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# <sup>1</sup> Coconut shell based activated carbon–iron oxide magnetic <sup>2</sup> nanocomposite for fast and efficient removal of oil spills

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#### A R T I C L E I N F O

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#### A B S T R A C T

An efficient magnetic adsorbent nanocomposite material is prepared by simple chemical methods using coconut shell based activated carbon and iron oxide nanoparticles. The composite material shows good oil retention capacity with fast kinetics and can be recovered along with the adsorbed oil by using an external magnet. The adsorbent material can be reused after recovering either by heat treatment of by solvent extraction. Hence, the magnetic nanocomposite is shown to be an efficient and recyclable potential candidate for removal of oil spills by magnetic separation.

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#### <sup>6</sup> Introduction

7 Our aquatic ecosystem is under constant threat due to the<br>8 possibility of oil spillage from different sources. Massive and <sup>8</sup> possibility of oil spillage from different sources. Massive and  $\frac{9}{2}$  momentary oil spillages came from the urgelage of china and oil <sup>9</sup> momentary oil spillages come from the wreckage of ships and oil<br> $\frac{10}{10}$  tankage whereas a clow and steady contribution somes from the 10 tankers, whereas a slow and steady contribution comes from the inductrial effluents or by the oil leakage from machineries and pine  $11$  industrial effluents or by the oil leakage from machineries and pipe<br> $12$  lines which eventually reaches the rivers and other subtervances  $12$  lines which eventually reaches the rivers and other subterranean  $13$  uniter systems  $[1]$ . Different techniques like skimmers, floating  $13$  water systems [\[1\].](#page--1-0) Different techniques like skimmers, floating<br>14 have expressive and the system of the selection of the polynomy 14 barriers, synthetic organophillic sorbent materials like polypropyl-<br>15 and polypthylope terms halote eilige agreeds reglites ergano  $15$  ene, polyethylene terephthalate, silica aerogels, zeolites, organo-<br> $16$  enhilia alays orgalisted graphics graphene frameworks cellulated  $^{16}$  phillic clays, exfoliated graphite, graphene frameworks, cellulose<br> $^{17}$  fiber cellagen fibers atc bays been employed in claaning up the oil 17 fiber, collagen fibers etc. have been employed in cleaning up the oil<br>18 field 1.5 l The meet important criteria that should be met by any <sup>18</sup> spills  $[1-5]$  $[1-5]$ . The most important criteria that should be met by any protocol to be used on large scale for such an environmental  $19$  material to be used on large scale for such an environmental  $20$  annieation are the efficiency recyclobility and biocompatibility. <sup>20</sup> application are the efficiency, recyclability and biocompatibility.<br>21 Even though manual the currently weilable expent materials estisfy <sup>21</sup> Even though many of the currently available sorbent materials satisfy<br>22 **Exercise in the suffer a major disclusive that the semand of** <sup>22</sup> these criteria, they suffer a major disadvantage that the removal of  $\frac{23}{100}$  seekent materials along with the adsorbed all from the agustic <sup>23</sup> sorbent materials along with the adsorbed oil from the aquatic  $\frac{23}{4}$ <sup>24</sup> system after the oil adsorption is tedious and time consuming task<br>25 september of the consumer of the consumer of the consuming task <sup>25</sup> considering that large quantity of oil has to be removed quite quickly  $^{26}$  and efficiently to prevent further spreading. This disadvantage can be 27 surpassed by adding a magnetic functionality to the sorbent material  $\frac{28}{100}$  which facilitates the fact resovery in the presence of a magnetic and which facilitates the fast recovery in the presence of a magnet and

<http://dx.doi.org/10.1016/j.jece.2015.04.028> 2213-3437/ $\circ$  2015 Published by Elsevier Ltd. thereby increasing the total efficiency of the process  $[5,6]$ . Therefore,  $^{29}$ <br>a composite made from a magnetic material and a suitable adsorbent  $^{30}$ a composite made from a magnetic material and a suitable adsorbent  $^{30}$ serves as a potential candidate for a fast oil clean up. However, the  $31$ composite as a whole and especially the magnetic material should be  $32$ <br>biocompatible to avoid any cocondary pollution in aquatic quotame biocompatible to avoid any secondary pollution in aquatic systems  $33$ <br>by the adocrhant/composite material along with the cost offective  $34$ by the adsorbent/composite material, along with the cost effective-<br>ness of the whole process and the ease of production of the  $35$ ness of the whole process and the ease of production of the  $\frac{35}{2}$  composite material in required bulk quantities  $\frac{23}{2}$ composite material in required bulk quantities.  $^{133}$ <br>Superparameteric iron oxide paperarticles SPIONs (Fe-O,  $^{37}$ 

Superparamagnetic iron oxide nanoparticles, SPIONs ( $Fe<sub>3</sub>O<sub>4</sub>$   $37$ )<br>de: Eq. O  $\lambda$  due their good magnetic proportion biogeomortibili and  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>), due their good magnetic properties, biocompatibili-<br>ty and low gut to visity find applications in targeted drug delivery. ty and low cytotoxicity, find applications in targeted drug delivery,  $\frac{39}{2}$ <br>magnetic byparthermia, as MPL contrast ophaneoment agent, atc.  $\frac{40}{2}$ magnetic hyperthermia, as MRI contrast enhancement agent, etc.  $\frac{40}{21}$  and they have been studied as the magnetic part of the sorbent  $\frac{41}{21}$ [\[7\]](#page--1-0), and they have been studied as the magnetic part of the sorbent  $\frac{41}{2}$ <br>material [5.6]. Different, types of magnetic sorbents, such as  $\frac{42}{3}$ material [\[5,6\]](#page--1-0). Different types of magnetic sorbents such as  $42$ <br>collaren fiber SPION composites [5], Eo O @C care shall pape.  $43$ collagen fiber-SPION composites [\[5\],](#page--1-0) Fe<sub>2</sub>O<sub>3</sub>@C core–shell nano-<br>particles [\[6\]](#page--1-0), Fe–Carbon nanocomposites [\[8\]](#page--1-0), magnetic floating 44<br>forms [0] iron incorporated carbon papetube sponges [10] metal foams  $[9]$ , iron incorporated carbon nanotube sponges  $[10]$ , metal-<br>organic framework (MOF) derived porous carbon iron ovide organic framework (MOF) derived porous carbon–iron oxide <sup>46</sup><br>nanogeomogeita.[11] magnetic exfeliated graphita.[12] apexidinad 47 nanocomposite [\[11\],](#page--1-0) magnetic exfoliated graphite [\[12\],](#page--1-0) epoxidized  $47$ <br>natural rubber, magnetite nanocomposites [12], polystyreno, iron  $48$ natural rubber–magnetite nanocomposites [\[13\]](#page--1-0), polystyrene–iron <sup>48</sup><br>oxide panocomposites [14], palm shell, based astivated carbon 49 oxide nanocomposites [\[14\]](#page--1-0), palm shell based activated carbon– $\frac{49}{150}$ <br>ison oxide composite [15] ats, baye been studied for the remayal of 50 iron oxide composite  $[15]$  etc., have been studied for the removal of  $50$ <br>oil, by magnetic contration. Many of these materials, like the  $51$ oil by magnetic separation. Many of these materials like the  $51$ <br>magnetic floating forms magnetic fl macroporous carbon nanotubes, magnetic floating foams, mag-<br>notic syfoliated graphite. MOE derived persus explore iron syide netic exfoliated graphite, MOF derived porous carbon–iron oxide 53<br>composite and polygturens iron oxide composite are good in 54 composite and polystyrene–iron oxide composite are good in  $54$ <br>terms of their eil retartion expects. However, the synthesis of  $55$ terms of their oil retention capacity. However, the synthesis of  $^{55}$ <br>these materials includes relatively complex procedures and costly these materials includes relatively complex procedures and costly<br>chamicals with low vield so that a cost effective bulk production 57 chemicals, with low yield, so that a cost effective bulk production  $57$ <br>for real time application is impossible [9, 12,14]. Comparatively for real time application is impossible  $[9-12,14]$ . Comparatively

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 $59$  cheaper natural sorbent materials like collagen fibers, epoxidized  $60$  extend without material subsequently activited exthen  $^{60}$  natural rubber and palm shell based chemically activated carbon  $^{61}$  $^{61}$  have been proposed to overcome the major issues, after  $^{62}$  issues attention with different meanwhich proposational Haussman  $^{62}$  incorporating with different magnetic nanoparticles. However,<br> $^{63}$  they also suffer with either a low eil retention cancely or a very  $^{63}$  they also suffer with either a low oil retention capacity or a very<br> $^{64}$  clow response time which reduces the efficiency of the process  $^{64}$  slow response time which reduces the efficiency of the process  $^{65}$   $^{15}$  12.151 Therefore search for a chann and efficient material which  $^{65}$  [\[5,13,15\]](#page--1-0). Therefore, search for a cheap and efficient material which<br> $^{66}$  can actually be used for immediate containment and/or sudden  $^{66}$  can actually be used for immediate containment and/or sudden  $^{67}$  removal of large oil spills is still an open area of research  $^{67}$  removal of large oil spills is still an open area of research.<br> $^{68}$  Cocoput shell based carbon bas been extensively used

 $^{68}$  Coconut shell based carbon has been extensively used as an  $^{69}$  adsorbent for various applications because of its bigh surface area  $^{69}$  adsorbent for various applications because of its high surface area  $^{70}$  $^{70}$  and porosity. The microstructure of pyrolyzed carbon is known to  $^{71}$  depend critically on the carbon course and bence a persus carbon  $^{71}$  depend critically on the carbon source and hence a porous carbon  $^{72}$  source like cosoput shall can produce highly porous carbon with  $72$  source like coconut shell can produce highly porous carbon with  $73$  high surface area and good sorption properties on pyrolusis  $^{73}$  high surface area and good sorption properties, on pyrolysis  $^{74}$  [16.17] In this manuscript we report the use of a composite made  $^{74}$  [\[16,17\].](#page--1-0) In this manuscript, we report the use of a composite made<br> $^{75}$  from assessive shall derived astivated sarbon and SPIONs for  $^{75}$  from coconut shell derived activated carbon and SPIONs for  $^{76}$  containment and removal of oil spills. The main reason for the  $^{76}$  containment and removal of oil spills. The main reason for the  $^{77}$  coloction of seconal shall as the exploration course in the present work  $77$  selection of coconut shell as the carbon source in the present work<br> $78$  is its again availability and gost offertiveness which makes the  $^{78}$  is its easy availability and cost effectiveness which makes the  $^{79}$  $79$  material an ideal source for large scale production of activated  $80$  scale  $\mu$  and  $\mu$   $\frac{80}{100}$  carbon. In order to prepare stable composites with iron oxide and  $\frac{81}{1000}$  to calculate all attention acceleration of  $\frac{81}{1000}$  $\frac{81}{2}$  to enhance the oil retention capacity by increasing the porosity and  $\frac{82}{2}$  $\frac{82}{100}$  surface area, the carbon material was activated by two different 83 activation techniques before incorporating iron oxide nanopar-<br>84 ticles a liquid phase acid activation and a solid phase  $KOM$  $^{84}$  ticles, a liquid phase acid activation and a solid phase KOH<br> $^{85}$  activation at high temperatures activation at high temperatures.

# <sup>86</sup> Experimental

## <sup>87</sup> Materials used

88 Analytical grade iron(II) chloride tetrahydrate (FeCl<sub>2</sub>·4H<sub>2</sub>O),  $\frac{89}{1500}$  iron(II) chloride hovehydrate (FeCl<sub>2</sub> EU O),  $25\%$  ammonia colu <sup>89</sup> iron(III) chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O), 25% ammonia solu-<br><sup>90</sup> tion Conc. H SO conc. HNO and *VOH* were purchased from <sup>90</sup> tion, Conc. H<sub>2</sub>SO<sub>4</sub>, Conc. HNO<sub>3</sub> and KOH were purchased from<br><sup>91</sup> Marck Chamicals and used as received Locally available coconut 91 Merck Chemicals and used as-received. Locally available coconut  $92$  shall was used as the carbon source. For oil removal studies two  $^{92}$  shell was used as the carbon source. For oil removal studies, two  $^{93}$  kinds of oils were used, red colored new premium oil and black  $^{93}$  kinds of oils were used, red colored new premium oil and black<br> $^{94}$  colored used oil colored used oil.

### 95 Preparation of activated carbon

96 Dried coconut shell was pyrolyzed at  $1000^{\circ}$ C in a horizontal <sup>97</sup> tubular furnace under flowing nitrogen atmosphere. The pyrolyzed<br> $\frac{98}{200}$  carbon obtained was exubed and ground to fine pourder using an 98 carbon obtained was crushed and ground to fine powder using an  $\frac{99}{2}$ <sup>99</sup> agate mortar and pestle. For liquid phase acid activation, 10 g of the  $^{100}$  pyrolized carbon pouderwas refluxed with 125 ml of 20% (*vly*) HNO <sup>100</sup> pyrolyzed carbon powder was refluxed with 125 ml of 20% (v/v)HNO<sub>3</sub><br><sup>101</sup> and 125 ml of 20% (v/v) H\_SO\_at 110 % for 00 min [18]. The activated 101 and 125 ml of 20% (v/v)  $H_2$ SO<sub>4</sub> at 110 °C for 90 min [\[18\].](#page--1-0) The activated<br>102 cample was washed several times with double distilled water till <sup>102</sup> sample was washed several times with double distilled water till<br> $^{103}$  poutral pH and then dried in an oven (sample sede AC). The base <sup>103</sup> neutral pH and then dried in an oven (sample code AC). The base<br><sup>104</sup> activation was carried out by a liquid state KOH impregnation of the <sup>104</sup> activation was carried out by a liquid state KOH impregnation of the  $^{105}$  pyrolyzed carbon (5 g) at 1:3 carbon to KOH (15 g) weight ratio for <sup>105</sup> pyrolyzed carbon (5 g) at 1:3 carbon to KOH (15 g) weight ratio for  $106 - 24$  by followed by drying and beating at  $1000\degree$ C under argon  $106$  24h, followed by drying and heating at  $1000^{\circ}$ C under argon  $107$  atmosphere in a tubular furnace  $171$ . The activated sample was <sup>107</sup> atmosphere in a tubular furnace  $[17]$ . The activated sample was<br><sup>108</sup> washed till neutral pH with double distilled water and dried in an <sup>108</sup> washed till neutral pH with double distilled water and dried in an  $109$  oven (sample code KC) oven (sample code KC).

<sup>110</sup> Preparation of activated carbon–iron oxide composite

111 Activated carbon/iron oxide composites were prepared by in<br>112  $\frac{1}{2}$  situ so precipitation technique using both AC and KC 1191. The <sup>112</sup> situ co-precipitation technique using both AC and KC  $[19]$ . The  $[13]$  activated carbon to iron oxide weight ratio in the final composite <sup>113</sup> activated carbon to iron oxide weight ratio in the final composite<br><sup>114</sup> material was fixed as 1:1.0.5 g of AC was first dispersed in water to <sup>114</sup> material was fixed as 1:1.0.5 g of AC was first dispersed in water to  $\frac{115}{115}$  which a 2:1 malar minture of FoCl. EU Q (11.5770.5) and FoCl. <sup>115</sup> which a 2:1 molar mixture of FeCl<sub>3</sub>·6H<sub>2</sub>O (11.6770 g) and FeCl<sub>2</sub>·<br><sup>116</sup> 4H<sub>2</sub>O (4.2943 g) was added and stirred for 2 h, after de-aerating<br><sup>117</sup> with argon gas. The argon flow was maintained and the all was with argon gas. The argon flow was maintained and the pH was

then adjusted to 12 using 25% ammonia solution to precipitate the  $118$ <br>interval in the precipitation of the precipitation that iron oxide nanoparticles. The precipitate was then heated in the  $119$ <br>another linear at 2006 for 1 k to feelilists the hinding of the mother liquor at 80 °C for 1 h to facilitate the binding of the nanoparticles to the surface functionalities of activated carbon  $121$ <br>[10] The final magnetic composite was magnetically converted [\[19\].](#page--1-0) The final magnetic composite was magnetically separated  $122$ <br>from a small fraction of light weight non-magnetic part present in from a small fraction of light weight non-magnetic part present in <sup>123</sup><br>the superpatant colution and then washed several times till poutral 124 the supernatant solution and then washed several times till neutral  $124$ <br>nH. The weight of this discarded pertien was less than 0.5% of the pH. The weight of this discarded portion was less than 0.5% of the  $125$ <br>weight of *VC* or AC used during the synthesis. Hence, the quantity weight of KC or AC used during the synthesis. Hence, the quantity  $126$ <br>of this small portion lost during the preparation of the composite of this small portion lost during the preparation of the composite  $127$ <br>une preclected during the solution of the eil patenties are exitual was neglected during the calculation of the oil retention capacity of  $128$ <br>ACS and KCS with gasp as the the smaximal factivited earlier present ACf and KCf with respect to the amount of activated carbon present  $129$ <br>in the material. The product was then dried in an even to obtain AC in the material. The product was then dried in an oven to obtain AC  $^{130}$ <br>iron ovide composite material (cample sode: ACf), KC iron ovide  $^{131}$  $\frac{131}{131}$  –iron oxide composite material (sample code: ACf). KC–iron oxide  $\frac{131}{132}$ 00 composite material was prepared by a similar procedure using the  $132$ <br>same amount of KC and iron oxide precursors (sample code: KCf) same amount of KC and iron oxide precursors (sample code: KCf).

## <sup>134</sup> Determination of oil adsorption capacity

The oil adsorption capacities of AC, KC, ACf and KCf were  $135$ <br>termined by using weight measurements. For eil removal determined by using weight measurements. For oil removal  $136$ <br>studies  $2 \times 3$  we have denote the set studies, 2 g oil was poured on top of 10 ml water taken in a petridish to create an artificial oil spill. A weighed amount of the  $138$ <br>material superconduction is all and then united for a small spill. material was smeared over the oil and then waited for a specific  $139$ <br>time hefore the eil adocted material was separated from the time before the oil adsorbed material was separated from the  $140$ <br>artificial cpill. On performing the experiment with magnetic artificial spill. On performing the experiment with magnetic  $141$ <br>composite ACf and *VCf* the sil adsorbed composite was resourced  $142$  composite ACf and KCf, the oil adsorbed composite was recovered  $142$ <br>by magnetic concration using a permanent magnet and then dried by magnetic separation using a permanent magnet and then dried  $143$ <br>exergisht at 100 °C to remove water. However, when AC and  $K_C = 144$ overnight at 100 °C to remove water. However, when AC and KC  $144$ <br>were used to remove the oil from the artificial spillare, the oil were used to remove the oil from the artificial spillage, the oil  $145$ <br>adsorbed material was separated by filtration, and the filtered adsorbed material was separated by filtration, and the filtered  $146$ <br>material was then dried under similar conditions as in the case of material was then dried under similar conditions as in the case of  $147$ <br>using ACS and KCS. The sil patentian sensative (b) of ACS KCS, AC and using ACf and KCf. The oil retention capacity  $(k)$  of ACf, KCf, AC and  $148$ <br>  $\frac{148}{149}$ KC, per gram of carbon, was determined by using the relation  $149$ <br> $h_2(h_2 g)$  where 'q' is the woight (in gram) of the adsorbant  $k = (b - a)/a$ , where 'a' is the weight (in gram) of the adsorbent  $150$ <br>material smoored on top of the oil layer and 'b' is the weight (in material smeared on top of the oil layer and 'b' is the weight (in  $\frac{151}{252}$ gram) of the oil adsorbed material recovered from the artificial oil  $152$ <br>spill after drying. The retention capacity (k) of ACf and KCf was spill after drying. The retention capacity  $(k)$  of ACf and KCf was  $153$ <br>calculated with respect to the weight of carbon present in the calculated with respect to the weight of carbon present in the  $154$ <br>composites in order to compare the results with that of AC and KC composites in order to compare the results with that of AC and KC.

### <sup>156</sup> Characterization techniques

All materials were characterized using powder X-ray diffraction  $157$ <br>
2D) see Phillips Yleast Pre-different proprietor Gu K, and intitate  $158$ (XRD) on a Phillips X'pert Pro diffractometer using Cu K $\alpha$  radiation.  $158$ <br>Infrared (IB) another wave generaled are a Prysian Tenant 27 FT IB Infrared (IR) spectra were recorded on a Bruker Tensor-27 FT-IR  $^{159}$ <br>spectromater, and the magnetic measurement was performed  $^{160}$ spectrometer and the magnetic measurement was performed  $160$ <br>using a Quantum Dosign MPMS 7T SOUID VSM TEM images were  $161$ using a Quantum Design MPMS 7T SQUID VSM. TEM images were  $161$ <br>obtained using a FEL TECNAL C2 TE 20 transmission electron  $162$ obtained using a FEI, TECNAI G2 TF 30 transmission electron  $162$ <br>microscope. The surface area and perseity measurements were  $163$ microscope. The surface area and porosity measurements were  $163$ <br>porformed using a Quantashrome Quadrascrb automatic volu performed using a Quantachrome Quadrasorb automatic volu-<br>motric instrument Temperature dependent eil adsorption studies and 165 metric instrument. Temperature dependent oil adsorption studies  $165$ <br>were performed after maintaining the temperature using a  $166$ were performed after maintaining the temperature using a  $166$ <br>refrigerated simulating  $FQ$ UPATU refrigerated circulating EQUIBATH.

# Results and discussion and  $168$

### <sup>169</sup> Characterization of the materials

Both acid and base activations are known to introduce different  $170$ <br>here of overgon functionalities on the carbon surface by partial  $171$ types of oxygen functionalities on the carbon surface by partial  $171$ <br>oxidation of carbon [20.21]. However during KOH activation apart  $172$ oxidation of carbon  $[20,21]$ . However, during KOH activation, apart  $172$ <br>from the surface modification, large numbers of pores are also from the surface modification, large numbers of pores are also  $173$ <br>formed by positivity of scales through a spairs of chamical  $174$ formed by gasification of carbon through a series of chemical  $174$ <br>meeting [22.22] Polyni 700.06 the main and ute an actualism. reactions  $[22,23]$ . Below 700 °C, the main products are potassium  $175$ oxide, carbon monoxide, carbon dioxide, hydrogen and potassium

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