

Applications of Hydrogel/Zelite Composites : A Review

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Abstract: *The role of Hydrogel/Zelite composites, synthesized for various applications, specifically dye removal from waste water, controlled fertilizer release and transdermal drug delivery system, has been discussed in this review. The importance of zeolites and the role of hydrogels in these applications, owing to specific chemical and structural properties, have also been compiled. Based on the extensive research work and literature available, it has been observed that hydrogels are preferred over other adsorbents, due to their exceptional water retention ability, while the zeolites function as carriers or absorbers of ions. These composites have been used for slow and prolonged chemical release, selective absorption and enhanced water retention capacity of hydrogels. A synergistic effect of the chemical and physical properties of hydrogels and zeolites are put to widespread use in the chemical and medical sectors, which have been discussed in detail. This work also presents an evaluation of various factors that influence the functioning and end properties of the Hydrogel/Zelite composites.*

Keywords: Hydrogel, Zeolite, Composite, Adsorption, Absorption

1. Introduction:

Since the birth of Nano-sciences, a competitive study based on its applications has emerged. Polymeric composites: A subset of Nano-sciences has led to numerous inventions in this field. Discovery of Hydrogel/Zelite composites (H/Z) has unveiled a possibility of specialized functions with tremendous potential in chemical and medical sectors.

Owing to their structure and chemical composition, H/Z have unique properties which render them fit for specific applications. Hydrogels are three dimensional networks which swell extensively due to their ability to absorb and retain water without dissolution [1]. The functional property of hydrogels is observed due to their special and complex network, which are highly stable, chemically as well as physically [2]. These hydrogels are modified by insertion of functional groups, as well as enhancing their sensitivity to change in stimuli, externally. Additionally, complete regeneration, without a significant drop in adsorption capacity is observed due to the reversibility of the process of adsorption [3]. The functional groups present in the hydrogel network open up during swelling and thus make internal active sites available to the molecules being adsorbed [2]. Zeolites on the other hand, are crystalline

aluminosilicates with a three-dimensional structure containing pores to trap cations, water molecules and smaller organic molecules.

They are used in exchange of ions, catalysis as well as adsorption processes due to uniform pre-size distribution, selectivity and chemical and physical stability [2,4].

This review studies the role of various composites developed by varying types of Hydrogel polymers and Zeolites for their application in waste water treatment, drug delivery and in the agro industry.

2. Applications:

2.1 Waste water treatment:

Hydrogel/zeolite composites find widespread application in waste water treatment for removal of dyes, which are a matter of environmental concern, due to the toxicity of most dyes. Adsorption is known to play a pivotal role in industrial waste water treatment, owing to low-cost and innovations. V.V. Panic & S. J. Velickovic, in their work synthesized composites based on poly(methacrylic acid) (PMAA) and hydrophilic zeolite A as well as hydrophobic zeolite ZSM-5, for uptake and removal of cationic dye, basic yellow, called as BY28. In a zeolite structure, SiO_4 and AlO_4 tetrahedra are connected by oxygen atoms. The maximum possible amount of the tetrahedral structure of aluminosilicate as well as highest number of sites for exchange of cations are provided by a Si/Al molar ratio of approximately 1, in the case of zeolite A. This results in maximum number of cations, as well as the capacity to exchange ions. Whereas zeolite ZSM-5 has a large number of Si-O-Si groups, which are hydrophobic. Additionally, in case of the latter, a molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ of approximately 90 was preferred. These ratios and material were therefore made use of, in synthesis of the composite by the authors, thus providing an environment friendly solution [2].

In the work, PMAA/ zeolite A, as well as, PMAA/ zeolite ZSM-5 composites were synthesized with a zeolite loading of 15wt% and 30wt%. The method followed was free-radical polymerization, followed by crosslinking at a temperature of 80°C, in aqueous medium [2,5]. The variation in behavior of the four afore mentioned samples were studied. The effect of concentration of zeolite incorporation on the composite properties superseded the effect of zeolite type. An increase in storage modulus of 3-22 times was observed in the compo-

sites, thus implying higher stability under shear force, thereby rendering it more suitable for adsorption, when compared to PMAA. Swelling of material, when in contact with liquids, is an important property because, it affects the expansion of network within the composite and also the porosity [2]. A 10% reduction in the degree of swelling at equilibrium (SD_{eq}) was observed in the composites, as compared to pure PMAA. The strong interactions within the composites was known to be the cause for the same [2]. In distilled water, the PMAA/hydrophilic zeolite A, with 15wt% loading of zeolite (PMAA/15A) was found to have a lower value of SD_{eq} , as compared to PMAA/hydrophobic zeolite ZSM-5, with zeolite loading 15wt% (PMAA/15Z). The interaction density between the PMAA network and zeolite lattice affects the behavior of the composite [2,6]. It was also observed that in acidic media, the extent of swelling was negligible, while in case of basic media, the swelling was lower than that in distilled water. The reason for the former was stated to be the protonation of the existing carboxylic groups, whereas the latter was observed due to interaction of material with the buffer ions that existed in the solution [2].

Additionally, zeolite A, owing to its structure, possesses higher number of active sites, capable of interacting with carboxylate and carboxylic groups, as compared to ZSM-5, which has very low surface -OH groups but is rich in silica. Thus, PMAA/15A has higher strength of crosslinking, physically and the extent of swelling is also lesser, as compared to PMAA/15Z. The authors observed that the hydrophobic nature of ZSM-5 zeolite was lost at higher concentration, which was attributed to restricted movement of polymer chain in the proximity of zeolite particles, beyond a specific critical concentration. The space in composite pores are occupied by these particles, thus lowering the penetration of water [2,6,7].

Thus, in accordance with the trends in various parameters, the hydrogel/zeolite composites were used to adsorb cationic dye BY28 thus aiding their removal from waste water [2]. The composites, therefore, function by adsorbing the dye, followed by cation exchange.

Similar to the above work, A. Almasian *et al.* synthesized poly(acrylic acid)/zeolite composite adsorbents for removal of cationic dyes Basic Red 46 (BR46) and Basic Blue 41 (BB41), with ammonium persulfate (APS) as the initiator for polymerization [8]. Pollutants can be removed by increasing the adsorption capacity of inorganic particles by polymerizing different monomers onto them [9]. Poly(acrylic acid) is known to be a super absorbent polymer and is capable of adsorbing dyes, in large amounts [10-12]. The zeolite functioned as the inorganic substrate, while the acrylic acid (AA) monomer was used as adsorbent to form a nano adsorbent [8].

The composites were prepared by dispersing 2g of zeolite in distilled water with 70% Cetyl trimethyl ammonium bromide (CTAB) and 10% sodium chloride, followed by stirring for 3hours at 80°C, centrifuged and washed with distilled water several times [8]. The paste was dried at 50°C [13-15]. Various amounts of AA and APS were added to the zeolite at various stirring times at a temperature of 70°C. In the final stage, the samples were centrifuged and washed by continuous agitation/centrifugation with distilled water, followed by drying at 60°C [8].

The maximum wavelengths for determination of remnant concentrations of BR46 and BB41, in the solution were 530nm and 590nm, respectively, using UV-visible spectrophotometry.

The extent and possibility of interaction between the dye molecules and the composite particles depend on the number and type of adsorption sites in the solution [8,16]. It was observed that the adsorption process, though rapid initially, slowed down and ultimately reached equilibrium stage.

The authors of the work reasoned that the initial phenomenon was due to the large number of vacant sites available for adsorption of the dyes and interaction with them [8,17]. But further on, the adsorption rate decreased due to the adsorption sites becoming saturated and a drop in the dye concentration. It was further observed that as the adsorbent dosage increased, though there was an increase in the adsorption percentage, a decrease in the adsorption capacity was seen. The increase in adsorption percentage was due to the increase in availability of adsorption sites, while a drop in the adsorption capacity was due to some adsorption sites remaining unsaturated during the process. The studies carried out with various adsorbent dosages led to 0.005g of adsorbent being chosen as the optimum value for adsorption of both dyes.

Thus, incorporation of acrylic acid on the zeolite was found to significantly improve the adsorption capacity of the composites, for both the dyes.

2.2 Transdermal Drug Delivery:

Transdermal Drug Delivery System (TDDS) is a method used to administer a drug through skin at a controlled rate into the blood stream. The difficulties in issuing TDDS include hindered drug diffusion due to the drug size and lipophilic nature of the skin which is inapt for delivering an ionic or hydrophilic drug [18-20]. Nophawan Paradee *et al.* [21], developed a Hydrogel/Zeolite composite as a drug carrier/matrix for TDDS via electrophoresis which enabled encapsulation and release of an ionic drug in a controlled fashion. The use of

zeolites for entrapping and releasing drugs is renowned (e.g. mitoxantrone [22], ibuprofen [23], 5-fluorouracil [24,23] and sulfonamide antibiotics [25,26]) however, its application in controlled drug delivery (CDD) in a powdered form is limited due to aggregation of its particles. Hence a composite of Zeolite and Hydrogel matrix makes Zeolites viable. Nophawan Paradee *et al.*, fabricated H/Z with Sodium Alginate hydrogel and Zeolite Y. They studied the effect of Si/Al ratio in Zeolite, Mesh size and electric field on the release of a model cationic drug: Folic acid.

The composite was prepared by initially loading the Zeolite with Folic acid followed by incorporation of the loaded zeolite powder into the reaction mixture of Na-Alg hydrogel before cross-linking. Further, CaCl_2 was added as a cross-linker in various proportions. The solution was cast into a nearly 0.3mm film within 48 hours. The H/Z nano composite was labelled as FAY/Alg hydrogel.

Folic Acid release characteristics were studied using a modified Franz-diffusion cell. Modified Franz-diffusion cell contains two chambers: Donor and Receptor. The receptor chamber was charged with a buffer solution (pH 5.5) at 37°C, and was kept in a circulated water jacket. Above the receptor chamber, the loaded H/Z composite was placed over a nylon mesh. The buffer solution was stirred during the experiment for 48hrs. Electric field was applied by placing an aluminum electrode connected to a battery on surface of the hydrogel. To check the amount of FA released into the buffer solution, 0.1ml of sample was taken out from receptor chamber and equal amount of fresh buffer solution was added.

The effect of increase in Si/Al ratio was studied and it was observed that the decrease in aluminum content resulted in weaker H-bonding of Zeolite hydroxyl group with FA molecules. This in turn led to lesser loading of FA into the Zeolite moieties. As for the electric conductivity, it decreased with a lower value of Si/Al ratio. This was due the increased FA content in loaded zeolites which retarded the electron mobility. A summary of results is given in Table 1. The amount of drug released into the buffer solution was governed by the Aluminum content. With stronger H-bonding, the ease of drug diffusion decreased as aluminum content increased hence with an increasing Si/Al ratio, FA release enhanced [24,27].

Table 1. Change in pore volume and electrical conductivity vs. Si/Al ratio [3].

Si/Al ratio	Pore volume (cm^3/g)		Electrical conductivity of Loaded H/Z (S/cm)
	Unloaded H/Z	Loaded H/Z	
5.1	0.394±0.01	0.300±0.01	8.57×10^{-5}
30	0.544±0.01	0.500±0.02	8.79×10^{-5}
60	0.562±0.03	0.547±0.03	8.96×10^{-5}

The incorporation of Zeolite into Hydrogel also reduced its mesh size (MS) as the zeolite particles occupied the voids resulting in reduced absorption ability of hydrogel [28]. MS was known to decrease with an increasing cross-linking ratio (Ratio of moles cross linker to moles of uronic acid monomer units) which again led to lowered swelling ability.

The FA content release was found to vary inversely with the cross-linking ratio with was attributed to the decrease in MS and ultimately a further restricted pathway for the drug [29]. The drug was diffused through the skin via electrophoresis. While the anode, the positively charged electrode was placed onto the hydrogel, the FA cations repelled the electric field and were introduced to the receptor chamber [30,31]. As the electric field was gradually increased the diffusion coefficient (D) of FA from Loaded H/Z was found to rise.

The sole purpose of encapsulating FA in zeolite and making a H/Z composite was to enable slow and prolonged release of the drug. Without applying electric field drug diffusion occurred due to ion exchange. Applying electric field improved D of FA and allowed timely application of the drug thus preventing the risk of before time administration.

2.3 Fertilizer release:

Fertilizers have become an inevitable requirement in the Agro industries [32]. Slow release fertilizers (SRFs) are used to consistently provide nutrients to the plants which coincides with its nutrient requirement hence decreasing loss of nutrient potency. Azam Rashidzadeh *et al.* [33], developed a Hydrogel/Zeolite composite for controlled release of a water-soluble fertilizer. The reason was ascribed to a low cost of production, ability of hydrogels to retain water and slow release of the fertilizers [34-36]. Clinoptilolite with Sodium Alginate Hydrogel composed the required H/Z composite.

Dried composite was used to coat (NPK) fertilizer. Studies were based water retention ability of the soil with the composite, water absorbency by H/Z and NPK coated with H/Z and Fertilizer release.

NPK coated with Hydrogel/Zeolite composites were prepared by placing fabricated dried H/Z composite samples in a pan

containing NPK fertilizer. Distilled water was sprinkled onto the pan and immediately shaken to provide a uniform coating of H/Z composite on NPK. Finally, the core-shell composite obtained was dried in a 70°C oven overnight to achieve the final product: Hyd/CL/NPK [33].

2.3.1 Water absorption studies:

It was found that water retaining ability of core-shell composite was lower as compared to Hydrogel/Clinoptilolite. Hyd/CL/NPK achieved equilibrium in 8hrs with 22.4g/g as water absorption capacity where as Hyd/Clinoptilolite composite achieved it after 60hrs with 34g/g equilibrium water absorbency. This trend was explained by the repulsive nature between COO- groups and the negatively charged surface of Clinoptilolite which expanded the hydrogels 3D network and hence increased water retaining volume of the composite.

A higher water retention in soil was observed once it was mixed with Hyd/CL/NPK thus proving the potential it holds in saving water for plant growth. Water retention capacity with Hyd/CL/NPK and without Hydrogel reached 69.42% and 53.27% within 15 days of study.

A comparison study between direct use of NPK fertilizer, Hyd/CL/NPK in water and Hyd/Clinoptilolite in soil was also made. The release of entire NPK into the soil was acquired just within 20 days on study whereas a reduced rate of release was displayed by Hyd/CL/NPK.

Even after 60 days, the percent of fertilizer released into water and soil was undetermined. The reason for such behavior was credited to the solubility of NPK in water and the structure of Hyd/CL/NPK. NPK being soluble in water, the nutrients easily seeped into the soil sample.

As for the release characteristics of Hyd/CL/NPK in water and soil, the water when absorbed by Hydrogel in the composite in large amounts slowly enters the fertilizer boundary, it dissolves the fertilizer and is slowly released out to the medium. Over other granular fertilizers, this method of fertilizer release displays numerous advantages. Along with a slow release system and reduced loss of fertilizer, it aids to the water retention of soil hence optimizing the water usage. Above all, since the

material of hydrogel composite is Sodium-alginate which is biodegradable and Clinoptilolite which is again a natural mineral, the entire system is soil friendly. There is no accumulation of non-biodegradable polymers in soil hence no damage This makes it an apt choice for sustainable agriculture.

to its structure or quality. This makes it an apt choice for sustainable agriculture.

The following table (Table 2) summarizes the applications covered in this study.

Table 2. Applications of Hydrogel/Zeolite composites. [2,8,21,33]

S. No	Appli- cation	Type of Hydro- gel	Type of Zeolite	Role of composite in the given application
1.	Dye (BY28)	Poly(methacrylic acid)	ZSM-5, Zeolite A	Adsorption and cation exchange
2.	Dye (BR46, BB41)	Poly (acrylic acid)	Zeolite 4A	Improved adsorption capacity and easy cation exchange
3.	TDDS	Sodium Alginate	Zeolite Y	Controlled drug delivery, in presence of electric field.
4.	Fertilizer	Sodium Alginate	Clinoptilolite	Controlled release of fertilizer and improved water retention.

Conclusion: The role of Hydrogel/Zeolite composites in waste water treatment, drug delivery and agriculture was reviewed in this study. It was observed that the adsorption of dyes from waste water was enhanced by usage of Hydrogel/zeolite composites. Poly(methacrylic acid)/zeolite A as well as ZSM-5 were used for uptake of dye BY28 and showed improved adsorption properties, functioning via adsorption and cation exchange. Similarly, a composite of Poly(acrylic acid)/zeolite 4A was used for removal of BR46 and BB41. The adsorption rate increased with increase in adsorbent dosage but saturated beyond a specific critical concentration. Thus, the optimal adsorbent dosage was fixed at 0.005g, for both the dyes. In case of drug delivery, slow and prolonged release of folic acid was achieved by transdermal drug delivery via electrophoresis. Use of Hydrogel/Zeolite composite to coat fertilizer NPK also proved to be beneficial for slow release of fertilizer and water retention of soil.

References:

- i. Ahmed EM. Hydrogel: Preparation, characterization, and applications: A review. *Journal of advanced research*. 2015 Mar 1;6(2):105-21.
- a. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.jare.2013.07.006>
- ii. Panic VV, Velickovic SJ. Removal of model cationic dye by adsorption onto poly (methacrylic acid)/zeolite hydrogel composites: kinetics, equilibrium study and image analysis. *Separation and Purification Technology*. 2014 Feb 10;122:384-94.
- a. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.seppur.2013.11.025>
- iii. Pan B, Pan B, Zhang W, Lv L, Zhang Q, Zheng S. Development of polymeric and polymer-based hybrid adsorbents for pollutants removal from waters. *Chemical Engineering Journal*. 2009 Aug 15;151(1-3):19-29.
- a. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.cej.2009.02.036>
- iv. Davis ME. Ordered porous materials for emerging applications. *Nature*. 2002 Jun;417(6891):813.
- a. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1038%2Fnature00785>
- v. Panic V, Adnadjevic B, Velickovic S, Jovanovic J. The effects of the synthesis parameters on the xerogels structures and on the swelling parameters of the poly (methacrylic acid) hydrogels. *Chemical Engineering Journal*. 2010 Jan 1;156(1):206-14.
- a. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.cej.2009.10.040>
- vi. Adnadjevic B, Jovanovic J. Investigation of the effects of NAA-type zeolite on PDMS composites. *Journal of applied polymer science*. 2000 Aug 8;77(6):1171-6.
- a. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1002%2F1097-4628%2820000808%2977%3A6%3C1171%3A%3Aaid-app1%3E3.0.co%3B2-c++>
- vii. Amnuaypanich S, Patthana J, Phinyocheep P. Mixed matrix membranes prepared from natural rubber/poly (vinyl alcohol) semi-interpenetrating polymer network (NR/PVA semi-IPN) incorporating with zeolite 4A for the pervaporation dehydration of water-ethanol mixtures. *Chemical Engineering Science*. 2009 Dec 1;64(23):4908-18.
- a. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.ces.2009.07.028>
- viii. Almasian A, Parvinzadeh Gashti M, Olya ME, Chizari Fard G. Poly (acrylic acid)-zeolite nanocomposites for dye removal from single and binary systems. *Desalination and Water Treatment*. 2016 Sep 19;57(44):20837-55.
- a. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1080%2F19443994.2015.1112841>
- ix. Huyen DN, Tung NT, Thien ND, Thanh LH. Effect of TiO₂ on the gas sensing features of TiO₂/PANi nanocomposites. *Sensors*. 2011 Feb 1;11(2):1924-31.
- a. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.3390%2Fs110201924>
- x. Wu J, Lin J, Zhou M, Wei C. Synthesis and properties of starch-graft-polyacrylamide/clay superabsorbent composite. *Macromolecular Rapid Communications*. 2000 Oct 1;21(15):1032-4.
- a. [https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1002%2F1521-3927\(20010301\)22:6<422::aid-marc422>3.0.co;2-r](https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1002%2F1521-3927%2820001001%2921%3A15%3C1032%3A%3Aaid-marc1032%3E3.0.co%3B2-n+)
- xi. Lin J, Wu J, Yang Z, Pu M. Synthesis and properties of poly (acrylic acid)/mica superabsorbent nanocomposite. *Macromolecular Rapid Communications*. 2001 Mar 1;22(6):422-4.
- a. [https://doi.org/10.1002/1521-3927\(20010301\)22:6<422::aid-marc422>3.0.co;2-r](https://doi.org/10.1002/1521-3927(20010301)22:6<422::aid-marc422>3.0.co;2-r)
- xii. Lee WF, Chen YC. Effect of intercalated reactive mica on water absorbency for poly (sodium acrylate) composite superabsorbents. *European Polymer Journal*. 2005 Jul 1;41(7):1605-12..
- a. <https://doi.org/10.1016/j.eurpolymj.2005.02.011>
- xiii. Gashti MP, Almasian A. UV radiation induced flame retardant cellulose fiber by using polyvinylphosphonic acid/carbon nanotube composite coating. *Composites Part B: Engineering*. 2013 Feb 1;45(1):282-9.
- a. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.compositesb.2012.07.052>
- xiv. Parvinzadeh M, Eslami S. Optical and electromagnetic characteristics of clay-iron oxide nanocomposites. *Research on Chemical Intermediates*. 2011 Sep 1;37(7):771.
- xv. Gashti MP, Eslami S. Structural, optical and electromagnetic properties of aluminum-clay nanocomposites. *Superlattices and Microstructures*. 2012 Jan 1;51(1):135-48. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.spmi.2011.11.008>
- xvi. Liu ZS, Rempel GL. Preparation of superabsorbent polymers by crosslinking acrylic acid and acrylamide copolymers. *Journal of Applied Polymer Science*. 1997 May 16;64(7):1345-53. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1002%2F%28sici%291097-4628%2819970516%2964%3A7%3C1345%3A%3Aaid-app14%3E3.0.co%3B2-w+>
- xvii. Turabik M. Adsorption of basic dyes from single and binary component systems onto bentonite: simultaneous analysis of Basic Red 46 and Basic Yellow 28 by first order derivative spectrophotometric analysis method. *Journal of hazardous materials*. 2008 Oct 1;158(1):52-64. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.jhazmat.2008.01.033>
- xviii. Keleb E, Sharma RK, Mosa EB, Aljahwi AA. Transdermal drug delivery system-design and evaluation. *International Journal of Advances in Pharmaceutical Sciences*. 2010 Jul 1;1(3).
- xix. Latheeshjilal L, Phanitejaswini P, Soujanya Y, Swapna U, Sarika V, Moulika G. Transdermal drug delivery systems: an overview. *International Journal of PharmTech Research*. 2011;3(4):2140-8.
- xx. SHINGADE G. Review on: recent trend on transdermal drug delivery system. *Journal of Drug Delivery and Therapeutics*. 2012 Jan 19;2(1). <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.22270%2Fjddt.v2i1.74>
- xxi. Paradee N, Sirivat A. Encapsulation of folic acid in zeolite Y for controlled release via electric field. *Molecular pharmaceutics*. 2015 Nov 25;13(1):155-62. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1021%2Facs.molpharmaceut.5b00592>
- xxii. Grund S, Doussineau T, Fischer D, Mohr GJ. Mitoxantrone-loaded zeolite beta nanoparticles: preparation, physico-chemical characterization and biological evaluation. *Journal of*

colloid and interface science. 2012 Jan 1;365(1):33-40.
<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.jcis.2011.09.003>+

xxiii. Horcajada P, Márquez-Alvarez C, Rámila A, Pérez-Pariante J, Vallet-Regí M. Controlled release of Ibuprofen from dealuminated faujasites. *Solid State Sciences*. 2006 Dec 1;8(12):1459-

65.<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.solidstatesciences.2006.07.016>+

xxiv. Datt A, Burns EA, Dhuna NA, Larsen SC. Loading and release of 5-fluorouracil from HY zeolites with varying SiO₂/Al₂O₃ ratios. *Microporous and Mesoporous Materials*. 2013 Feb 1;167:182-7.

<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.micromeso.2012.09.011>+

xxv. Braschi I, Blasioli S, Gigli L, Gessa CE, Alberti A, Martucci A. Removal of sulfonamide antibiotics from water: evidence of adsorption into an organophilic zeolite Y by its structural modifications. *Journal of Hazardous Materials*. 2010 Jun 15;178(1-3):218-25.

<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.jhazmat.2010.01.066>+

xxvi. Braschi I, Gatti G, Paul G, Gessa CE, Cossi M, Marchese L. Sulfonamide antibiotics embedded in high silica zeolite y: A combined experimental and theoretical study of host-guest and guest-guest interactions. *Langmuir*. 2010 Feb 25;26(12):9524-32.
<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1021%2F1a9049132>+

xxvii. Narang KK, Singh VP, Bhattacharya D. 5-Fluorouracil and 5-fluorouracil-histidine complexes with Al^{III}, Cr^{III} and Fe^{III} ions and their antitumour activity. *Polyhedron*. 1997 Jan 1;16(14):2491-7.

<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fs0277-5387%2896%2900551-7>+

xxviii. Vicoso AL, Gomes AC, Soares BG, Paranhos CM. Effect of sepiolite on the physical properties and swelling behavior of rifampicin-loaded nanocomposite hydrogels. *Express Polym Lett*. 2009 Aug 1;3:518-24.

<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.3144%2Fexpresspolymlett.2009.64>+

xxix. Paradee N, Sirivat A, Niamlang S, Prissanaroon-Ouajai W. Effects of crosslinking ratio, model drugs, and electric field strength on electrically controlled release for alginate-based hydrogel. *Journal of Materials Science: Materials in Medicine*. 2012 Apr 1;23(4):999-1010.

<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1007%2Fs10856-012-4571-0>+

xxx. Murdan S. Electro-responsive drug delivery from hydrogels. *Journal of controlled release*. 2003 Sep 19;92(1-2):1-7.
<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fs0168-3659%2803%2900303-1>+

xxxi. Juntanon K, Niamlang S, Rujiravanit R, Sirivat A. Electrically controlled release of sulfosalicylic acid from crosslinked poly(vinyl alcohol) hydrogel. *International journal of pharmaceutics*. 2008 May 22;356(1-2):1-1.

<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.ijpharm.2007.12.023>+

xxxii. Khan S, Hanjra MA. Footprints of water and energy inputs in food production—Global perspectives. *Food Policy*. 2009 Apr 1;34(2):130-40.

a. <https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.foodpol.2008.09.001>+

xxxiii. Rashidzadeh A, Olad A, Reyhanitabar A. Hydrogel/clinoptilolite nanocomposite-coated fertilizer: swelling, water-retention and slow-release fertilizer properties. *Polymer Bulletin*. 2015 Oct 1;72(10):2667-84.

<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1007%2Fs00289-015-1428-y>+

xxxiv. Hussien RA, Donia AM, Atia AA, El-Sedfy OF, El-Hamid AR, Rashad RT. Studying some hydro-physical properties of two soils amended with kaolinite-modified cross-linked poly-acrylamides. *Catena*. 2012 May 1;92:172-8.

<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.catena.2011.12.010>+

xxxv. Lee WF, Chen YC. Effect of intercalated reactive mica on water absorbency for poly (sodium acrylate) composite superabsorbents. *European Polymer Journal*. 2005 Jul 1;41(7):1605-12.
<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fj.eurpolymj.2005.02.011>+

xxxvi. Wu J, Wei Y, Lin J, Lin S. Study on starch-graft-acrylamide/mineral powder superabsorbent composite. *Polymer*. 2003 Oct 1;44(21):6513-20.

<https://search.crossref.org/?q=https%3A%2F%2Fdoi.org%2F10.1016%2Fs0032-3861%2803%2900728-6>+