Environmentally benign, copper nanoparticles supported on walnut shell as highly durable nanocatalyst for synthesis of the propargylamines

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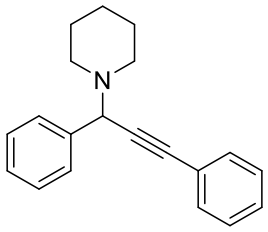
Content

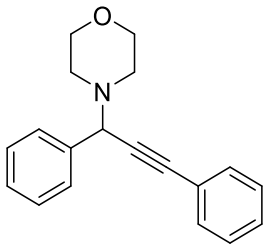
Characterizations of products

1-(1, 3-diphenylprop-2-yn-1-yl) piperidine (Table 3, entry 1):



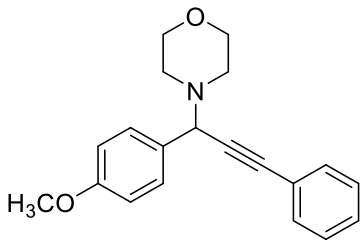
^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.51-7.65 (m, 2H), 7.57 (d, 2H, *J*=5 Hz), 7.35-7.39 (m, 6H), 4.85 (s, 1H), 2.62 (br, 4H), 1.67-1.48 (m, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 137.95, 131.8, 129.7, 128.3, 128.1, 127.6, 123.18, 88.17, 85.6, 62.4, 50.7, 25.92, 24.3.

4-(1, 3-diphenylprop-2-yn-1-yl) morpholine (Table 3, entry 2):



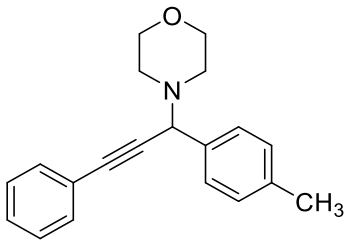
^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.62-7.65 (m, 2H), 7.52 (m, 2H), 7.24-7.37 (m, 6H), 4.80 (s, 1H), 3.73 (br, 4H), 2.64 (br, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 137.73, 131.8, 128.6, 128.21, 127.77, 122.94, 88.5, 85.02, 67.13, 62.03, 49.86.

4-(1-(4-methoxyphenyl)-3-phenylprop-2-yn-1-yl) morpholine (table 3-2 entry 13):



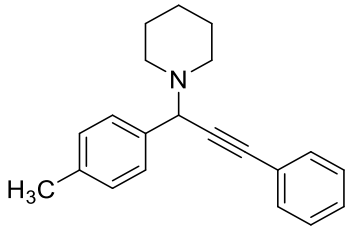
^{1}H NMR ($CDCl_3$, 250 MHZ): δ 7.52-7.55 (m, 4H), 7.27-7.33 (m, 3H**),** 6.68-6.92 (d, 2H), 4.74 (s, 2H), 3.82 (s, 3H), 3.74 (br, 4H), 2.62 (br, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 159.18, 131.77, 129.71, 128.27, 128.19, 123.01, 113.56, 87.95, 85.34, 67.07, 61.44, 55.27, 49.76.

4-(3-phenyl-1-(*p*-tolyl) prop-2-yn-1-yl) morpholine (Table 3, entry 4):



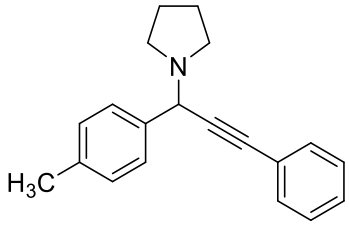
^{1}H NMR ($CDCl_3$, 250 MHZ): δ 7.34-7.52 (m, 4H), 7.16-7.33 (m, 5H), 4.75 (s, 1H), 3.72 (br, 4H), 2.63 (br, 4H), 2.36 (s, 3H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 137.49, 134.78, 131.78, 129.14, 128.90, 128.50, 128.27, 128.18, 123.09, 88.23, 85.32, 67.13, 61.78, 49.86, 21.10.

1-(3-phenyl-1-(*p*-tolyl) prop-2-yn-1-yl) piperidine (Table 3, entry 5):



^{1}H NMR ($CDCl_3$, 250 MHZ): δ 7.44-7.48 (m, 4H), 7.16-7.34 (m, 5H), 4.71 (s, 1H), 2.55-2.59 (m, 4H), 2.36 (s, 3H), 1.44-1.61 (m, 6H); ^{13}C NMR ($CDCl_3$, 62.9MHz): 137.19, 135.63, 131.79, 128.74, 128.47, 128.35, 127.98, 123.51, 87.59, 86.46, 62.22, 50.65, 26.15, 24.55, 21.2.

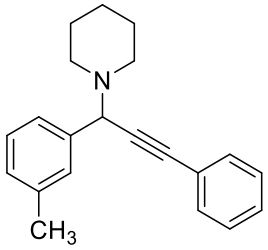
1-(3-phenyl-1-(*p*-tolyl) prop-2-yn-1-yl) pyrrolidine (Table 3, entry 6):



^{1}H NMR ($CDCl_3$, 250 MHZ): δ 7.30-7.48 (br, 4H), 7.15-7.26 (m, 5H), 4.93 (s, 1H), 2.72 (br, 4H),

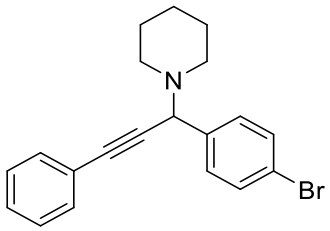
2.39 (s, 3H), 1.81 (br, 4H); ^{13}C NMR ($CDCl_3$, 62.9MHz): 137.3, 131.77, 128.89, 128.19, 128.24, 128.01, 123.41, 87.62, 86.6, 58.75, 50.22, 23.4, 21.04.

1-(3-phenyl-1-(*m*-tolyl) prop-2-yn-1-yl) piperidine (Table 3, entry 7):



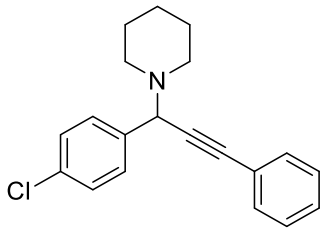
^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.18-7.48 (m, 8H), 7.09-7.12 (m, 1H), 4.75 (s, 1H), 2.53 (br, 4H), 2.38 (s, 3H), 1.38-1.55 (br, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 138.52, 137.63, 131.79, 129.25, 128.99, 128.48, 128.23, 128.02, 127.9, 125.71, 123.42, 87.7, 86.30, 62.45, 50.78, 30.23, 26.15, 24.43, 21.55.

1-(1-(4-bromophenyl)-3-phenylprop-2-yn-1-yl) piperidine (Table 3, entry 8):



^{1}H NMR ($CDCl_3$, 250 MHZ): δ 7.45-7.55 (m, 6H), 7.33-7.35 (m, 3H), 4.75 (s, 1H), 2.52-2.56 (br, 4H), 1.45-1.62 (m, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 145.41, 137.8, 131.8, 131.14, 130.18, 129.01, 128.51, 128.21, 123.05, 121.36, 88.27, 85.23, 61.76, 50.62, 26.11, 24.36.

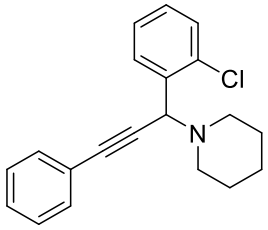
1-(1-(4-chlorophenyl)-3-phenylprop-2-yn-1-yl) piperidine (Table 3, entry 9):



^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.41-7.55 (m, 4H), 7.21-7.39 (m, 5H), 4.71 (s, 1H), 2.48 (br, 4H),

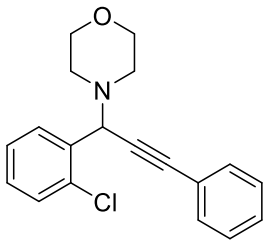
1.44-1.6 (m, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 137.02, 131.79, 129.51, 128.95, 128.50, 128.29, 128.22, 123.11, 87.54, 85.58, 61.42, 50.34, 26.13, 24.08.

1-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl) piperidine (Table 3, entry 10):



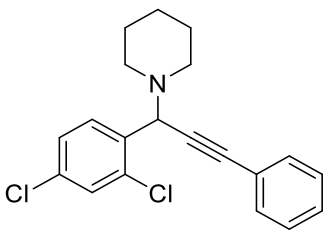
^{1}H NMR ($CDCl_3$, 250 MHZ): δ 7.76-7.73 (m, 2H), 7.49 (br, 2H), 7.26-7.41 (m, 5H), 5.10 (s, 1H), 2.61 (br, 4H), 1.55-1.60 (m, 4H), 1.42-1.46 (m, 2H); ^{13}C NMR ($CDCl_3$, 69.2 MHz): 136.39, 134.63, 131.77, 130.55, 129.76, 128.73, 128.25, 128.1, 126.15, 123.05, 87.50, 85.8, 59.23, 50.73, 26.12, 24.43.

4-(1-(2-chlorophenyl)-3-phenylprop-2-yn-1-yl) morpholine (Table 3, entry 11):



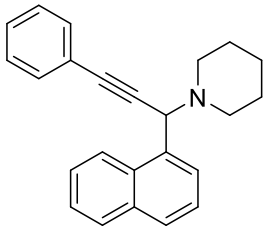
^{1}H NMR ($CDCl_3$, 250 MHZ): δ 7.70 (br, 1H), 7.50 (br, 2H), 7.26-7.43 (m, 6H), 5.14 (s, 1H), 3.715 (br, 4H), 2.68 (br, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 135.45, 134.63, 131.80, 130.56, 129.88, 129.67, 129.15, 128.31, 126.37, 122.75, 88.37, 84.38, 67.03, 58.92, 49.82.

1-(1-(2,4-dichlorophenyl)-3-phenylprop-2-yn-1-yl)piperidine (Table 3, entry 12) :



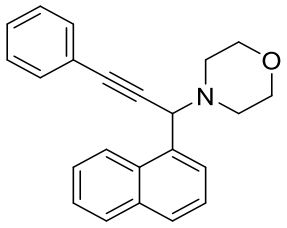
^{1}H NMR ($CDCl_3$, 250 MHZ): δ 7.72(d, J= 10 Hz, 1H), 7.25-7.49 (m, 7H), 5.05 (s, 1H), 2.60 (br, 4H), 1.43-1.57 (br, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 135.28, 133.94, 131.79, 131.44, 129.55, 128.31, 126.57, 122.8, 88.14, 84.97, 58.83, 50.75, 25.95, 24.3.

1-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl) piperidine (Table 3, entry 13):



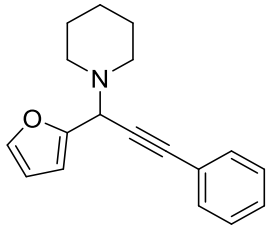
^{1}H NMR ($CDCl_3$, 250 MHZ): δ 8.475 (d, J=7.5 Hz, 1H), 7.74-7.91 (m, 3H), 7.27-7.51 (m, 8H), 5.51 (s, 1H), 2.62 (br, 4H), 1.51-1.60 (m, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 134.08, 132.35, 131.88, 128.63, 128.44, 128.35, 128.10, 126.96, 125.81, 125.60, 125.04, 124.82, 123.47, 88.62, 85.9, 60.52, 50.76, 26.28, 24.6.

4-(1-(naphthalen-1-yl)-3-phenylprop-2-yn-1-yl) morpholine (Table 3, entry 14):



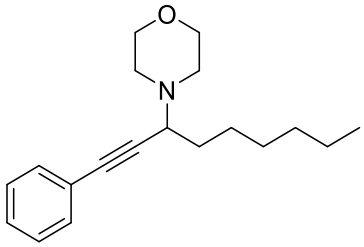
^{1}H NMR ($CDCl_3$, 250 MHZ): δ 8.345 (d, J= 7.5 Hz 1H), 7.50-7.90 (m, 3H), 7.21-7.49 (m, 8H), 5.45 (s, 1H), 3.64-3.69 (br, 4H), 2.71-2.73 (br, 4H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 134.08, 133.11, 131.75, 131.6, 128.90, 128.43, 128.33, 128.25, 128.18, 127.11, 125.90, 125.69, 124.72, 123.05, 88.95, 84.98, 67.14, 60.17, 49.7.

1-(1-(furan-2-yl)-3-phenylprop-2-yn-1-yl) piperidine (Table 3, entry 15):



^{1}H NMR ($CDCl_3$, 250 MHZ): δ 7.43-7.52 (m, 3H), 7.26-7.34 (m, 3H), 6.485 (d, J=2.5 Hz, 1H), 6.355 (d, J=2.5 Hz, 1H), 4.87 (s, 1H), 2.59 (br, 4H), 1.42-1.70 (m, 6H); ^{13}C NMR ($CDCl_3$, 62.9 MHz): 151.62, 142.53, 131.83, 128.25, 122.93, 109.94, 109.20, 86.37, 83.83, 56.53, 50.51, 25.94, 24.28.

4-(1-phenyl-non-1-yn-3-yl) morpholine (Table 3, entry 16):



^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.43 (br, 2H), 7.20-7.30 (br, 3H), 3.75-3.78 (br, 4H), 3.48 (t, 1H, *J*=7.2 Hz), 2.72 (br, 2H), 2.59 (br, 2H), 1.67-1.73 (m, 2H), 1.31-1.50 (m, 9H), 0.86-0.89 (m, 3H). ^{13}C NMR ($CDCl_3$, 62.9 MHz): 131.70, 128.19, 127.92, 123.25, 87.17, 86.12, 67.13, 58.13, 49.73, 32.93, 31.72, 29.65, 29.01, 26.53, 22.59, 14.05.

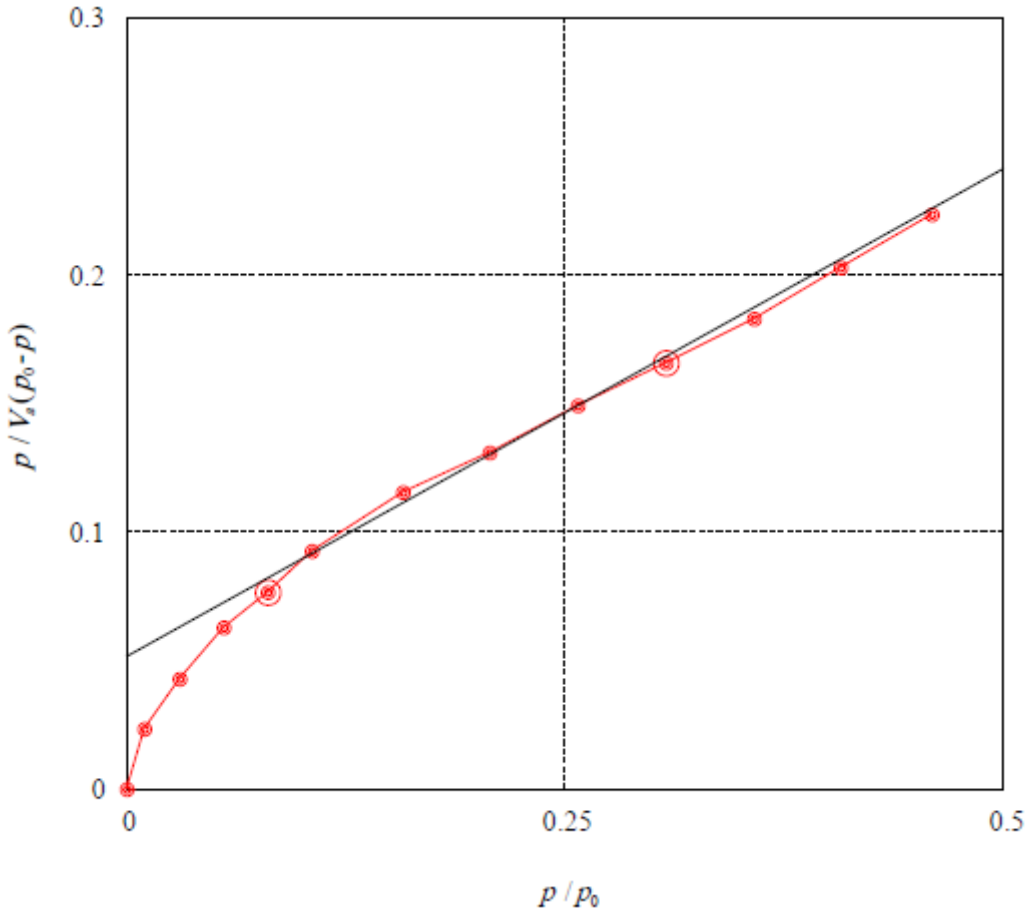


Fig. A1. BET-Plot of walnut shell (WS).

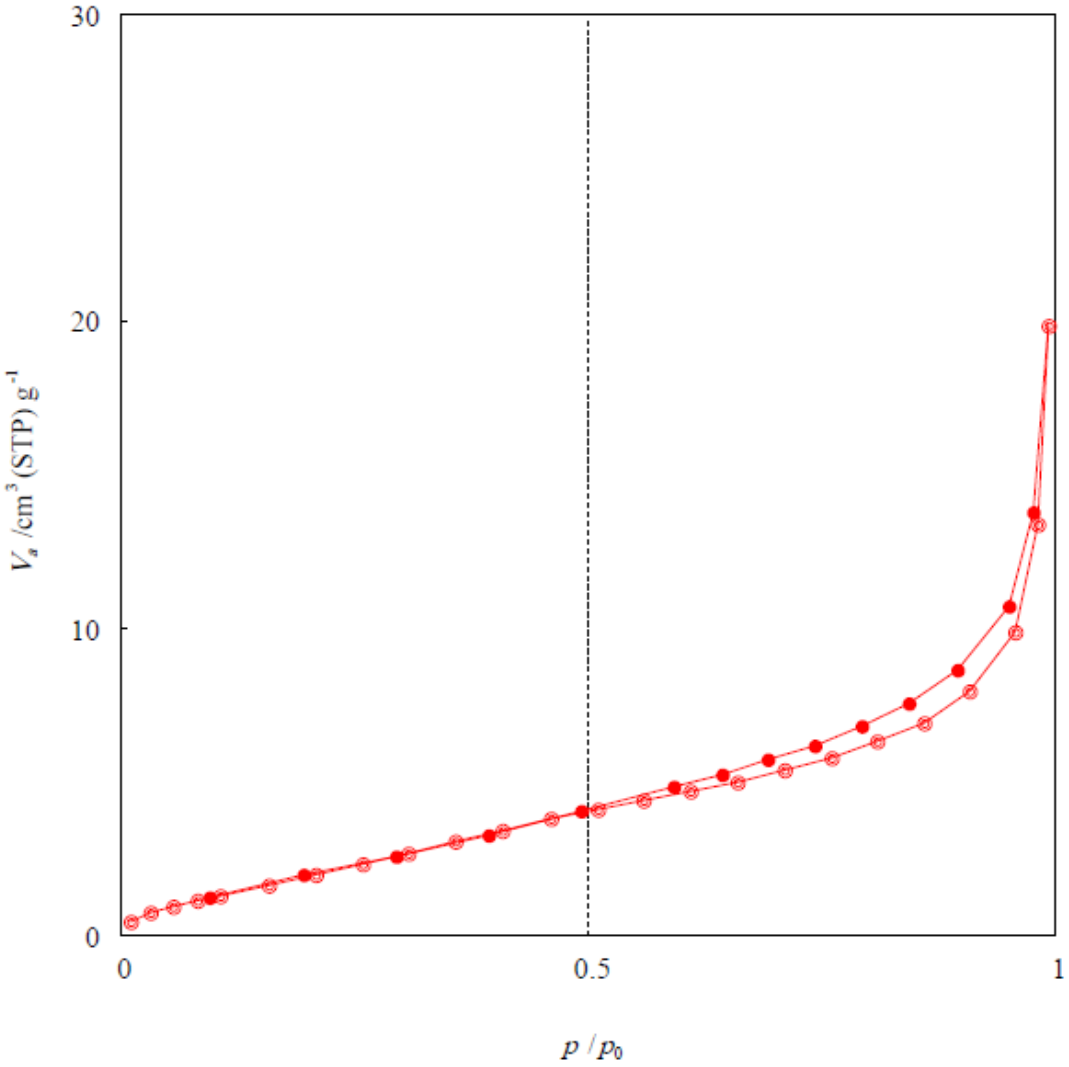


Fig. A2. Adsorption / desorption isotherm of walnut shell (WS).

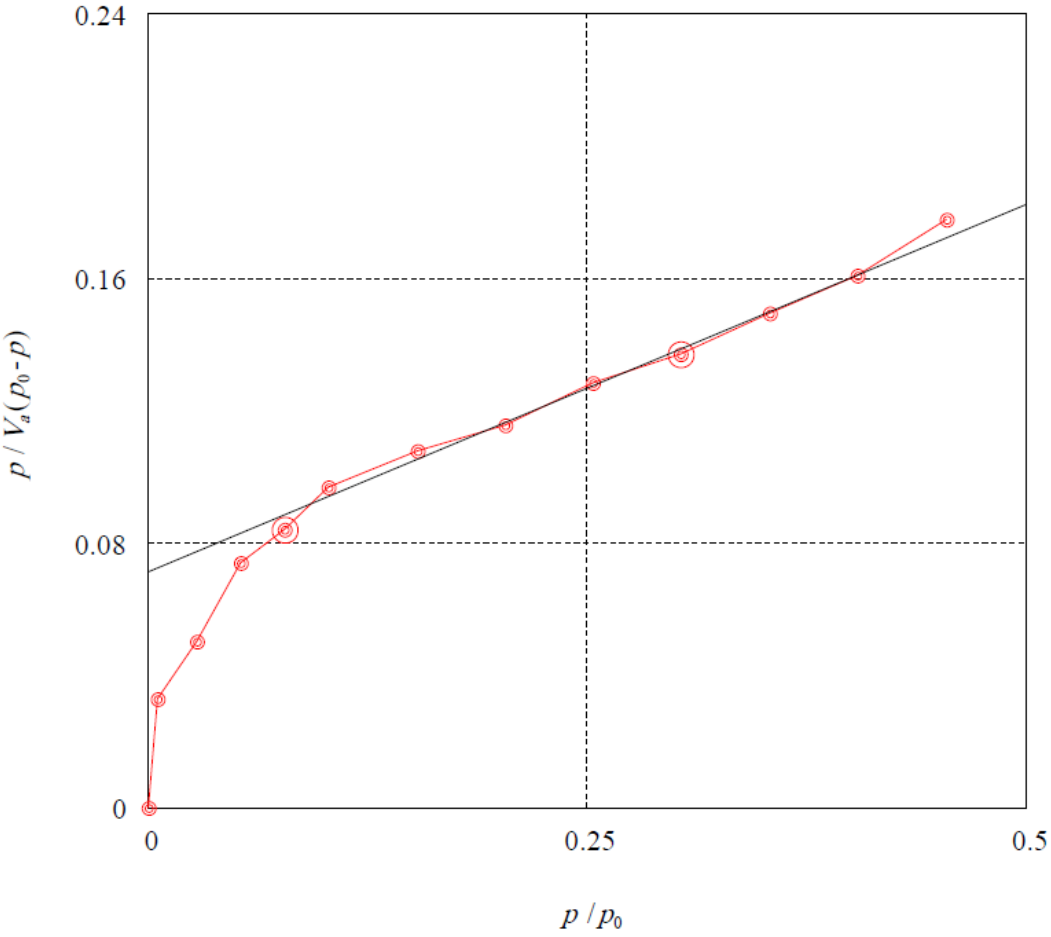


Fig. A3. BET-Plot of Cu nanoparticles supported on walnut shell (CuNPs@WS)

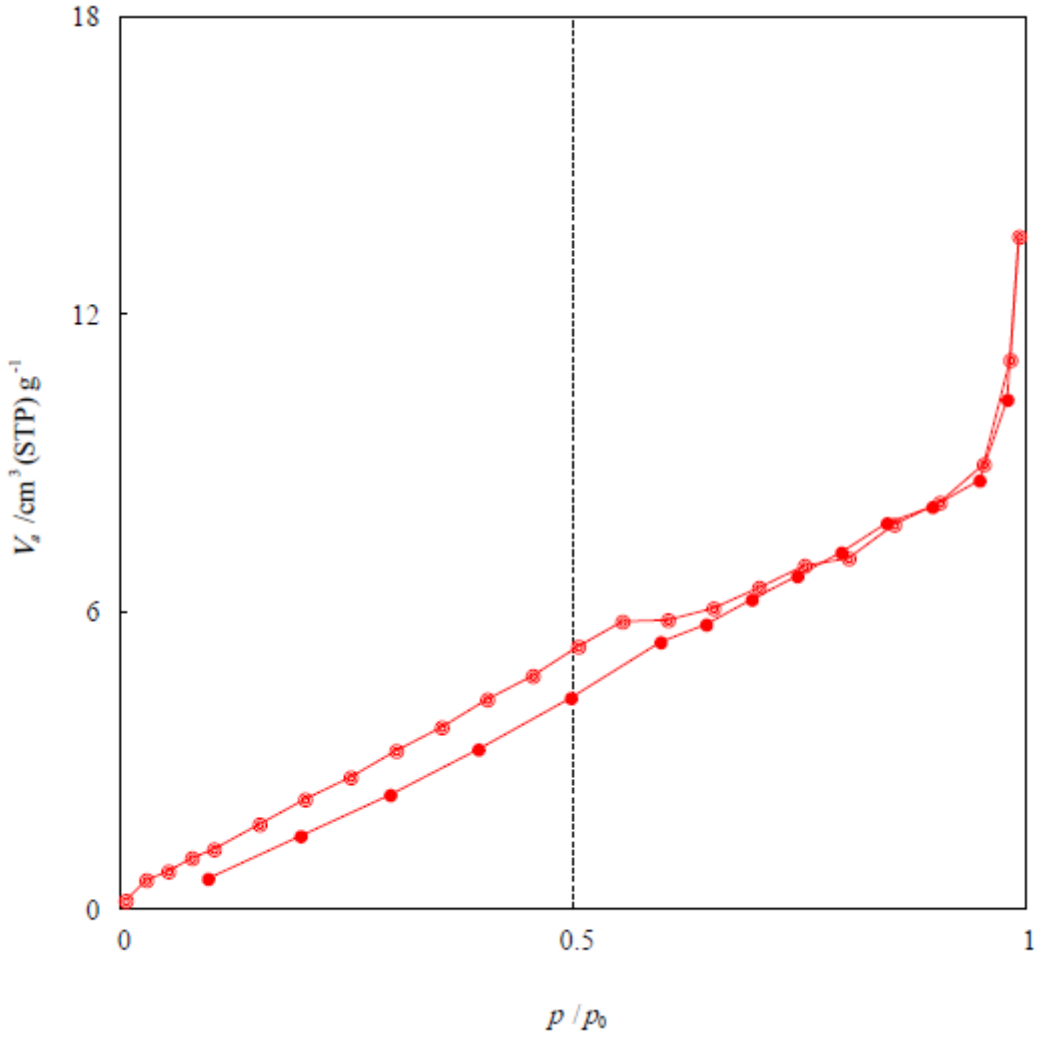


Fig. A4. Adsorption / desorption isotherm of Cu nanoparticles supported on walnut shell (CuNPs@WS).