International Journal of Research in Engineering and Science (IJRES)
ISSN (Online): 2320-9364, ISSN (Print): 2320-9356
www.ijres.org Volume 10 Issue 5 ǁ 2022 ǁ PP. 86-92

ZSM-5 A promising Drug Delivery Platform for Quercetin

Pourya Zarshenas
Department of Inorganic Chemistry, Faculty of Chemistry & Petroleum Sciences
ShahidBeheshti University (SBU), Tehran, Iran

Abstract
In pursuit of development of a drug carrying platform for delivery of Quercetin, an anti-cancer drug, a porous metal–organic frameworks (MOFs), ZMS-5, was synthesized and used. The unique structure of ZSM-5 which are built of inorganic nodes and organic ligands lead to successful encapsulation of different ions and molecules.Following our recent study, ZMS-5 was prepared and characterized using variety of analytical methods containing FTIR, FESEM, and EDS. The loading and releasing profile of Quercetin in the synthesized platform ZSM-5 were evaluated. The in vitro cytotoxicity results revealed ZSM-5-Quercetin was able to increase cytotoxicity compared to that of Quercetin on HT-29 cancerous cells indicating the remarkable role of this drug delivery system.

Keywords:*ZSM-5, MOF, drug delivery, Quercetin, Cytotoxicity*

Date of Submission: 15-05-2022 Date of acceptance: 29-05-2022

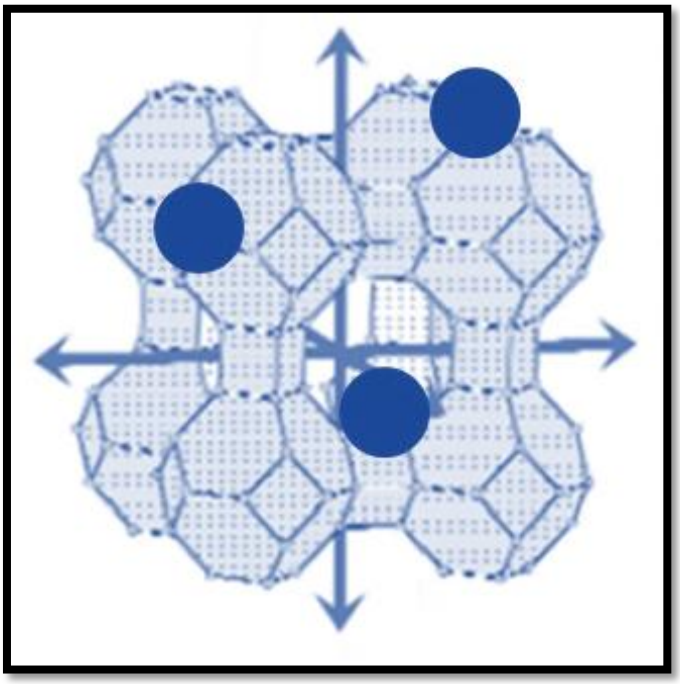

Fig1. Placement of drug in the structure of Zeolite.

I. Introduction

Recently, developing effective therapeutics become as an urgent demand due to its major impact on the patient's quality of life.Accumulated studies have been devoted to finding the effective therapeutic agents [1, 2].

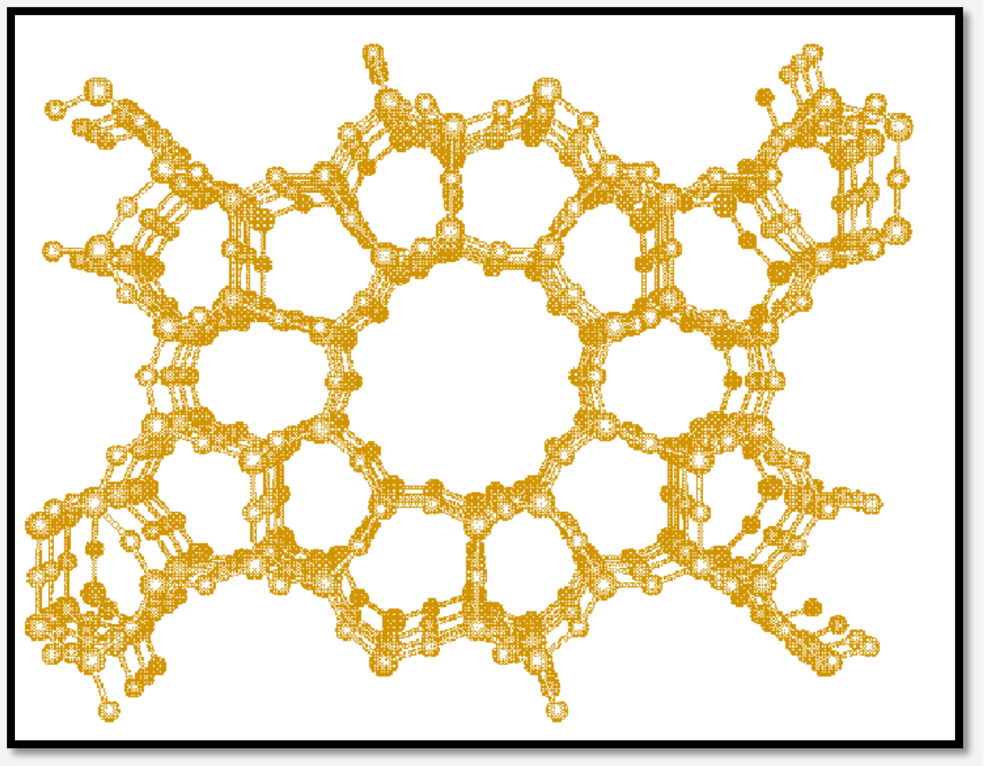

Fig2. The framework structure of ZSM-5.

Zeolite

Zeolites are a group of crystalline materials made up of evenly sized pores and tunnel systems. When purifying VOCs and hydrocarbons, we use a synthetic hydrophobic zeolite. When the contaminated air passes through the material, the hydrocarbons are adsorbed. The material can adsorb a certain amount of hydrocarbons before needing to be regenerated. [16], [17]

A smaller flow of hot air is then directed through the material so that the hydrocarbons release from the zeolite in a higher concentration. This enables more cost-effective incineration. One of its strengths is that it is non-combustible–meaning it can withstand very high temperatures. [18] This means that we are also able to purify volatile hydrocarbons such as fumes emitted from vulcanization, plastic smoke and styrene, all of which require very high temperatures during regeneration. The resistance to high temperatures and the structure of the material also allows the zeolite to be completely regenerated – meaning that the VOCs completely release from the zeolite when heated. This means that the system maintains its high purification rate year after year and that the material does not have to be replaced, which gives it a long lifespan and a minimal need for maintenance. [19] Our systems have an availability of over 99% and a lifespan exceeding 25 years. Combining the benefits of zeolite with our 30 years of experience in working with air purification gives our customers a supremely sustainable and customized system with low operating costs and high availability.

ZSM-5 is composed of several pentasil units linked together by oxygen bridges to form pentasil chains. A pentasil unit consists of eight five-membered rings. In these rings, the vertices are Al or Si and an O is assumed to be bonded between the vertices. The pentasil chains are interconnected by oxygen bridges to form corrugated sheets with 10-ring holes. Like the pentasil units, each 10-ring hole has Al or Si as vertices with an O assumed to be bonded between each vertex. Each corrugated sheet is connected by oxygen bridges to form a structure with "straight 10-ring channels running parallel to the corrugations and sinusoidal 10-ring channels perpendicular to the sheets." Adjacent layers of the sheets are related by an inversion point. The estimated pore size of the channel running parallel with the corrugations is 5.4–5.6 Å.The crystallographic unit cell of ZSM-5 has 96 T sites (Si or Al), 192 O sites, and a number of compensating cations depending on the Si/Al ratio, which ranges from 12 to infinity. The structure is orthorhombic (space group Pnma) at high temperatures, but a phase transition to the monoclinic space group $P2_1/n$.1.13 occurs on cooling below a transition temperature, located between 300 and 350 K.

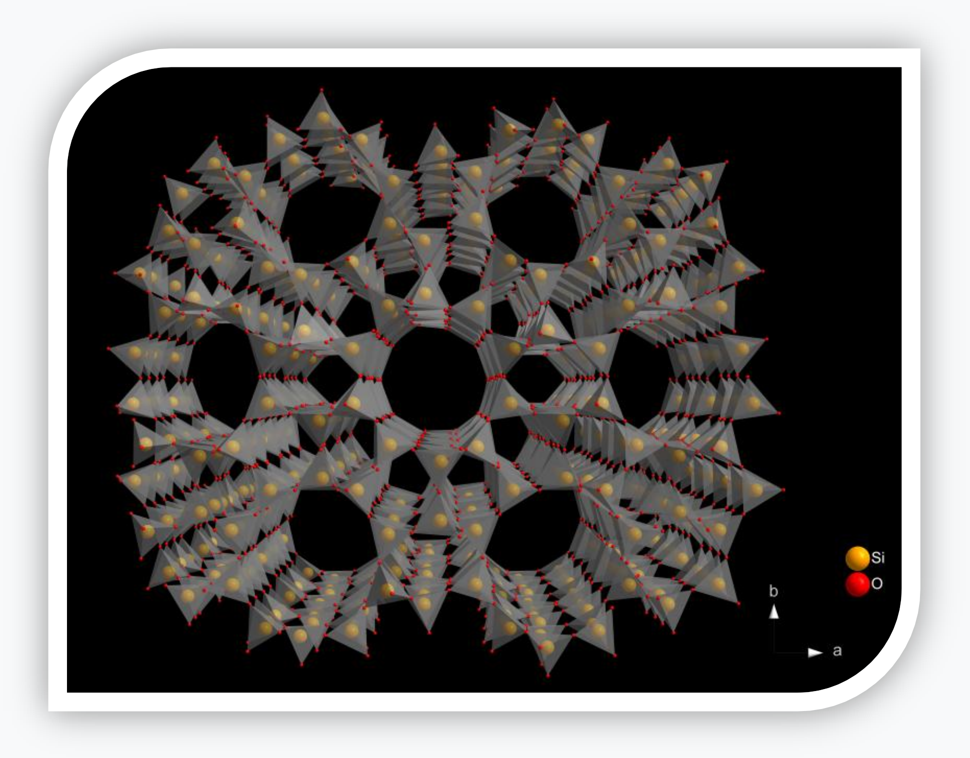

Fig3. The molecular structure of ZSM-5 zeolite, showing well defined pores and channels in the zeolite. Yellow balls represent Si and red balls represent O.

ZSM-5 catalyst was first synthesized by Argauer and Landolt in 1969. It is a medium pore zeolite with channels defined by ten-membered rings. The synthesis involves three different solutions. The first solution is the source of alumina, sodium ions, and hydroxide ions; in the presence of excess base the alumina will form soluble $Al(OH)_4^-$ ions. The second solution has the tetrapropylammoniumcation that acts as a templating agent. The third solution is the source of silica, one of the basic building blocks for the framework structure of a zeolite. Mixing the three solutions produces supersaturated tetrapropylammonium ZSM-5, which can be heated to recrystallize and produce a solid.

Background of the invention

Pentasil-zeolites are defined by their structure type, and more specifically by their X-ray diffraction patterns. ZSM-5 is the trade name of a pentasil-zeolite.

As early as 1967, Argauer and Landolt worked out parameters for the synthesis of pentasilzeolites, particularly those relating to the following molar ratios: OH^-/SiO_2 = 0.07–10, SiO_2/Al_2O_3 = 5–100, H_2O/SiO_2 = 1–240. However, the Argauer and Landolt procedure succeeded in synthesizing a reasonably pure phase ZSM-5 zeolite only if organic amines with a structure-giving function (i.e. template function), such as tetrapropyleneammonium compounds were used. Subsequent publications have disclosed methods of conducting the synthesis of pentasil-zeolites without requiring the very expensive, toxic and easily inflammable organic amine templates. Still other subsequent publications have disclosed substitutes for these amines. In addition to their expense, toxicity and flammability, such amines are disfavored because they are subject to thermal decomposition which can destroy the zeolite structure. Further publications have disclosed modifications of the Argauer and Landolt process directed towards improving the reactivity of the SiO_2 and Al_2O_3 starting materials.

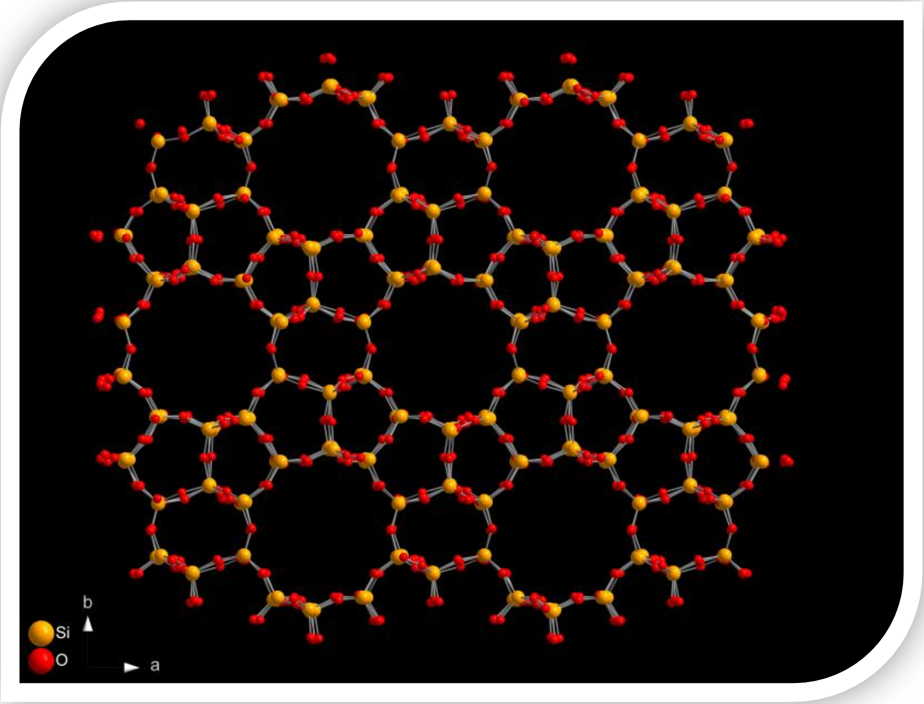

Fig4. The molecular structure of ZSM-5 zeolite, showing well defined pores and channels in the zeolite. Yellow balls represent Si and red balls represent O.

Synthesis

ZSM-5 is a synthetic zeolite, closely related to ZSM-11. There are many ways to synthesize ZSM-5; a common method is as follows:

An aqueous solution of silica, sodium aluminate, sodium hydroxide, and tetrapropylammonium bromide are combined in appropriate ratios

$$SiO_2 + NaAlO_2 + NaOH + N(CH_2CH_2CH_3)_4Br + H_2O \rightarrow \text{ZSM-5} + \text{analcime} + \text{alpha-quartz}$$

ZSM-5 is typically prepared at high temperature and high pressure in a Teflon-coated autoclave and can be prepared using varying ratios of SiO_2 and Al containing compounds.

Uses

ZSM-5 has a high silicon to aluminum ratio. Whenever an Al^{3+} cation replaces a Si^{4+} cation, an additional positive charge is required to keep the material charge-neutral. With proton (H^+) as the cation, the material becomes very acidic. Thus the acidity is proportional to the Al content. The very regular 3-D structure and the acidity of ZSM-5 can be utilized for acid-catalyzed reactions such as hydrocarbon isomerization and the alkylation of hydrocarbons. One such reaction is the isomerization of meta-xylene to para-xylene. Within the pores of the ZSM-5 zeolite, para-xylene has a much higher diffusion coefficient than meta-xylene. When the isomerization reaction is allowed to occur within the pores of ZSM-5, para-xylene is able to traverse along the pores of the zeolite, diffusing out of the catalyst very quickly. This size-selectivity allows the isomerization reaction to occur quickly in high yield.[9]

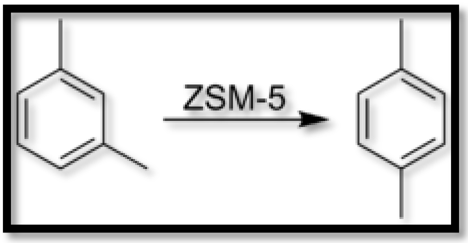

Fig5. Isomerisation of meta-xylene to para-xylene on passing through a ZSM-5 catalyst.

ZSM-5 has been used as a support material for catalysis. In one such example, copper is deposited on the zeolite and a stream of ethanol is passed through at temperatures of 240 to 320 °C as a vapor stream, which causes the ethanol to oxidize to acetaldehyde; two hydrogens are lost by the ethanol as hydrogen gas. It appears that the specific pore size of ZSM-5 is of benefit to this process, which also functions for other alcohols and oxidations. The copper is occasionally combined with other metals, such as chromium, to fine tune the diversity and specificity of the products, as there is likely to be more than one. Acetic acid is an example of one possible byproduct from hot copper oxidation.

ZSM-5 is also used to convert alcohols directly into gasoline. One such process is known as the Methanol to Gasoline (MTG) process, patented by Mobil.

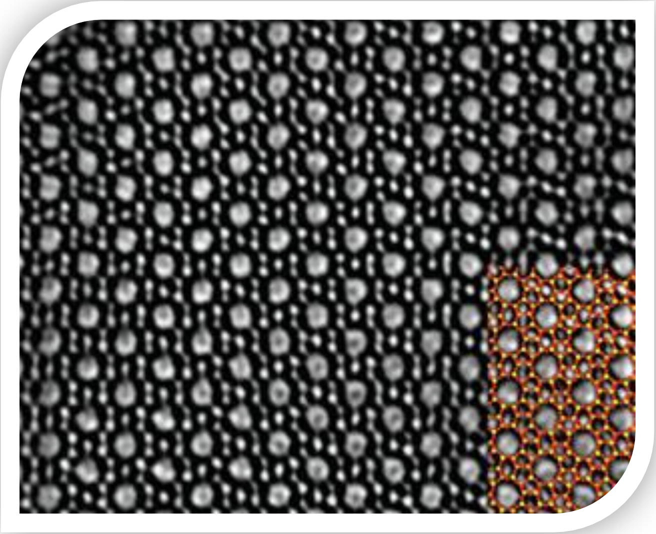

Fig6. Bragg-filtered HR-TEM image of MFI nanosheet with the overlaid crystal structure along [010] direction.

II. Results And Discussion

Characterization

The chemical structure of the zsm-5-Quercetin was characterized with different analytical methods such as XRD, SEM & TEM.

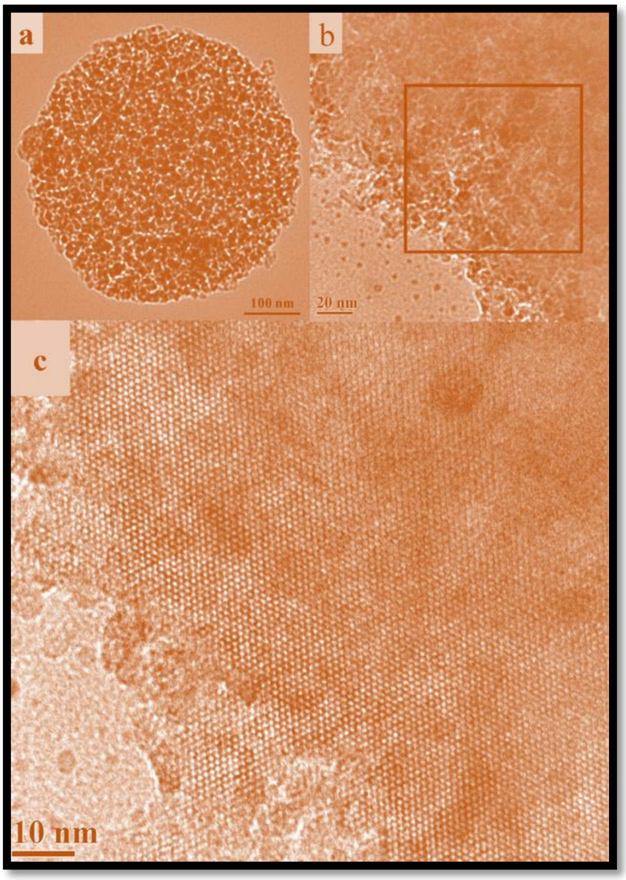

Fig7. TEM images (a, b) of mesoporous ZSM-5 microsphere of different magnifications and the HR-TEM image (c) from the area marked by a black square in (b).

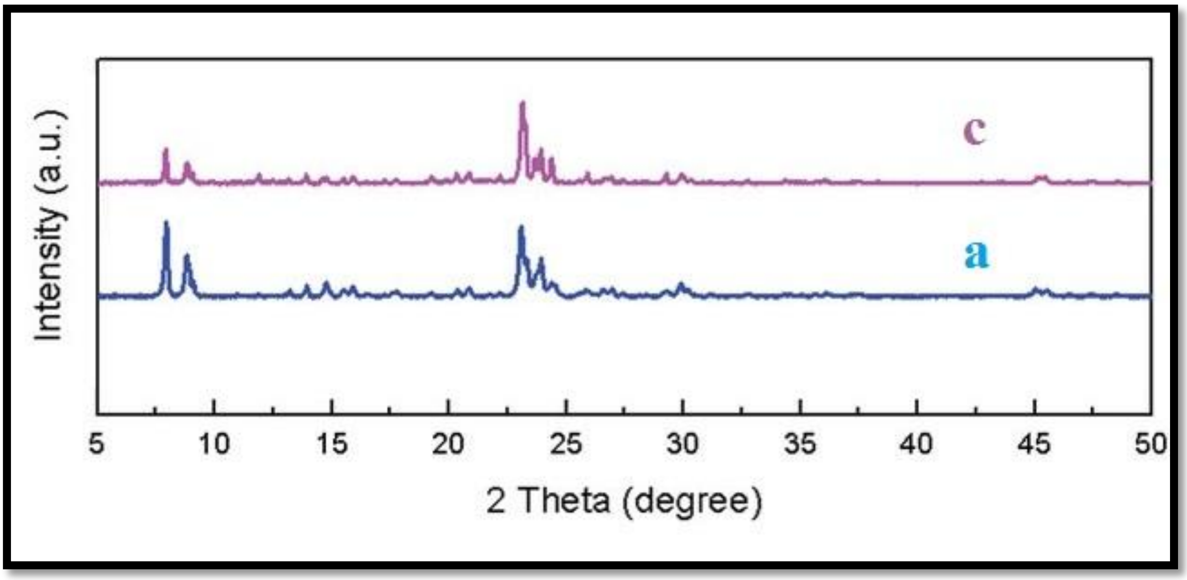

Fig8. XRD patterns of ZSM-5 samples obtained Quercetin: (a) ZSM-5 (c) ZSM-5-Quercetin.

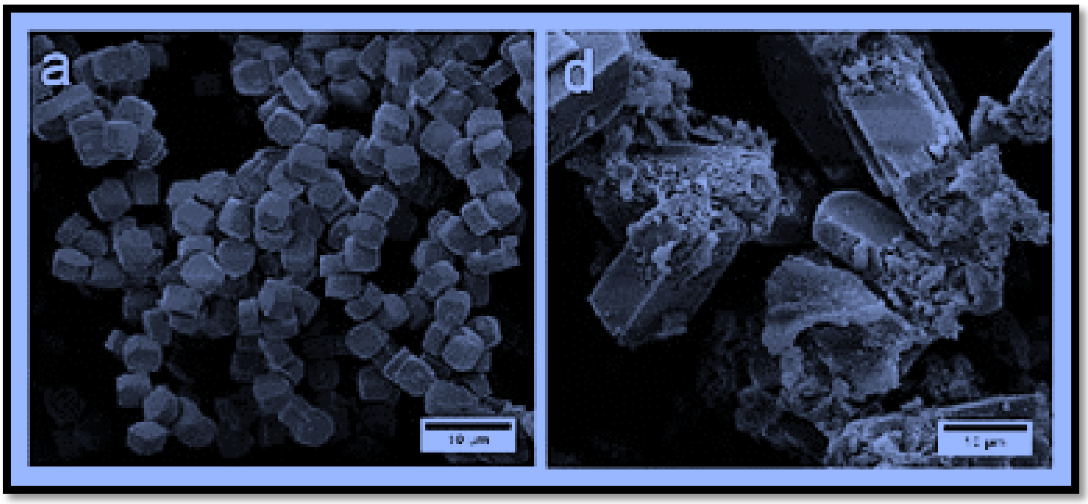

Fig9. SEM images of ZSM-5 samples obtained Quercetin:
(a)ZSM-5, (d) ZSM-5-Quercetin.

III. Conclusion

In this study, ZSM-5- as a drug carrier was applied for delivery of Quercetin. The obtained nanostructure poses spherical morphology with an average diameter of 39-52 nm. The results showed the high loading capacity (82%) and sustained drug release behavior for Quercetin after 48h. In addition, upon exposure by ZSM-5— Quercetin, the growth inhibition was increased compared to those for ZSM-5- and Quercetin drug against HT-29 cells. Collectively, ZSM-5—may could be used as a promising drug delivery system for Quercetin.

References

[1]. O. Zarei, F. Azimian, M. Hamzeh-Mivehroud, J. Shahbazi Mojarrad, S. Hemmati, S. Dastmalchi. Medicinal Chemistry Research 2020**,** 29, 1438-1448.
[2]. S. Rojas, T. Devic, P. Horcajada. Journal of Materials Chemistry B 2017**,** 5, 2560-2573.
[3]. B.-H. Song, X. Ding, Z.-F. Zhang, G.-F. An. Journal of the Iranian Chemical Society 2019**,** 16, 333-340.
[4]. E. Tawfik, M. Ahamed, A. Almalik, M. Alfaqeeh, A. Alshamsan. Saudi Pharmaceutical Journal 2017**,** 25, 206-213.
[5]. N.M. Mhaidat, M. Bouklihacene, R.F. Thorne. Oncology letters 2014**,** 8, 699-704.
[6]. W. Cai, J. Wang, C. Chu, W. Chen, C. Wu, G. Liu. Advanced Science 2019**,** 6, 1801526.
[7]. Song, Y., Chen, y., Xu, M., Wei, W., Zhang, Y., Yang, G., Ran, R., Wei, Z., &Zongping, S. (2020). "A Cobalt-Free Multi-Phase Nanocomposite as Near-Ideal Cathode of Intermediate-Temperature Solid Oxide Fuel Cells Developed by Smart Self-Assembly." Advanced Materials, 32(8), 1906979. https://doi.org/10.1002/adma.201906979
[8]. Rane, A. V., Kanny, K., Abitha, V.K., & Thomas, S. (2018). "Methods for synthesis of nanoparticles and fabrication of nanocomposites. In S. M. Bhagyaraj, O. S. Oluwafemi& S. Thomas (Eds.), “Synthesis of inorganic nanomaterials (pp. 121-139). Woodhead Publishing. https://doi.org/10.1016/B978-0-08-101975-7.00005-1
[9]. Lopez, N., Janssens, T.V.W., Clausen, B.S., Xu, Y., Mavrikakis, M., Bligaard, T., &Nørskov, J.K. (2004). "On the origin of the catalytic activity of gold nanoparticles for low-temperature CO oxidation". Journal of Catalysis, 223(1), 232-235. 10.1016/j.jcat.2004.01.001
[10]. Hubbe, Martin A., et al. "Cellulosic nanocomposites: a review." BioResources 3.3 (2008): 929-980.
[11]. Kornmann, Xavier, Henrik Lindberg, and Lars A. Berglund. "Synthesis of epoxy–clay nanocomposites: influence of the nature of the clay on structure." Polymer 42.4 (2001): 1303-1310.
[12]. Fornes, T. D., and D. R. Paul. "Modeling properties of nylon 6/clay nanocomposites using composite theories." polymer 44.17 (2003): 4993-5013.
[13]. Wagner, H. D., et al. "Stress-induced fragmentation of multiwall carbon nanotubes in a polymer matrix." Applied physics letters 72.2 (1998): 188-190.
[14]. Gu, Dongdong, et al. "Selective laser melting of TiC/Ti bulk nanocomposites: Influence of nanoscale reinforcement." ScriptaMaterialia 67.2 (2012): 185-188.
[15]. Fechete, Ioana, Ye Wang, and Jacques C. Védrine. "The past, present and future of heterogeneous catalysis." Catalysis Today 189.1 (2012): 2-27.
[16]. Dąbrowski, A. "Adsorption—from theory to practice." Advances in colloid and interface science 93.1-3 (2001): 135-224.
[17]. Shahabuddin, M., et al. "A review on the production of renewable aviation fuels from the gasification of biomass and residual wastes." Bioresource Technology 312 (2020): 123596.
[18]. Khan, Faisal I., and Aloke Kr Ghoshal. "Removal of volatile organic compounds from polluted air." Journal of loss prevention in the process industries 13.6 (2000): 527-545.
[19]. Rathje, William L., and Cullen Murphy. Rubbish!: the archaeology of garbage. University of Arizona Press, 2001.
[20]. Gorse, Christopher, David Johnston, and Martin Pritchard. A dictionary of construction, surveying, and civil Engineering. Oxford University Press, 2012.
[21]. Malamis, S., and E. Katsou. "A review on zinc and nickel adsorption on natural and modified zeolite, bentonite and vermiculite: examination of process parameters, kinetics and isotherms." Journal of hazardous materials 252 (2013): 428-461.