Degradation of Diclofenac from Water Using Photo Catalyst

Riaz Ahmed Soomro[1], Sheeraz Ahmed Memon[1], Khan Muhammad Brohi1, Rafi O Zaman Brohi[1], Azeem Panhwar[1]

[1]*Institue of Environmental Engineering and Management, Mehran UET, Jamshoro, Sindh, Pakistan*

***Abstract*: The diclofenac is the NSAID compound. It is developing poison in nature. The fundamental wellspring of diclofenac in the earth is pharmaceutical wastewater and local wastewater. It can't be evacuated by ordinary treatment strategies, so it requires an exceptional treatment technique to expel from water bodies. Advance oxidation process is most recent water treatment strategy which use free extreme response to straightforwardly debase natural contaminations utilizing impetus. In this examination, the Mn/Ni based impetus was integrated by compound decrease strategy in which the proportion of Manganese and Nickel was 3:1. The Characterization of photograph impetus, for example, molecule size and SEM was done to analyze shape and size of impetus. The zeta molecular size demonstrated that the normal molecule size was 524 nm and SEM results showed that the particles were round fit as a fiddle. The group explore was done in which different parameters, for example, impact of photo catalyst dose and concentration of diclofenac were studied. During this research the improved parameters were observed that optimum photo catalytic dose was 25 mg and concentration of diclofenac 20 ppm. The maximum degradation of 90±0.5 % were achieved during this research. After debasement the lingering diclofenac focus was resolved utilizing UV-Visible spectrophotometer (UV-1800 SHIMADZU CORPORATION Kyoto Japan).**

***Keywords*: Diclofenac, Advance oxidation process, photo catalyst Bimetallic.**

I. INTRODUCTION

Now a days the personal care product and pharmaceutical and personal care product in the environment are emerging pollutant in water and soil and it has potential impact on human life as well as environment [1, 2]. Likewise, this significant rising natural contamination by PPCPs and their metabolites in the oceanic condition has raised expanding concern [3]. Pharmaceutical contamination is expanding in the oceanic condition since numerous pharmaceuticals are not entirely evacuated during their entry through wastewater treatment plants. PPCPs comprise of a wide scope of intensifies whose conduct is hard to anticipate on the grounds that it is regularly constrained by collaborations with explicit utilitarian gatherings or confused pH subordinate speciation, etc [4]. The persistent contribution of such mixes may prompt incessant low level introduction and gathering, bringing about negative impacts on life and the earth [5], plus undesired collateral generation of microbial resistances [6]. One of the most expended meds compares to the order of the non-steroidal calming drugs (NSAIDs). NSAIDs have been recognized in effluents from emergency clinics [7] effluent of WWTP [7–11], in rivers, lakes, and surface water [12, 13], as well as in sea water [14]. Diclofenac is a non-steroidal anti-inflammatory drug use to pain relief medication with different non-rheumatic diseases and rheumatic [15]. These days, the hurtful impacts of Diclofenac on various life forms in reasonable oceanic conditions have been illustrated [16]. For instance, diclofenac can cause renal disappointment in the Indian vulture and changes of the gills of rainbow trout. It additionally can impact the biochemical elements of fish and lead to tissue harm [17]. The potential risk on environment and on human society demonstrated at trace level. The studied conducted on decline in Vultures population also in Pakistan was mainly due to Diclofenac residues. When Vultures eat dead bodies of animals, the residue in meat and blood of dead animals damage the renal systems such as Kidneys of Vultures. This is major cause in decline. [18]. Because of the polar no-unstable nature, diclofenac appropriation in the earth occurred basically through the oceanic medium movement and evolved way of life collection [19]. Through conventional treatment techniques such as aerobic, anaerobic process and activated carbon and other methods used were not so effective in the removal of this environmental concern [20]. In this manner, propelled systems are important, and ought to critically be investigated to manage this natural issue. Notwithstanding, as far as anyone is concerned, PC expulsion degradation of diclofenac by fluid TiO_2 suspensions [21]. To protect the water resources the new methods for the elimination of diclofenac in water were developed. For that reason different non-classical and chemicals oxidation method such as irradiation or sonolysis with UV- light or microwave are present. Under UV-light irradiation such as Fenton reaction in the presence of H_2O_2 or ozone methods were describe recently [22, 23, and 24]. The degradation of organic pollutant from water and wastewater such as dyes or pesticides and the removal of biological contaminant through ultrasound irradiation method a number of publication have published in recent years [25, 26, 27, 28, 29, 30 and 31]. Without additional oxidizing chemicals in water appears practicable in technical scales of ultrasonic irradiation [32].From the published research on the water and wastewater treatment , advance oxidation process are well known technology for the removal of organic compound in the water such as pharmaceutical compounds. Along with the Advance oxidation process the photo catalyst also use then removal efficiency will also be increased [32]. Through activation of catalyst surfaces Ultrasound can also modified in catalytic oxidation processes. Synergetic effects can be used for water treatment in advanced oxidation process (AOP) [33]. In sonolysis use of catalyst is another quite new aspect in this field of investigations [34, 35, 36, 37 and 38]. In literature the commonly described catalyst are Fenton ($Fe2+/ H2O2$) and titanium dioxide (P25) [39]. Keeping in account the above studies were concluded that the occurrence of Diclofenac drugs in water bodies is an issue of emerging environmental concern. Therefore we propose this study for the degradation of Diclofenac in water to develop cost effective and simple treatment method for remediation one of most widely used Diclofenac drug.

II. MATERIALS & METHODS

A. *Chemicals 1*

Sodium Diclofenac use as a standard and also as a pollutant in spiked water was purchased from the GSK pharmaceutical Pvt. Ltd company Karachi. Methanol employed to make stock solution of diclofenac purchased from DAE JUNG Chemicals and metals co. Ltd. Nickel sulfate and manganese sulfate to synthesize the photo catalyst was purchased from the DAE JUNG Chemicals and metals co. Ltd. Sodium borohyderad used as a reducing agent in the synthesize of photo catalyst also purchased from the DAE JUNG Chemicals and metals co. Ltd. Sodium hydroxide and Hydrochloric acid also used form the pH study was purchased from DAE JUNG Chemicals and metals co. Ltd. All the chemicals used in this study are employed any further purification, Deionized water used through this study.

B. *Fabrication of Photo Catalyst 2*

The bimetallic photo catalyst were prepared by using Sodium borohyderad (NaBH4) reduction method with some modification [40]. Briefly, 0.1775 M of MnSO4.H2O was mixed with nickel sulfate 0.06M having ratio of 3:1 and were dissolved in deionized water. Mixture was then stirred mechanically and 0.2 % of NaBH4 was added drop wise while stirring the solution, finally brownish black precipitate were formed which were washed several times with deionized water, filtered and dried overnight in to oven at 50 ◦C.

C. *Photo Catalyst degradation experiment 3*

In each experiment 50 ml of diclofenac solution with known concentration was added to 0.02 g of perlite in 100 ml of glass beaker at 34±0.5 ℃ and put the beaker into the digital ultrasonic cleaner (WINCOM company Ltd china) under the 100 watt tungsten bulb, whose emitting spectrum was similar to sunlight was used as light source [41]. The sample were taken at present time interval and photo catalyst was separated from the solution by filtration assembly. The concentration of supernatant solution was analyze to determine the residual concentration of diclofenac and was measured before and after treatment with double bean UV-Visible spectrophotometer (UV-1800 SHIMADZU CORPORATION Kyoto Japan). All experiment carried out twice and average value of concentration are taken. Two parameters like pH and photo catalyst dose in visible light will be performed. Photo catalyst dose optimization will be carried out using 10 mg, 15 mg, 20 mg and 25 mg, 30 mg and 35 mg doses, similarly concentration study of diclofenac also be done.

D. *Kinetics Models*

The methods for adsorption reaction can be analysis through the equation of adsorption kinetics. Pseudo first order and Pseudo second order are widely use, which were also analyzed in this study.

Pseudo First Order

The equation for Pseudo first order is (Eq.04)

$$\text{Log}\,(Qe - Qt) = \text{Log}\,Qe - K1 * t \quad \ldots\ldots\ldots. \quad (04)$$

Where,

Qe = ration of equilibrium uptake of diclofenac on the absorbent surface as mg/g

Qt = adsorption on the adsorbent on the time t

K1 = Pseudo first order constant basis on g/ (mg. mint)

The graph is plot Log (Qe-Qt) versus t is linear so the reaction follow this model [42].

Pseudo Second order model

This is empirical model which is define as the rate of adsorption used with proportional to the square of the number of sites involved. Eq. (05) is the linear form of this model.

$$t/Qt = 1/K_2 * Qe^2 + t/Qe \quad \ldots\ldots\ldots.. \quad (05)$$

Where,

K_2 (g/(mg. mint))is the pseudo second order constant. A linear graph is plot t/Qt verses t and slop of $1/K_2 * Qe^2$ and 1/Qe respectively [43].

E. Analytical procedures

The sample were filtered with 0.45 micro meter filter paper through filtration assembly to remove the catalyst particles. The filtered sample than run on UV-spectrophotometer to check the remaining concentration of diclofenac from the water samples at the absorbance of 276 nm [44 and 45].

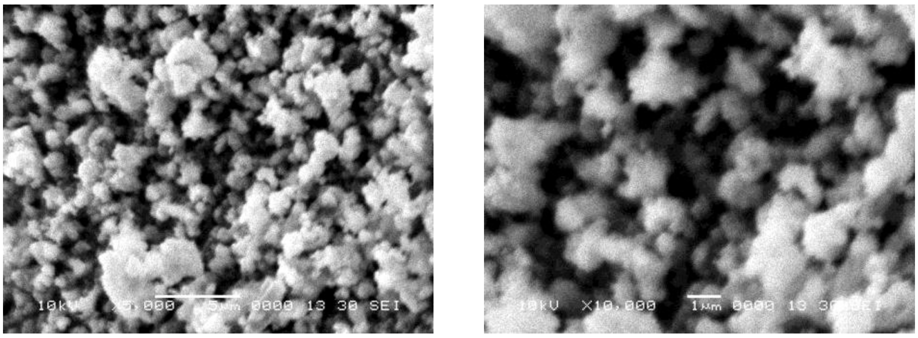
F. Characterization of Photo Catalyst

The morphology and structure of the Nano-particle of Mn/Ni is done through the different techniques such as Particle size analysis using master sizer 3000 of Malvern instruments Ltd, X-ray diffraction (XRD) by using D8 ADVANCE X-ray diffract meter from Bruker AXS, Scanning electronic microscope (SEM) by using scanning electronic microscope model JSM 7500 F Geol Ltd company Tokyo Japan working at 10KV and Fourier trans formation infra-red radiation (FTIR) using Fourier transform infrared spectroscope having model iS10 USA and spectrum range 600 to 4000 cm-1.

III. RESULTS

A. Scanning electronic microscope (SEM) and Particle size analysis

The top view of Mn/Ni photo catalyst crystals are shown in fig.1. The Mn/Ni crystals are spherical and spherical like structures, which has the spherical diameters about 525 nm.



(a) (b)

Fig. 1: SEM image of Mn/Ni (a) at 1 µm zoom (b) at 5 µm zoom

B. Effect of photo catalyst dosage on diclofenac:

Photo catalytic loading rate is the primary option in the bimetallic photo catalytic. In this experiment the concentration of 20 ppm of sodium diclofenac is taken and the dose of photocatalystic was varied from 10mg – 35 mg to check the effect t of catalytic amount. The diclofenace was irradiated for 3 hrs at the pH of 3. The maximum removal efficiency achieved at 25 mg with 75% of diclofenac removal as shown in fig 02.

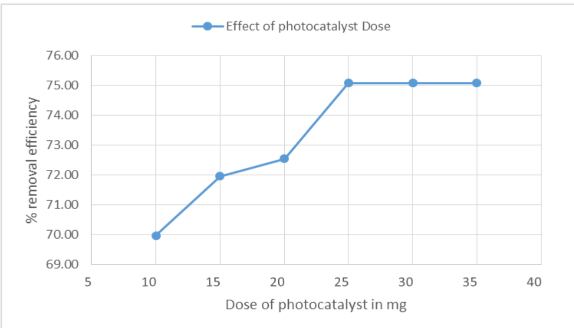


Figure.02: Influence of catalytic dose on the removal of diclofenac from water

C. Effect of Diclofenac concentration:

The effect of diclofenac was examine on the degradation of bimetallic photo catalyst. The experiment were carried out in a range of diclofenac initial concentration (1, 2.5, 5, 7.5, 10, and15) with removal efficiency of 90, 89, 79, 76, 63 and 55% respectively. The diclofenac decreases as the initial concentration increases as shown in fig 03. From this results it is clear that the diclofenac and the catalyst adsorption of present photon has good competition leading to the degradation of diclofenac. On the one hand diclofenac has cross relaxations between the photolysis regimes and excited state of diclofenac. On the other hand due to the high absorbance of light through the diclofenac the photon available for the activation of catalyst are not good to maintain an efficient process. Similar results achieved from the different literature for the degradation of diclofenac and other organic compounds [46].

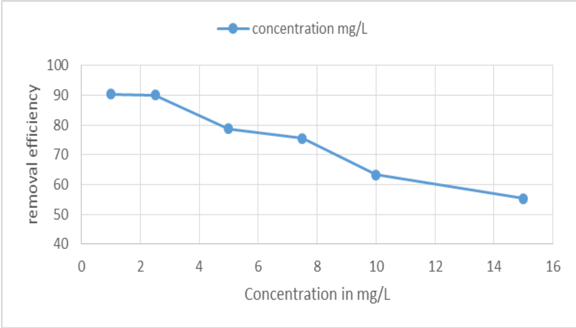
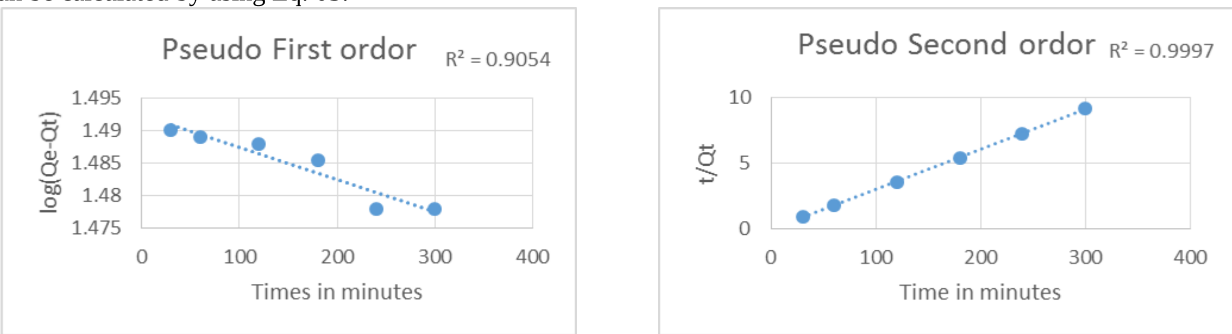


Figure.03: The concentration removal of diclofenac from water at optimum dose, pH and contact time.

D. Kinetic study of diclofenac

The adsorption dynamics of adsorbent can be better understand through the kinetic adsorption. In the modelling and design of any adsorption process the kinetic parameters play an important role. This knowledge give path to design a large system. The kinetic adsorption of diclofenac on photo catalyst was calculated using Eq. 01. In this work two kinetic models were used (Pseudo first order and pseudo second order). The pseudo Fist order is plot in figure 7 (a) and Pseudo second order is plot in figure 4 (b). It was observed during the study that diclofenac adsorption on Mn/Ni photocatalyst followed pseudo second order kinetic rather than pseudo first order with R2 value is 0.9997 as indicate in figure.04 (b). The pseudo second order constant value can be calculated by using Eq. 05.



(a) (b)

Figure. 04- Adsorption kinetic study of diclofenac on adsorbent (a) Pseudo First Order (b) Pseudo second order model

IV. CONCLUSIONS

During this study the Manganese and Nickel bimetallic photocatalyst were prepared through the sodium borohydrat method which were used for the treatment of diclofenac through the advance oxidation method. It was observed that the removal efficiency of functionalized Mn/Ni was 90±0.5 % at the adsorption capacity of 33.412 mg/g at optimum conditions. The adsorption kinetics followed Pseudo second order model.

V. ACKNOWLEDGEMENT

I acknowledged the institute of Environmental Engineering and management Mehran University of Engineering and Technology Jamshoro for support and help in my research.

REFERENCES

[1] Kosma, C.I., Lambropoulou, D.A. and Albanis, T.A., 2014. Investigation of PPCPs in wastewater treatment plants in Greece: occurrence, removal and environmental risk assessment. Science of the Total Environment, 466, pp.421-438.

[2] Kumar, A. and Xagoraraki, I., 2010. Pharmaceuticals, personal care products and endocrine-disrupting chemicals in US surface and finished drinking waters: a proposed ranking system. Science of the Total Environment, 408(23), pp.5972-5989.

[3] Calza, P., Sakkas, V.A., Villioti, A., Massolino, C., Boti, V., Pelizzetti, E. and Albanis, T., 2008. Multivariate experimental design for the photocatalytic degradation of imipramine: Determination of the reaction pathway and identification of intermediate products. Applied Catalysis B: Environmental, 84(3-4), pp.379-388.

[4] Kibbey, T.C., Paruchuri, R., Sabatini, D.A. and Chen, L., 2007. Adsorption of beta blockers to environmental surfaces. Environmental science & technology, 41(15), pp.5349-5356.

[5] Zuccato, E., Calamari, D., Natangelo, M. and Fanelli, R., 2000. Presence of therapeutic drugs in the environment. The lancet, 355(9217), pp.1789-1790.

[6] Sanderson, H., Johnson, D.J., Reitsma, T., Brain, R.A., Wilson, C.J. and Solomon, K.R., 2004. Ranking and prioritization of environmental risks of pharmaceuticals in surface waters. Regulatory toxicology and pharmacology, 39(2), pp.158-183.

[7] Kümmerer, K., 2001. Drugs in the environment: emission of drugs, diagnostic aids and disinfectants into wastewater by hospitals in relation to other sources–a review. Chemosphere, 45(6-7), pp.957-969.

[8] Carballa, M., Omil, F., Lema, J.M., Llompart, M., García-Jares, C., Rodríguez, I., Gomez, M. and Ternes, T., 2004. Behavior of pharmaceuticals, cosmetics and hormones in a sewage treatment plant. Water research, 38(12), pp.2918-2926.

[9] Clara, M., Strenn, B., Gans, O., Martinez, E., Kreuzinger, N. and Kroiss, H., 2005. Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. Water research, 39(19), pp.4797-4807.

[10] Spongberg, A.L. and Witter, J.D., 2008. Pharmaceutical compounds in the wastewater process stream in Northwest Ohio. Science of the total environment, 397(1-3), pp.148-157.

[11] Perez, S. and Barceló, D., 2008. Applications of LC-MS to quantitation and evaluation of the environmental fate of chiral drugs and their metabolites. TrAC Trends in Analytical Chemistry, 27(10), pp.836-846.
[12] Boyd, G.R., Reemtsma, H., Grimm, D.A. and Mitra, S., 2003. Pharmaceuticals and personal care products (PPCPs) in surface and treated waters of Louisiana, USA and Ontario, Canada. Science of the total Environment, 311(1-3), pp.135-149.
[13] Muñoz, I., López-Doval, J.C., Ricart, M., Villagrasa, M., Brix, R., Geiszinger, A., Ginebreda, A., Guasch, H., de Alda, M.J.L., Romaní, A.M. and Sabater, S., 2009. Bridging levels of pharmaceuticals in river water with biological community structure in the Llobregat river basin (northeast Spain). Environmental Toxicology and Chemistry, 28(12), pp.2706-2714.
[14] Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B. and Buxton, H.T., 2002. Pharmaceuticals, hormones, and other organic wastewater contaminants in US streams, 1999− 2000: A national reconnaissance. Environmental science & technology, 36(6), pp.1202-1211.
[15] Calza, P., Sakkas, V.A., Medana, C., Baiocchi, C., Dimou, A., Pelizzetti, E. and Albanis, T., 2006. Photocatalytic degradation study of diclofenac over aqueous TiO2 suspensions. Applied Catalysis B: Environmental, 67(3-4), pp.197-205.
[16] Stülten, D., Zühlke, S., Lamshöft, M. and Spiteller, M., 2008. Occurrence of diclofenac and selected metabolites in sewage effluents. Science of the Total Environment, 405(1-3), pp.310-316.
[17] Mehinto, A.C., Hill, E.M. and Tyler, C.R., 2010. Uptake and biological effects of environmentally relevant concentrations of the nonsteroidal anti-inflammatory pharmaceutical diclofenac in rainbow trout (Oncorhynchus mykiss). Environmental science & technology, 44(6), pp.2176-2182.
[18] Chiron, S. and Duwig, C., 2016. Biotic nitrosation of diclofenac in a soil aquifer system (Katari watershed, Bolivia). Science of the Total Environment, 565, pp.473-480.
[19] Acuña, V., Ginebreda, A., Mor, J.R., Petrovic, M., Sabater, S., Sumpter, J. and Barceló, D., 2015. Balancing the health benefits and environmental risks of pharmaceuticals: Diclofenac as an example. Environment international, 85, pp.327-333.
[20] Bouju, H., Nastold, P., Beck, B., Hollender, J., Corvini, P.F.X. and Wintgens, T., 2016. Elucidation of biotransformation of diclofenac and 4′ hydroxydiclofenac during biological wastewater treatment. Journal of hazardous materials, 301, pp.443-452.
[21] Calza, P., Sakkas, V.A., Medana, C., Baiocchi, C., Dimou, A., Pelizzetti, E. and Albanis, T., 2006. Photocatalytic degradation study of diclofenac over aqueous TiO2 suspensions. Applied Catalysis B: Environmental, 67(3-4), pp.197-205.
[22] Ravina, M., Campanella, L. and Kiwi, J., 2002. Accelerated mineralization of the drug diclofenac via Fenton reactions in a concentric photo-reactor. Water research, 36(14), pp.3553-3560.
[23] Vogna, D., Marotta, R., Napolitano, A., Andreozzi, R. and d'Ischia, M., 2004. Advanced oxidation of the pharmaceutical drug diclofenac with UV/H2O2 and ozone. Water Research, 38(2), pp.414-422.
[24] Pérez-Estrada, L.A., Maldonado, M.I., Gernjak, W., Agüera, A., Fernández-Alba, A.R., Ballesteros, M.M. and Malato, S., 2005. Decomposition of diclofenac by solar driven photocatalysis at pilot plant scale. Catalysis Today, 101(3-4), pp.219-226.
[25] Petrier, C. and Francony, A., 1997. Ultrasonic waste-water treatment: incidence of ultrasonic frequency on the rate of phenol and carbon tetrachloride degradation. Ultrasonics sonochemistry, 4(4), pp.295-300.
[26] Tezcanli-Guyer, G. and Ince, N.H., 2003. Degradation and toxicity reduction of textile dyestuff by ultrasound. Ultrasonics Sonochemistry, 10(4-5), pp.235-240.
[27] Manousaki, E., Psillakis, E., Kalogerakis, N. and Mantzavinos, D., 2004. Degradation of sodium dodecylbenzene sulfonate in water by ultrasonic irradiation. Water Research, 38(17), pp.3751-3759.
[28] Rehorek, A., Tauber, M. and Gübitz, G., 2004. Application of power ultrasound for azo dye degradation. Ultrasonics Sonochemistry, 11(3-4), pp.177-182.
[29] Okitsu, K., Iwasaki, K., Yobiko, Y., Bandow, H., Nishimura, R. and Maeda, Y., 2005. Sonochemical degradation of azo dyes in aqueous solution: a new heterogeneous kinetics model taking into account the local concentration of OH radicals and azo dyes. Ultrasonics Sonochemistry, 12(4), pp.255-262.
[30] Tiehm, A. and Neis, U., 2005. Ultrasonic dehalogenation and toxicity reduction of trichlorophenol. Ultrasonics sonochemistry, 12(1-2), pp.121-125.
[31] Mason, T.J., 2003. Sonochemistry and sonoprocessing: the link, the trends and (probably) the future. Ultrasonics Sonochemistry, 10(4-5), pp.175-179.
[32] Aguinaco, A., Beltrán, F.J., García-Araya, J.F. and Oropesa, A., 2012. Photocatalytic ozonation to remove the pharmaceutical diclofenac from water: influence of variables. Chemical Engineering Journal, 189, pp.275-282.
[33] Lifka, J., Ondruschka, B. and Hofmann, J., 2003. The use of ultrasound for the degradation of pollutants in water: aquasonolysis–a review. Engineering in life sciences, 3(6), pp.253-262.
[34] Harada, H., 2001. Sonophotocatalytic decomposition of water using TiO2 photocatalyst. Ultrasonics sonochemistry, 8(1), pp.55-58.
[35] Pandit, A.B., Gogate, P.R. and Mujumdar, S., 2001. Ultrasonic degradation of 2: 4: 6 trichlorophenol in presence of TiO2 catalyst. Ultrasonics Sonochemistry, 8(3), pp.227-231.
[36] Kubo, M., Matsuoka, K., Takahashi, A., Shibasaki-Kitakawa, N. and Yonemoto, T., 2005. Kinetics of ultrasonic degradation of phenol in the presence of TiO2 particles. Ultrasonics sonochemistry, 12(4), pp.263-269.
[37] Wang, J., Guo, B., Zhang, X., Zhang, Z., Han, J. and Wu, J., 2005. Sonocatalytic degradation of methyl orange in the presence of TiO2 catalysts and catalytic activity comparison of rutile and anatase. Ultrasonics sonochemistry, 12(5), pp.331-337.
[38] Yano, J., Matsuura, J.I., Ohura, H. and Yamasaki, S., 2005. Complete mineralization of propyzamide in aqueous solution containing TiO2 particles and H2O2 by the simultaneous irradiation of light and ultrasonic waves. Ultrasonics sonochemistry, 12(3), pp.197-203.
[39] Neppolian, B., Park, J.S. and Choi, H., 2004. Effect of Fenton-like oxidation on enhanced oxidative degradation of para-chlorobenzoic acid by ultrasonic irradiation. Ultrasonics Sonochemistry, 11(5), pp.273-279.
[40] Fang, Z., Qiu, X., Chen, J. and Qiu, X., 2011. Debromination of polybrominated diphenyl ethers by Ni/Fe bimetallic nanoparticles: influencing factors, kinetics, and mechanism. Journal of Hazardous Materials, 185(2-3), pp.958-969.
[41] Lin, Y., Li, D., Hu, J., Xiao, G., Wang, J., Li, W. and Fu, X., 2012. Highly efficient photocatalytic degradation of organic pollutants by PANI-modified TiO2 composite. The Journal of Physical Chemistry C, 116(9), pp.5764-5772.
[42] El Nemr, A., 2009. Potential of pomegranate husk carbon for Cr (VI) removal from wastewater: Kinetic and isotherm studies. Journal of Hazardous Materials, 161(1), pp.132-141.
[43] Ho, Y.S. and McKay, G., 1999. Pseudo-second order model for sorption processes. Process biochemistry, 34(5), pp.451-465.
[44] Naddeo, V., Belgiorno, V., Kassinos, D., Mantzavinos, D. and Meric, S., 2010. Ultrasonic degradation, mineralization and detoxification of diclofenac in water: optimization of operating parameters. Ultrasonics sonochemistry, 17(1), pp.179-185.
[45] Rizzo, L., Meric, S., Kassinos, D., Guida, M., Russo, F. and Belgiorno, V., 2009. Degradation of diclofenac by TiO2 photocatalysis: UV absorbance kinetics and process evaluation through a set of toxicity bioassays. Water research, 43(4), pp.979-988.
[46] Pecini, E.M. and Avena, M.J., 2013. Measuring the isoelectric point of the edges of clay mineral particles: The case of montmorillonite. Langmuir, 29(48), pp.14926-14934.