد أن السعه العظمى للسرمة بالنسبة لايونات الهيدروجين والمستنتجة من المعادلتين متطابقة وتســـــاوى ٢ ٥, ٠ مجم / جم

كما أوضحت عمليات معالجة المياه المتعادله أن السرمه تطلق أيونات الهيدروجين بدرجة طفيفه الى الوسط المعالج ،

ABSTRACT

Rice husks (RH), a major agricultural waste by-rpoduct, has been chosen to be employed in several environmental pollution control applications. A survey about RH including production, composition, utilization and usage limitation is given. Due to the known effect of pH on removal processes of many substances from wastewaters, the present work concerns also with studying the effect of RH on the pH of the treated aqueous solutions as well as to investigate the possibility of cations and anions removal from these solutions by adsorption onto RH surface. The obtained results showed that RH considerably changed the pH of the treated acidic and alkaline waters and both hydrogen and hydroxyl ions, which of them existed in excess, were removed from aqueous solutions by RH. Treatment of neutral water with RH revealed also that, the latter slightly released hydrogen ions to the treated solutions.

1-INTRODUCTION

Rice husks are the dry outer envelopes of the rice kernels. They are separated as a by-product during dehulling process at rice mills. The quantity, quality, size, colour, and other apparent properties of RH vary with many different factors such as temperature, season of harvest, type of soil, and method of agriculture. The international annual yield of paddy reaches about 300 million tons and in Egypt the annual yield of paddy reaches about 2.4 million tons. Rice husks represent 16-20 % of the output products of rice milling process [1,2]. So, the annual yield of RH in Egypt is about half million ton. Due to its general characteristics, which will be discussed shortly, RH constitute one of the major waste products of the agricultural industry.

Many investigations have been made to utilize husks[3-7]. Historically, RH has been burnt as a source of energy. Other forms of fuels such as coal, producer gas and liquid fuels may also be obtained from RH by appropriate treatment of the latter, e.g., by burning in a limited amount of air, by thermal decomposition in absense of oxygen, and by suitable chemical, thermochemical and biological treatment. RH is used also in poultry and cattle feeding and ground RH is used as a filling materials in livestock fodder. RH may also be used in building materials to produce products of light weights and insulation properties. In addition, RH may be used as a filling materials in rubber industry and RH ash may be used in some glass industry. Furthermore, RH may be used in production of more valuably products such as silicon carbide and nitride, furfural, active carbon. etc. There are also several other secondary uses of RH. Unfortunately, reports pointed out that utilization of RH in the fields outlined above still economically unsuccessful process. Some literature[8,9] revealed that RH possess some special characteristics that may limit their economical use. These include :

a) Actual RH density is 0.735 g/cm^3 and bulk density is only about 0.13 g/cm^3 which creates great difficulties during withdrawal, transportation, and storage.

b)   RH cannot be stored outdoors in forms of piles because it can
     be easily scattered by air and, in the same time, storage indoors
     needs relatively large chambers which makes this process to
     be very costly.

c)   RH have high content of silica and cellulose in their
     structure which make them very hard. Furthermore, RH have a
     needle shape with very sharp ends and have a very abrasive
     nature. These factors cause high consumption of the tools
     in grinding machines due to rapid wear of their surfaces.

d)   There is a risk in using RH as a fodder in poultry and cattle
     feeding because they have hard tissue and harmful needle
     structure that may irritate the alimentary canal and cause
     dyspepsia[2].

e)   Low content of proteins, vitamins, and valuable minerals make
     them of little nourishing value and limit their use as a
     nutriment. For example, 100 kg of RH has the same nourishing
     value of 2.5 kg of starch.

f)   High ash content, consisting mainly of silica, hinders their
     complete combution in case of direct burning and lowering
     their calorific value. Besides, evolved gases and flying
     ash are considered as air pollutants.

g)   Due to low content of alpha-cellulose (portion of
     holocellulose that is insoluble in strong sodium hydroxide)
     in RH and due to their short fibers, RH, is not suitable
     for paper industry.

     Accordingly, possible uses of RH have been surveyed as an
universal problem [8,9] and as a local one [5]. Therefore,
further attention should be paid to research for new
technological methods that would be most efficient. The sought
methods will be the key to put an end to the care problem of RH
accumulation in rice mills. The authors tried to find some other
useful application of RH [10,11] and several studies have been
conducted to use it in the field of environmental pollution
control.

     RH as a material to be used in environmental pollution
control enjoys a good advantage that it is available in large
quantities at a central collection points. Thus costs of
applications will be very cheap. Among the studied applications
is the use of RH in the treatment of industrial wastewaters
before their discharge into receiving water ways. Due to the
known effect of the pH on the removal processes of many
substances from wastewaters (e.g.,the fractional percent of
different adsorbate species , the extent of hydrolysis of many
ions , the number of available adsorption sites on the adsorbent
surface , etc., are pH dependent) the study is started by
finding the effect of RH on the pH of the treated aqueous
solutions. The study also investigates the possibility of

removal of different cations and anions from the treated solutions by adsorption onto RH surface.

2- EXPERIMENTAL, RESULTS, AND DISCUSSION

2.1. Materials:

Rice husks are obtained from a local mill.   It was washed, dried, ground and sieved. The fraction of grain size 160~500 m was the one used in all conducted experiments.   Stirring was conducted using a home-made stitter, Figure,1, where six mixtures could be stirred at the same time.   Experiments were conducted at room temperature (25 $\pm$ 2 ^{o}C).   The standard deviation in replicate experiments did not exceed $\pm$ 0.1.

2.2. Effect of Initial pH

To determine the effect of initial pH on ΔpH of the treated solutions, the following experiments were carried out. Aliquots of water (100 ml) of known pH (1.0-12.0) were introduced into beakers each contained one gram of RH.   The mixtures were agitated for 2 hours and the final pH of each mixture was measured.   The obtained results are plotted in Figure 2 which indicates that the change of pH value per weight of RH,Δ pH/g, is strongly dependent on the initial pH of the treated solutions. The change was ranged from -2.0 at pH 10 to 2.4 at pH 4.5, under the used experimental conditions.   The increase in the pH value (+ ve ΔpH) in the acidic region (1-6.5) indicates that hydrogen ions were removed from acidic solutions by RH.   In the same time, the decrease in the pH value (-veΔ pH) in the alkaline region (12-7.5) indicates that hydroxyl ions were removed from alkaline solutions by RH.

Figure 3 shows the dependence of the percentage removal of hydrogen and hydroxyl ions per gram of RH on initial pH values of the treated solutions. The figure illustrates that maximum removal occured at pH 4.5 for the hydrogen ions and at pH 10 for hydroxyl ions.

Removal of both hydrogen and hydroxyl ions from equeous solutions indicates that the surface of RH have different groups which are able to react with and adsorb both ions.

2.3. Treatment of Alkaline Solutions :

Figure 2 shows that ΔpH had a zero value when the initial pH of the treated solution was 7.3 under the used experimental conditions.   This leads to the suggestion that hydrogen ions is probably supplied to the treated medium from RH.
To examine the effect of RH on solutions at pH values about neutral (7.0$\pm$0.5), equal volumes of water (100 ml each) at pH 7.3 were agitated with different RH weights (0.5-10g) for 2 hours and

the final pH of each mixture was measured. The mixtures were
covered and left for 24 hours and their pH values were remeasured
again.   The obtained results are plotted in Figure 4.   The drop
in the pH values of different mixtures (curves A and B)
demonstrate that hydrogen ions are released to the solutions from
RH.   Furthermore, the liberated amount of hydrogen ions depends
on contact time. Figure 4 (curves C and D) illustrates also that
for RH concentration greater than 2.5% by weight, the change in
pH values per gram of RH is almost constant specially after 2
hours agitation period.   It is expected that the release of
hydrogen ions from RH will be suppressed in acidic media and
enhanced in alkaline media.

2.4. Treatment of Alkaline Solutions :

     Equal volumes of water at pH 11.0 were treated with
different weights of RH.   The final pH of the mixtures were
measured after agitation for 1 hour and remeasured after 48
hours from agitation.   The obtained results are shown in Figures
5 and 6 which conform the previously obtained results that
hydroxy ions are removed from alkaline solutions when these
solutions are treated with RH.   Figure 5 shows that the final pH
values of te mixtures decrease linearly with the concentration of
RH for the two contact time periods and the value of the pH drop
depends on the contact time period. Figure 6 C and D reveal that
the amounts of the hydroxyl ions removed from the treated
solutions per weight of RH tend to be constant as   the
concentration of RH in these solutions is increased. The removal
of hydroxyl ions from the treated alkaline solutions by RH is
mainly occured by two mechanisms:
a)   Hydroxyl   ions are removed due to the action of different
      adsorption   and chemisorption forces.
b)   Reaction of hydroxl ions with hydrogen ions released by RH
      to the surrounding solutions . The releasement is further
      enhanced   by the alkalinity of the treated medium.
The predomination of one of the two mechanisms will depend on
the solution pH, concentration of RH, and contact time period.

2.5. Treatment of Acidic Solutions :

     Water at pH 3.0 was used to conduct this experimental part.
To find the agitation time necessary to reach equilibrium, a
mixture of RH concentration 10 g/l was stirred and the pH after
different stirring time periods was measured. The relation between
measured pH and the stirring period is given in Figure 7.   The
shape of the curve in Figure 7 indicates that approximately
2 hours stirring period are needed to reach equilibrium.
     The effect of RH weight on the final pH of treated solutions
at pH 3.0 is shown in Figure 5. The shape of the curve in Figure 5
is similar to that obtained in acid-base titration where hydrogen
ions are gradually removed from the titrated solution by the
successive addition of the base to it.   The gradual increase in
the concentrations of RH from one solution to another replaces

the gradual addition of the base. The pH change and the pH
change per gram as function of RH weight are given in Figure 9.
Figure 9B reveales that maximum ΔpH/g is obtained at RH
concentration of 12 g/l under the mentioned experimental
conditions.

Data collected during an adsorption test will describe the
performance of the adsorbent and will yield valuable information
if properly interpreted. The presentation of the ammount of
solute adsorbed per unit weight of adsorbent as a function of the
equilibrium concentration in bulk solution at constant
temperature, is commonly termed the adsorption isotherm. So, the
adsorption isotherm in the present case will be the relation
between the amount of hydrogen ions adsorbed per gram of RH and
the equilibrium concentration of hydrogen ions. However, it is
seen that a more useful and visible isotherm may be obtained by
plotting ΔpH/g as a function of equilibrium pH, Figure 9.
The figure reveals also that maximum change in ΔpH/g occurs at
RH concentration of 12 g/l.

Several mathematical relationships have been developed to
describe the equilibrium distribution of solute between the solid
and liquid phases and thus aid in the interpretation of
adsorption data. Among these relations are those of Langmuir
and Freundlich[12].
The reciprocal of Langmuir equation yields the equation :

$$m/x = (1/b) + (1/ab)(1/C_e)$$

where x is the amount of material adsorbed (mg), m is the weight
of adsorbent (g), C_e the equilibrium concentration of the solute
(mg/l) and a,b are constants. If adsorption follows the
Langmuir, linear trace should result when the quantity (m/x) is
plotted against (1/C_e). Values of constants a and b can be
determined from the slope and intercept of the plot where the
slope is equal (1/ab) and the intercept is equal (1/b).The value
of constant b is important since it represent the maximum or
monolayer adsorption capacity of the adsorbent. The influence of
isotherm shape on whether adsorption is favourable of
unfavourable for Langmuir isotherm , can be classified by a
term " r ". A dimensionless constant, called separation factor.

$$r = 1 / (1 + a C_o)$$

where C_o is the initial adsorbate concentration (mg/l). The
value of r must be less than unity and greater than zero for
favourable adsorption process. The plots of m/x versus 1/C_e gave
straight line, part of the straight line is shown in Figure 10 .
Langmuir parameters have been compouted and are listed in
Table 1. The value of r shows that adsorption of hyderogen ions
is a favourable process.

Table 1. Langmuir Parameters For the Adsorption of Hydrogen
Ions at pH 3.0 on Rice Husks .

intercept (1/b)	slope (1/ab)	correlation coefficient	ab	b (mg/g)	a (1/mg)	r
8.4	0.1	1.0	10	0.12	83.3	0.01

The linear form of Freundlich equation is the following :

$$\log (x/m) = \log k + (1/n) \log C_e$$

where x,m, and C_e have the same meaning as in Langmuir equation
and k and n, are constants characteristic of the system. Values
of constants n and k can be determined from the slope and the
intercept of the plot. From these constants the ultimate
capacity, $k \, C_e^{1/n}$, of the adsorbent for a given adsorbate can be
determined. Plotting log x/m versus log C_e is given in Figure
1. The plot showed some sort of curvature. In such cases,
these results can be better represented by more than one straight
line [13]. The best slope 1/n and intercept, log k , for each
section are obtained by the least squares method. These
parameters as well as the ultimate capacity for each section are
given in Table_2.

Table 2. Freundlich Constants for Adsorption of Hydrogen Ions at
pH 3.0 Onto Rice Husks.

	intercept (log k)	slope (1/n)	correlation coefficient	k (1/mg)	n (g/1)	$k \, C_e^{1/n}$ (mg/g)
first section	-0.92	0.06	1	0.12	16.7	0.12
second section	-0.30	0.27	0.98	0.50	3.7	0.5

The magnitude of the exponent, n, gives an indication of the
favourability and capacity of the adsorbent/adsorbate system. It
is generally stated that values of n greater than one represent
favourable adsorption conditions [13]. Therefore, the adsorption
of hyderogen ions onto RH surface is a favourable process
according to Freundlich interpretation. The maximum or monolayer
adsorption capacity "b" obtained from Langmuir isotherm is 0.12
mg/g which is in a complete agreement with ultimate capacity
obtained from the first section of Freundlich isotherm.

3- CONCLUSION

The performed experiments clearly show that :
1) The   pH   values   of   the   treated   aqueous   solution   were significatly affected by the use of RH.

2) Both hyderogen and hydroxyl ions were removed from acidic and alkaline solutions , respectively , by RH .   The amount of ions   removed   depend on pH of the treated solution, concentration of RH , and contact time period.

3) Treatment of neutral solutions shows that hydrogen ions were released by RH to the treated medium.

4) The application of Langmuir and Freundlich isotherms showed that adsorption of hydrogen ions from acidic media onto RH surface was a favourable process. The Langmuir maximum capacity (b value) and the Freundlich ultimate capacity $(k \ C_o^{1/n})$ for adsorption of hydrogen ions onto RH surface were in agreement and found to be 0.12 mg/g.

5) Experimental results obtained in addition to the availability and the very low price of rice husks make this technique appears promising for wastewater treatment in situations involving acidic or alkaline wastes.

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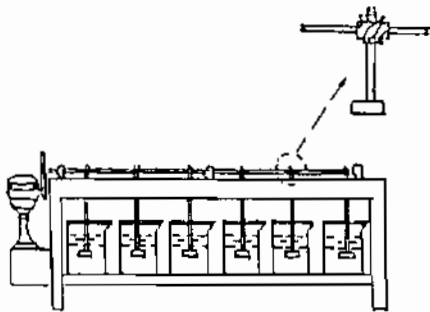
Figure 1- Schematic of the
stirring device.
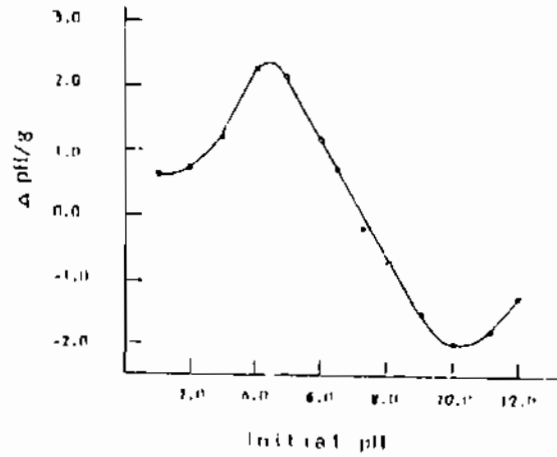
Figure 2 :   Effect of initial pH on pH
change per gram of RH.
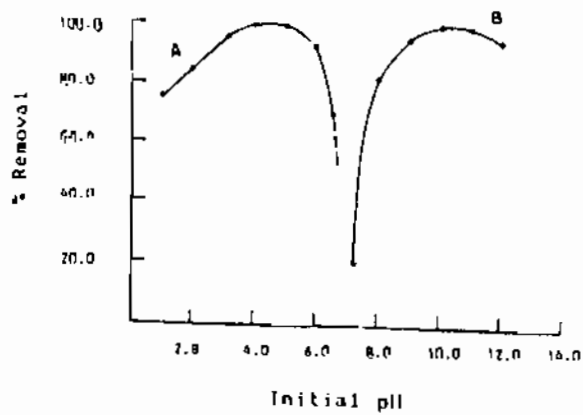
Figure 3 :   Effect of initial pH of the solutions treated by
RH on percent removal of hydrogen ions (Curve A)
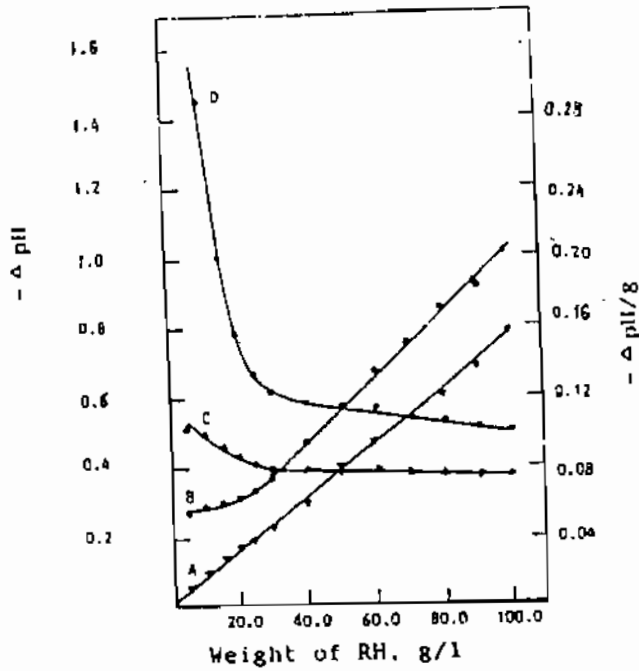and hydroxyl ions (Curve B).

Figure 4 : Effect of RH weight on   pH (Curves A and B)
and Δ pH/g (Curves C and D) ; initial pH of
the treated water is 7.3.
- A and C : After agitation for 2 hours.
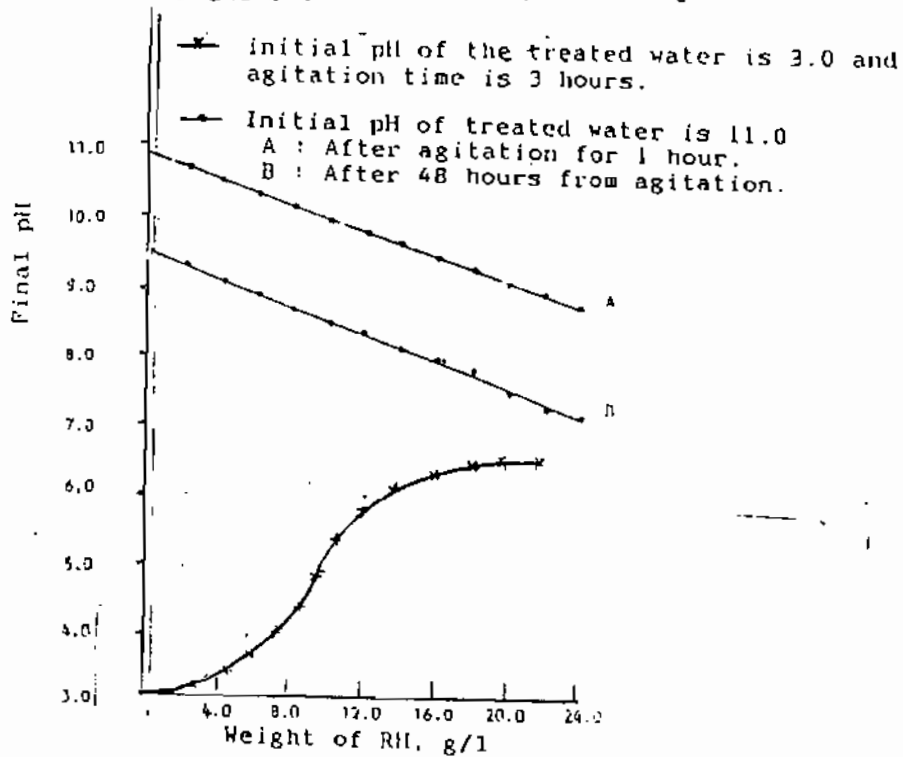- B and D : After 24 hours from agitation.

Figure 5- Relation between final pH of treated water
and weight of RH used in the treatment.
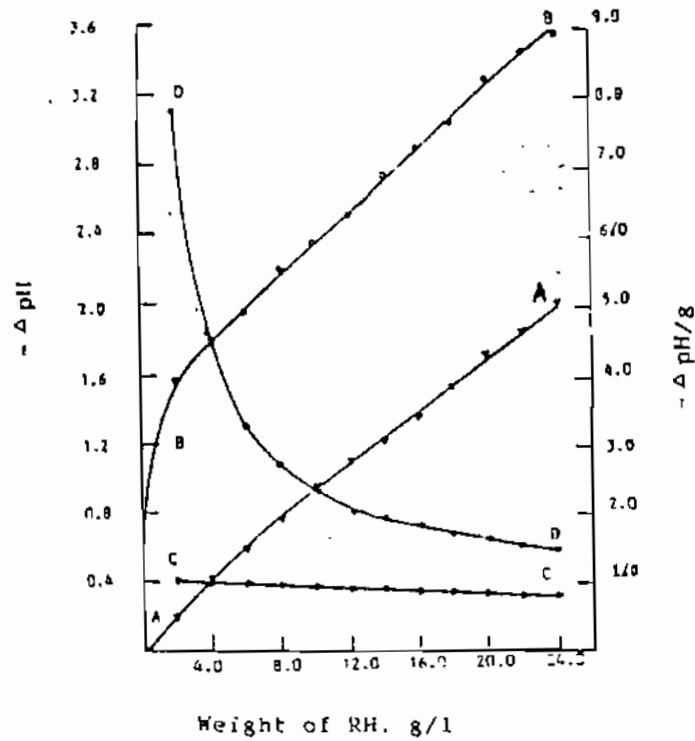
Figure 6- Dependence of pH (Curves A and B) and
Δ pH/g (Curves C and D) on RH weight.
- A and C : After agitation for 2 hours.
- B and D : After 48 hours from agitation.

Initial pH of treated water is 11.0

Initial pH of the treated water is 3
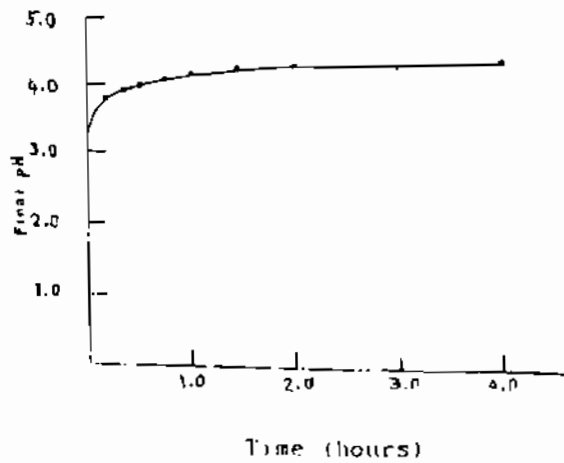
Figure 7- Effect of contact time on the final
pH of water treated with RH.
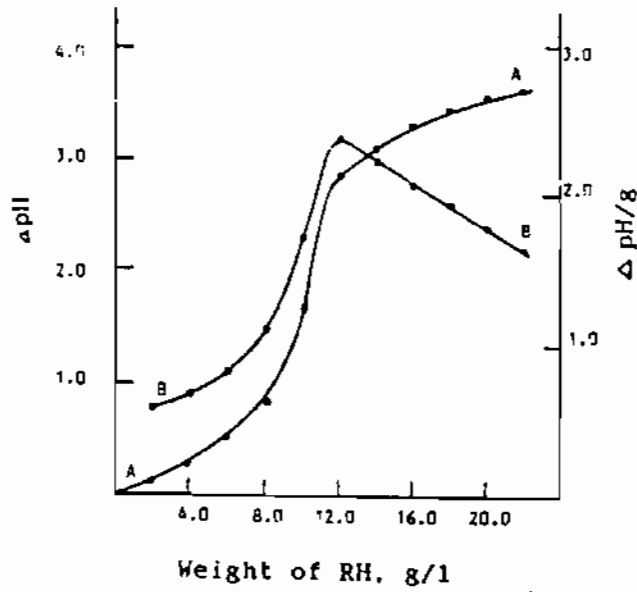
Figure 8- Dependence of ΔpH (Curve A) and ΔpH/g (Curve B)
on the RH weight. Initial pH of the treated
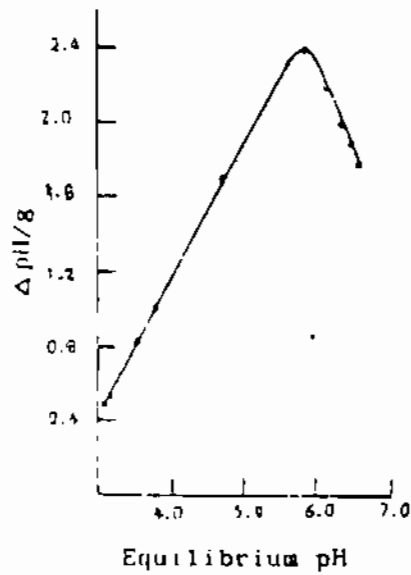water is 3.0 and agitation time is 3 hours.

Figure 9- Relation between ΔpH/g and equilibrium
pH of water treated with RH at 10 g/l ;
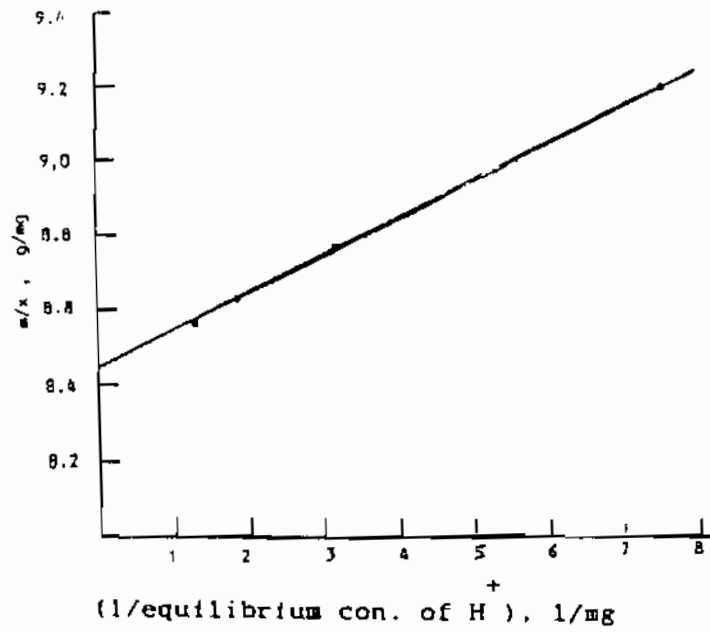initial pH of the treated water is 3.0.

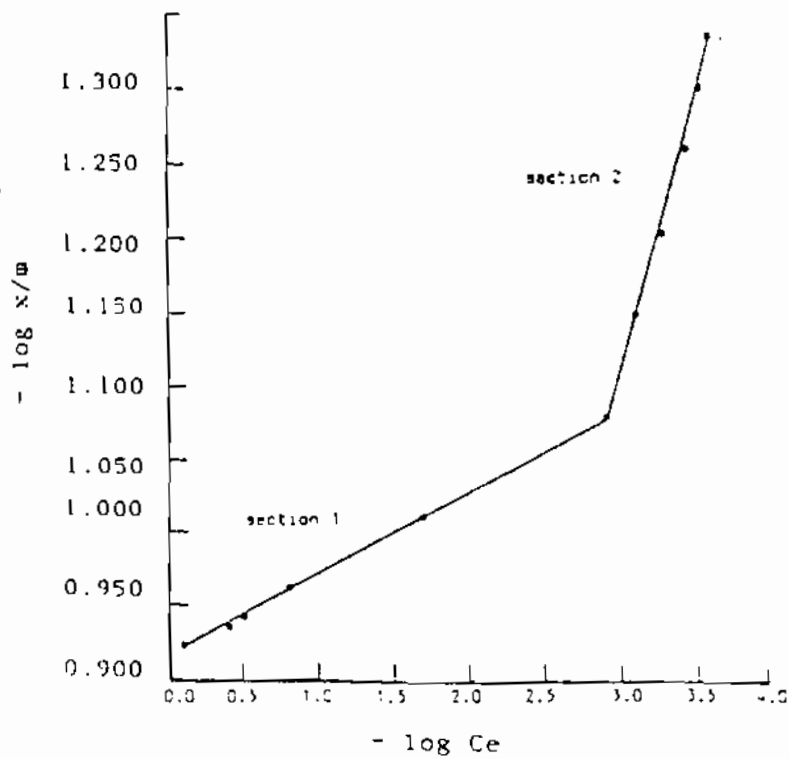Figure 10- Langmuir adsorption isotherm of hydrogen ion on RH.

Figure 11- Freundlich adsorption isotherm of hydrogen ions on RH.