ISSN: 2641-1784

Review Article

Advance in Environmental Waste Management & Recycling

Utilization of Waste Paper to Manufacture of Hydrogels

Michael Ioelovich

Designer Energy Ltd, Israel

***Corresponding author**
Michael Ioelovich, Designer Energy Ltd, 2 Bergman Str, Rehovot 7670504, Israel.

Submitted: 24 Apr 2020; **Accepted:** 30 Apr 2020; **Published:** 05 May 2021

Citation: *Michael Ioelovich (2021) Utilization of Waste Paper to Manufacture of Hydrogels Adv Envi Was Mana Rec, 4 (2):52-55.*

Abstract
Huge volumes of mixed waste paper (MWP) pollute the environment. Nevertheless, it is an abundant, renewable and inexpensive material, so finding a new way of utilization it is very important. In this article, MWP has been used as initial material for the production of hydrogels. It was found that when MWP is treated with a cold solvent, namely with an aqueous solution of 7%NaOH/12%Urea (N/U), at solvent to initial paper ratio $R \geq 5$, complete amorphization of the cellulose component of the paper occurs, as a result of which a hydrogel is formed. In addition, if the alkali of the solvent is neutralized with phosphoric acid, then the resulting hydrogel will contain PN-fertilizer and can be applied in agriculture. Studies have shown that this hydrogel promotes seed germination, increases the water retention of the soil, and then completely decomposes in a short time under the action of enzymes secreted by microorganisms present in the soil.

Keyword: Mixed waste paper, Utilization, Treatment with solvent, Hydrogel, Agricultural application

Introduction

Hydrogels are class of polymeric materials, the hydrophilic structure of which renders them capable of holding large amounts of water in their three-dimensional networks [1, 2]. In fact, they are highly water-swollen polymeric materials. In recent years, hydrogels based on various synthetic and natural polymers have received considerable attention due to their wide range of applications [3,4]. The hydrogels can be used in biomedicine, hygiene, pharmaceutics, food processing, chemistry and physicochemistry, chromatography, water purification, agriculture, soil technology and other areas.

Many publications have discussed details of the use of hydrogels in agriculture and soil technology, such as protectors of plant and seed, water keepers, depots for slow release of fertilizers and agrochemicals, aids for preventing soil erosion, sorbents for soil cleaning from heavy metals, etc. [5-10]. However, the widespread use of hydrogels in agriculture and soil technology is limited by the high cost of hydrogel polymers, their low production volume, and biostability of synthetic polymers polluting the environment. The solution to this problem is search for cheap, available and biodegradable natural materials for the production of hydrogels. Such promising natural-based material can become a waste paper, which contains mainly cellulose and other natural polymers, hemicellulose and lignin.

World pulp and paper industry produces about 300-350 million tons of various types of paper and board [11]. From third to half of the used paper is recycled, but hundred million tons of the residual paper waste is thrown out or landfilled and pollute the environment. Since waste paper is regarded as abundant, renewable and inexpensive material, it is important to find a new way of its utilization, such as the production of hydrogels.

To achieve a swollen state, the starting paper material must be soaked by suitable solvent, followed by regeneration with water. Various solvents can be used: ionic liquids (IL), NMMO, LiCl/DMAA, DMSO/PFA, DMSO/DEA/SO2, o-phosphoric acid, etc. [12-17]. However, these solvents are expensive: the average price of o-phosphoric acid, DMSO, DEA and DMAA is $1.5-2 per kg, NMMO $10-20 per kg and IL $100-150 per kg. The traditional solvents of cellulose-based materials, CS_2/NaOH system and Cuproxam, used in XX century, are currently prohibited due to high toxicity and environmental hazard.

The cheapest solvent for hydrogel production the is probably aqueous solution of 7% NaOH/12% Urea [18, 19] denoted as N/U, which has cost of $0.05 per kg due to low price of commercial chemicals. The problem is that this solvent was previously only used for pure cellulose. Therefore, the purpose of this research was to adapt the N/U solvent for paper materials in order to find the optimal conditions for preparation of hydrogels.

Experimental

Materials and chemicals

Mixed waste paper (MWP), containing waste of paper towels, paper wipes and blotting/absorbing paper (Amnir Recycling, Hadera, Israel), were used as initial material. Sodium hydroxide and urea were supplied from Sigma-Aldrich Co. These chemicals were used to prepare an N/U - solvent, such as aqueous solution containing 7% NaOH and 12% Urea.

Study of chemical composition

The chemical composition of MWP was determined by conventional method of chemical analysis [20].

Preparation of hydrogel samples

The initial material was cut into 10-15 mm pieces and placed in a glass beaker cooled with ice/salt mixture having temperature of -15°C. Then, a cold N/U - solvent was added at the ratio of the solvent to paper material (R) from 3 to 10 (v/w) while periodically stirred for 1 h, and after which left in a freezer at -15°C for 5 h.

The solvent-treated samples aimed for structural investigations, swelling and water retention were washed with tap water, neutralized with 1% sulfuric acid to pH 7, washed with distilled water and finally frieze-dried. Other hydrogel samples intended for study of germination index and biodegradation was prepared as follows. The solvent-treated samples were neutralized with 50% o-phosphoric acid to pH 7. The unabsorbed excess of aqueous phase was removed by vacuum filtration. As a result, hydrogel samples containing PN –fertilizer were obtained

Wide-angle X-ray scattering (WAXS)

Structural state of the cellulose component in samples was studied by WAXS-method using Rigaku-Ultima Plus diffractometer (CuK_α–radiation, λ=0.15418 nm [21]. The X-ray diffractograms were recorded in the range of 2θ angle from 5 to 50°. For WAXS experiments, the freeze-dry samples of the equal mass were pressed into tablets. The incoherent background was subtracted from the diffractograms, whereas intensities of the peaks were corrected and normalized. Then, the total integrated intensity (area) of the corrected diffractogram is separated into areas of crystalline and non-crystalline scatterings. The degree of crystallinity (X) is calculated, as follows:

$$X = \int(Jc\, d\varphi) / \int (Jo\, d\varphi) \quad (1)$$

The degree of amorphicity (Y) can be also found:

$$Y = 1 - X \quad (2)$$

where J_c and J_o are the corrected and normalized intensities of X-ray diffraction from crystallites only and whole sample, respectively; $\varphi = 2\theta^o$.

Swelling value

The freeze-dried samples (1 g) were placed into tea bags and then immersed in distilled water at 25°C for 5 days. The swelling value was measured by weighing the freeze-dried samples before and after immersion in distilled water. The excess of water was absorbed from surface of the tea bag by clean and soft paper tissues. The swelling value (SW) was calculated, as follows:

$$SW = 100\% (W_s - W_d)/W_d \quad (3)$$

where W_s is weight of the swollen hydrogel and W_d is weight of the freeze-dried sample.

Water retention

The water retention was measured using the sandy soil. Freeze-dried hydrogel samples (5 g) were thoroughly mixed with 50 g of dry soil and the mixture was placed in a plastic container (15 cm in diameter). Then, 100 mL of deionized water was added into the container, and the weight of filled container was controlled within the 60-day test period. The value of water retention was calculated according to the following equation [10]:

$$WR = 100\% (W_t - W_s)/(W_o - W_s) \quad (4)$$

where Wt is weight of container with wet soil and swollen sample at time t; W_o is weight of container with wet soil and dry sample at time zero; Ws is weight of container with dry soil.

Germination index

Seeds of cucumber were placed in Petri dishes (15 seeds per dish). Dishes were filled with 10 mL of distilled water (control) or with hydrogels containing PN-fertilizer additionally wetted with water. Dishes were placed in a growth chamber at 25°C for 72 h in dark conditions [22]. Six replications were carried out for each hydrogel sample to obtain an average value of germination index (GI). The GI was determined using the following simplified equation:

$$GI = 100\% (N/N_o) \quad (5)$$

where N is number of germinated seeds in presence of hydrogel; No is number of germinated seeds in control experiment.

Biodegradation test

The soil contains numerous microorganisms that secrete enzymes destroying cellulose and other biopolymers of paper or board [23]. These enzymes are isolated from microorganisms for use them in scientific research and biotechnology. In this work, the commercial enzyme preparation CTec-3 (Novozymes A/S, Bagsvaerd, Denmark) was used to study the biodegradation of hydrogels samples. The dose of enzyme in relation to solid sample was 1-3%. Enzymatic hydrolysis of the samples was carried out in 50-mL polypropylene tubes. The hydrogel samples containing 1 g of solid matter were put into tubes, and the needed amount of the enzyme was added. Then, acetate buffer (pH =4.8) was supplemented to obtain concentration of the substrate (C_o) 50 g/L. The tubes closed with covers were placed in a shaker incubator at 50°C and shaken for various times. Finally, the residue was separated from liquid phase by centrifugation at 4,000 rpm for 10 min, washed with distilled water to pH=7, rinsed with ethanol and dried at 60°C to constant weight. The weight loss (WL) of the sample during hydrolysis was calculated, as follows:

$$WL = 100\% (W_o - W_t)/W_o \quad (6)$$

where W_t and W_o is dry weight of the hydrolyzed and initial sample, respectively.

Results and discussion

Chemical analysis showed that initial MWP sample contains 81% cellulose, 6% hemicelluloses, 4% lignin and 9% of other components (starch, inorganic substances, etc.). Cellulose component of MWP is typical crystalline allomorph of CI having crystalline peaks at 2θ angle of 15-16° and 22.5° (Figure 1, diffractogram 1). Crystallinity degree of this sample is evaluated to be 0.56 and amorphicity degree to 0.44, respectively. After treatment the initial MWP sample with N/U-solvent at R =3, the CI allomorph is transformed into CII allomorph with a low crystallinity degree of about 0.20. However, when the initial sample is treated with the N/U-solvent at R ≥ 5, a completely amorphous material is formed, with a broad diffuse X-ray scattering and maximum at 2θ angle of 19-20° (Figure 1, diffractogram 3).

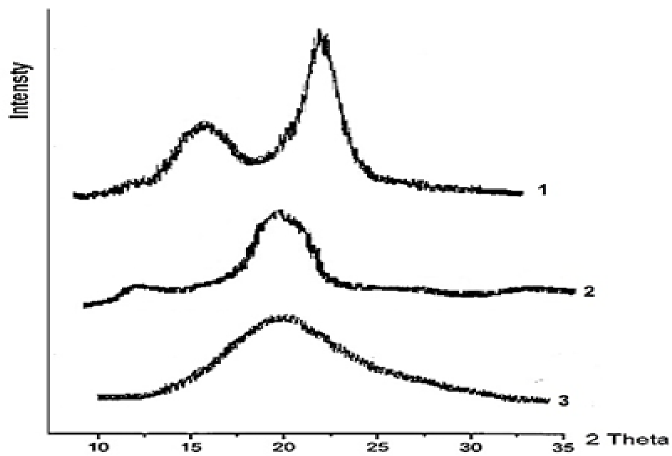

Figure 1: X-ray diffractograms of initial MWP (1) and solvent-treated samples at R=3 (2) and R=5 (3)

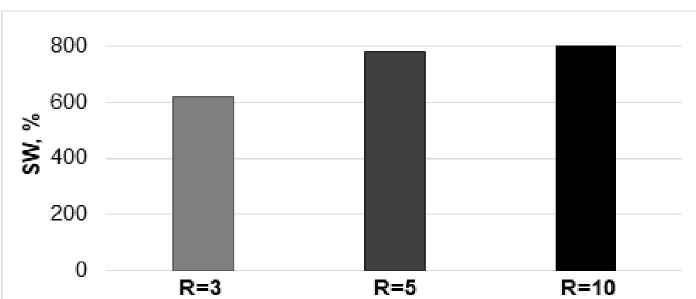

Figure 2: Swelling value of solvent-treated samples at different R-values

After immersion of the obtained samples in water, the swelling value reaches 600-800%, and this value for complete amorphous samples is the highest (Figure 2).

If the soil contains an additive of hydrogel with amorphous structure, then its water retention is significantly improved (Figure 3), which allows to reduce the frequency of watering the soil when growing cultivated plants, and thereby save valuable water resources.

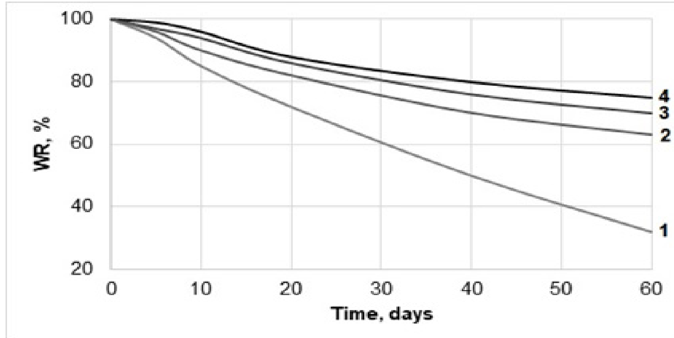

Figure 3: Kinetics of water retention only for soil (1) and for soil with the additive of hydrogel obtained at R = 3 (2), R = 5 (3) and R = 10 (4)

Hydrogels containing PN-fertilizer also help to increase the seed germination (Figure 4).

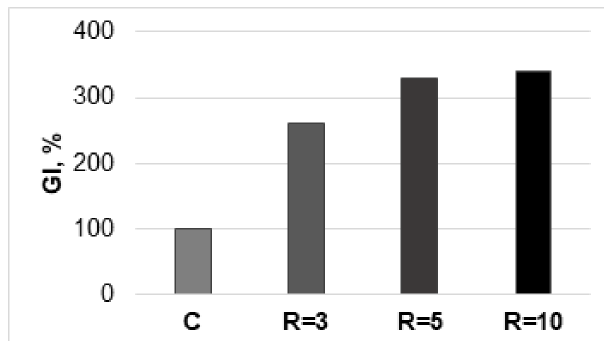

Figure 4: Index of seed germination for control conditions (C) and for hydrogel obtained at different R-values

As follows from the biodegradability test, the sample of amorphous hydrogel is degraded within five days with a relatively small dose of enzyme such as 1%. If the dose of enzyme is increased to 3%, then the amorphous hydrogel completely decomposes even in two days (Figure 4).

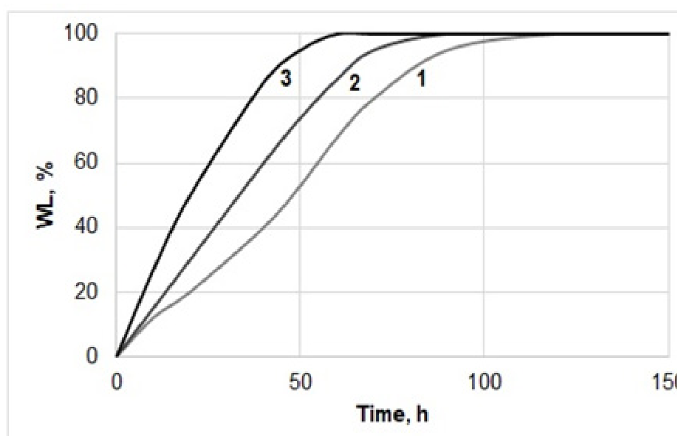

Figure 5: Decomposition kinetics of hydrogel sample obtained at R=5 using enzyme dose of 1% (1), 2% (2) and 3% (3)

Conclusions

In this article, mixed paper waste (MWP) was utilized as initial material for the production of hydrogels. For this purpose, this paper material was treated with a cold solvent, namely with an aqueous solution of 7%NaOH/12%Urea (N/U), at solvent to initial material ratio R of 3 to 10. It was found that when MWP is treated with N/U-solvent at ratio R ≥ 5, complete amorphization of the cellulose component of the paper occurs, as a result of which a hydrogel is formed. Moreover, if the alkali of the solvent is neutralized with phosphoric acid, then the resulting hydrogel will contain PN-fertilizer and can be applied in agriculture. Studies have shown that this hydrogel promotes seed germination, increases the water retention of the soil, and then completely decomposes in a short time under the action of enzymes secreted by microorganisms present in the soil. The increase of water retention of soil containing hydrogel additive allows to reduce the frequency of watering the soil when growing cultivated plants, and thereby save valuable water resources. The biodegradability test indicated that the sample of amorphous hydrogel is degraded within five days with a relatively small dose of enzyme such as 1%. If the dose of enzyme is increased to 3%, then the amorphous hydrogel completely decomposes even in two days

References

1. Ahmed EM, Aggor FS, Awad AM, El Aref AT (2013) An innovative method for preparation of nanometal hydroxide superabsorbent hydrogel. Carbohydrate Polym 91: 693-698.
2. Buchholz FL, Graham AT (1998) Modern superabsorbent polymer technology. New York: Wiley- VCH.
3. Yuhui L, Guoyou H, Xiaohui Z (2013) Magnetic hydrogels and their potential biomedical applications. Adv Funct Mater 23: 660-672.
4. Ahmed EM (2015) Hydrogel: preparation, characterization, and applications: a review. J Adv Res 6: 105-121.
5. Raju KM, Raju MP (2001) Synthesis of novel superabsorbing copo lymers for agricultural and horticultural applications. Polym Int 50: 946-951.
6. Shaviv A (2000) Advances in controlled release of fertilizers. Adv in Agronomy 71: 1-49.
7. Davidson DW, Verma MS, Gu FX (2013) Controlled root targeted delivery of fertilizer using an ionically crosslinked carboxymethyl cellulose hydrogel matrix. Springer Plus 2: 1-9.
8. Demitri C, Scalera F, Madaghiele M (2013) Potential of cellulose-based superabsorbent hydrogels as water reservoir in agriculture. Int J Polym Sci, 1-6.
9. Song Z, Liu J, Bai Y (2019) Laboratory and field experiments on the effect of vinyl acetate polymer-reinforced soil. Appl Sci 9: 1-15.
10. Liu S, Wu Q, Sun X (2021) Novel alginate-cellulose nanofiber-poly(vinyl alcohol) hydrogels for carrying and delivering nitrogen, phosphorus and potassium chemicals. Int J Biol Macromolec 172: 330-340.
11. Ioelovich M (2014) Waste paper as promising feedstock for production of biofuel. J Sci Res Report 3: 905-916.
12. Anantharam PD, Sasidhar V, Constange AS (2006) Enhancement of cellulose saccharification kinetics using an ionic liquid pretreatment step. Biotechnol Bioeng 95: 904-910.
13. Roseneau T, Potthast A, Sixta H, Kosma P (2001) The chemistry of side reactions and by-product formation in the system NMMO/cellulose (Lyocell process). Prog Polym Sci 26: 1763-1837.
14. Schroder LR, Gentile VM, Attala RH (1985) Non-degradative preparation of amorphous cellulose. IPC technical paper series, No 152. The Institute of Paper Chemistry: Appleton.
15. Ciolacu D, Ciolacu F, Popa VI (2011) Amorphous cellulose structure and characterization. Cellular Chem Technol 45: 13-21.
16. Zhang Ch, Liu R, Xiang J (2014) Dissolution mechanism of cellulose in N,N-Dimethylacetamide/Lithium Chloride: revisiting through molecular interactions. J Phys Chem, B, 118: 9507-9514.
17. Zhang YHP, Cui J, Lynd LR., Kuang LR (2006) A transition from cellulose swelling to cellulose dissolution by o-phosphoric acid: Evidence from enzymatic hydrolysis and supramolecular structure. Bio macromolecules 7: 644-648.
18. Egal M, Budtova T, Navard P (2008) The dissolution of microcrystalline cellulose in sodium hydroxide-urea aqueous solutions. Cellulose 15: 361-370.
19. Duchemin B, Le Corre D, Leray N (2016) All-cellulose composites based on microfibrillated cellulose and filter paper via a NaOH-Urea solvent system. Cellulose 23: 593-609.
20. Sluiter JB, Ruiz RO, Scarlata CJ, Sluiter AD, Templeton DW, et al. (2010) Compositional analysis of lignocellulosic feedstocks. Review and description of methods. J Agric Food Chem 58: 9043-9053.
21. Ioelovich M (2016) Models of supramolecular structure and properties of cellulose. J Polym Sci, A, 58: 925-943.
22. Montesano FF, Parente A, Santamaria P (2015) Biodegradable superabsorbent hydrogel increaseswater retention properties of growing media and plant growth. Agriculture and Agriculture Sci Proced 4: 451- 458.
23. Avellaneda Torres LM, Pulido CPG, Rojas ET (2014) Assessment of cellulolytic microorganisms in soils of Nevados Park. Colombia Braz J Microbiol 45:1211-1220.