**Ultrasonic assisted magnetic solid phase extraction based on the use of magnetic waste-tyre derived activated carbon modified with** **methyltrioctylammonium chloride adsorbent for the preconcentration and analysis of non-steroidal anti-inflammatory drugs in wastewater.**

Mpingana Ndilimeke Akawaa,b, K. Mogolodi Dimpea,b, Philliswa N. Nomngongo[[1]](#footnote-1)a,b,c

*aDepartment of Chemical Sciences, University of Johannesburg, Doornfontein Campus, P.O. Box 17011, Johannesburg, 2028, South Africa*

*bDSI/NRF SARChI Chair: Nanotechnology for Water, University of Johannesburg, Doornfontein 2028, South Africa*

*cDSI/Mintek Nanotechnology Innovation Centre, University of Johannesburg, Doornfontein, 2028, South Africa*

**Table S1.** Physical and chemical properties of the target NSAIDs

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **NSAID** | **Chemical Formula** | **Molecular** mass**(g/mol)** | **Chemical Structure** | **Solubility (mg/l, at 25 ºC)** | **pKa** | **Log KOW** |
| **Diclofenac** | C14H11Cl2NO2 | 96.16 |  | 2.37 | 4.00 | 4.51 |
| **Naproxen** | C14H14O3 | 230.27 |  | 15.9 | 4.19 | 3.18 |
| **Ketoprofen** | C16H14O3 | 254.29 |  | 20.4 | 4.45 | 3.12 |

**Table S2.** The experimental design and the percentage extraction recoveries (% ER) of the UA-MSPME method optimization.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|   |   |   |   |   | KET | NAP | DIC |
| Trial | pH | IS | ET | MA | % ER | % ER | % ER |
| 1 | 4.0 | 0.0 | 10.0 | 20.0 | 85.8 | 75.0 | 76.3 |
| 2 | 4.0 | 0.0 | 10.0 | 50.0 | 80.3 | 64.1 | 64.0 |
| 3 | 4.0 | 0.0 | 20.0 | 20.0 | 85.3 | 75.5 | 79.5 |
| 4 | 4.0 | 0.0 | 20.0 | 50.0 | 104.4 | 62.1 | 61.1 |
| 5 | 4.0 | 5.0 | 10.0 | 20.0 | 81.1 | 73.4 | 75.6 |
| 6 | 4.0 | 5.0 | 10.0 | 50.0 | 76.1 | 58.4 | 57.5 |
| 7 | 4.0 | 5.0 | 20.0 | 20.0 | 81.9 | 73.9 | 76.1 |
| 8 | 4.0 | 5.0 | 20.0 | 50.0 | 76.9 | 60.0 | 59.4 |
| 9 | 9.0 | 0.0 | 10.0 | 20.0 | 82.8 | 71.4 | 69.6 |
| 10 | 9.0 | 0.0 | 10.0 | 50.0 | 103.6 | 69.8 | 65.2 |
| 11 | 9.0 | 0.0 | 20.0 | 20.0 | 107.2 | 65.2 | 74.0 |
| 12 | 9.0 | 0.0 | 20.0 | 50.0 | 102.8 | 63.1 | 59.3 |
| 13 | 9.0 | 5.0 | 10.0 | 20.0 | 79.7 | 70.9 | 66.0 |
| 14 | 9.0 | 5.0 | 10.0 | 50.0 | 79.2 | 60.0 | 51.2 |
| 15 | 9.0 | 5.0 | 20.0 | 20.0 | 78.9 | 69.8 | 64.2 |
| 16 | 9.0 | 5.0 | 20.0 | 50.0 | 80.6 | 61.0 | 52.9 |
| 17 | 2.8 | 2.5 | 15.0 | 35.0 | 83.6 | 66.2 | 59.5 |
| 18 | 10.2 | 2.5 | 15.0 | 35.0 | 65.1 | 52.5 | 56.2 |
| 19 | 6.5 | -1.2 | 15.0 | 35.0 | 94.5 | 84.3 | 93.4 |
| 20 | 6.5 | 6.2 | 15.0 | 35.0 | 70.3 | 71.9 | 80.7 |
| 21 | 6.5 | 2.5 | 7.59 | 35.0 | 84.3 | 72.4 | 64.3 |
| 22 | 6.5 | 2.5 | 22.4 | 35.0 | 83.2 | 67.8 | 59.6 |
| 23 | 6.5 | 2.5 | 15.0 | 12.8 | 92.5 | 80.7 | 81.8 |
| 24 | 6.5 | 2.5 | 15.0 | 57.2 | 75.3 | 55.3 | 46.6 |
| 25 (C) | 6.5 | 2.5 | 15.0 | 35.0 | 85.6 | 69.3 | 60.5 |
| 26 (C) | 6.5 | 2.5 | 15.0 | 35.0 | 79.4 | 63.6 | 55.7 |

**Table S3** Analysis of variance (ANOVA) for response surface quadratic model

|  |  |
| --- | --- |
|  Factor | ANOVA;  |
| SS | df | MS | F | p |
| (1)pH (L) | 11.504 | 1 | 11.504 | 0.13033 | 0.724932 |
| pH (Q) | 65.109 | 1 | 65.109 | 0.73762 | 0.408750 |
| (2)IS (L) | 1540.347 | 1 | 1540.347 | 17.45054 | 0.001543 |
| IS (Q) | 212.722 | 1 | 212.722 | 2.40992 | 0.148848 |
| (3)ET (L) | 112.150 | 1 | 112.150 | 1.27055 | 0.283651 |
| ET (Q) | 26.958 | 1 | 26.958 | 0.30541 | 0.591562 |
| (4)MA (L) | 0.933 | 1 | 0.933 | 0.01057 | 0.919964 |
| MA (Q) | 28.998 | 1 | 28.998 | 0.32852 | 0.578060 |
| 1L by 2L | 91.840 | 1 | 91.840 | 1.04046 | 0.329626 |
| 1L by 3L | 0.077 | 1 | 0.077 | 0.00087 | 0.976943 |
| 1L by 4L | 12.056 | 1 | 12.056 | 0.13659 | 0.718715 |
| 2L by 3L | 126.563 | 1 | 126.563 | 1.43382 | 0.256308 |
| 2L by 4L | 94.522 | 1 | 94.522 | 1.07083 | 0.322972 |
| 3L by 4L | 0.174 | 1 | 0.174 | 0.00197 | 0.965421 |
| Error | 970.962 | 11 | 88.269 |   |   |
| Total SS | 3294.915 | 25 |   |   |   |

**Table S4** Analysis of variance (ANOVA) for response surface quadratic model

|  |  |
| --- | --- |
| Factor | ANOVA;  |
| SS | df | MS | F | p |
| (1)pH (L) | 0.210 | 1 | 0.210 | 0.00484 | 0.945764 |
| pH (Q) | 58.263 | 1 | 58.263 | 1.34288 | 0.271066 |
| (2)IS (L) | 77.726 | 1 | 77.726 | 1.79147 | 0.207755 |
| IS (Q) | 36.996 | 1 | 36.996 | 0.85270 | 0.375601 |
| (3)ET (L) | 5.142 | 1 | 5.142 | 0.11852 | 0.737135 |
| ET (Q) | 56.933 | 1 | 56.933 | 1.31222 | 0.276303 |
| (4)MA (L) | 1010.649 | 1 | 1010.649 | 23.29399 | 0.000530 |
| MA (Q) | 21.339 | 1 | 21.339 | 0.49184 | 0.497677 |
| 1L by 2L | 43.006 | 1 | 43.006 | 0.99122 | 0.340841 |
| 1L by 3L | 15.921 | 1 | 15.921 | 0.36696 | 0.556957 |
| 1L by 4L | 0.014 | 1 | 0.014 | 0.00033 | 0.985782 |
| 2L by 3L | 10.332 | 1 | 10.332 | 0.23813 | 0.635142 |
| 2L by 4L | 4.873 | 1 | 4.873 | 0.11232 | 0.743824 |
| 3L by 4L | 54.191 | 1 | 54.191 | 1.24902 | 0.287554 |
| Error | 477.253 | 11 | 43.387 |   |   |
| Total SS | 1872.849 | 25 |   |   |   |

**Table S5** Analysis of variance (ANOVA) for response surface quadratic model

|  |  |
| --- | --- |
| Factor | ANOVA; |
| SS | df | MS | F | p |
| (1)pH (L) | 16.561 | 1 | 16.561 | 0.17222 | 0.686126 |
| pH (Q) | 0.712 | 1 | 0.712 | 0.00740 | 0.932974 |
| (2)IS (L) | 125.053 | 1 | 125.053 | 1.30040 | 0.278361 |
| IS (Q) | 306.019 | 1 | 306.019 | 3.18221 | 0.102021 |
| (3)ET (L) | 37.537 | 1 | 37.537 | 0.39034 | 0.544864 |
| ET (Q) | 24.246 | 1 | 24.246 | 0.25213 | 0.625476 |
| (4)MA (L) | 1896.681 | 1 | 1896.681 | 19.72312 | 0.000993 |
| MA (Q) | 66.230 | 1 | 66.230 | 0.68871 | 0.424248 |
| 1L by 2L | 191.215 | 1 | 191.215 | 1.98840 | 0.186153 |
| 1L by 3L | 53.360 | 1 | 53.360 | 0.55488 | 0.471947 |
| 1L by 4L | 11.280 | 1 | 11.280 | 0.11729 | 0.738442 |
| 2L by 3L | 57.029 | 1 | 57.029 | 0.59303 | 0.457469 |
| 2L by 4L | 32.659 | 1 | 32.659 | 0.33961 | 0.571806 |
| 3L by 4L | 127.795 | 1 | 127.795 | 1.32891 | 0.273435 |
| Error | 1057.819 | 11 | 96.165 |   |   |
| Total SS | 4004.197 | 25 |   |   |   |

**Table S6. Regeneration studies showing the desoportion results after the adsorption-desorption cycles.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **Recovery (%)** |  |  |  |
| **Cycles** | **1** | **2** | **3** | **4** |
| **KET** | **92.5 ± 3** | **91.4 ± 2** | **89.0 ± 6** | **79.3 ± 4** |
| **NAP** | **82.1 ± 4** | **81.7 ± 5** | **80.0 ± 7** | **72.2 ± 2** |
| **DIC** | **94.1 ± 5** | **93.8 ± 3** | **91.7 ± 4** | **81.9 ± 3** |



**Fig. S1.** The FTIR spectrum of WTAC.



**Fig. S2.** The N2 adsorption-desorption isotherms for MWTAC@MeTOACl nanocomposite



**Fig. S3.** Choice of adsorbents between modified and unmodified magnetic waste tyre derived activated carbon (MWTAC). Conditions: extraction time: 10 min, desorption time: 5 min, pH of sample: 7, desorption volume: 2 mL and mass of adsorbent: 50 mg.



**Fig. S4. The Pareto charts of effects of optimization for ketoprofen (KET), naproxen (NAP) and diclofenac (DIC). Abbreviations: (4) MA=mass of adsorbent, (2) IS = % ionic strength, (3) ET = extraction time, (1) pH of sample, 2Lby3L = linear interaction between IS and ET, 2Lby4L = linear interaction between IS and MA , 1Lby2L = linear interaction between pH and IS, 1Lby4L = linear interaction between pH and MA, 3Lby4L = linear interaction between IS and MA and 1Lby3L = linear interaction between pH and ET.**



**Fig. S5.** The desirability of the parameter effects on the preconcentration of NSAIDs**.**

1. Correspondence: *Department of Chemical Sciences, University of Johannesburg*, pnnomngongo@uj.ac.za [↑](#footnote-ref-1)